Solar Selective Characteristics and Local Electronic Bonding States of 3d Transition Metal Oxide and Metal Nitride Based Thin Film Coatings

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This Thesis is submitted for the Degree of Doctor of Philosophy in the School of Engineering & Information Technology at Murdoch University

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DECLARATION

I hereby declare that the work presented in this thesis is my own account of research and contains as its main content work which has not been previously submitted elsewhere for the award of a degree at any tertiary education institution.

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(Mohammad Mahbubur Rahman)
ABSTRACT

The present study focused on the development of transition metal oxide and metal nitride based thin film coatings to be utilized as a cost-effective solar selective surface that constitute a new approach in maximizing the power conversion efficiency. Despite many developments on transition metal oxide and metal nitride based selective solar absorbers, these materials are yet to be commercialized for solar thermal conversion applications. Numerous studies on CuCoO and graphene oxide based thin films are dedicated for their optical applications and light harvesting purposes. However to the best of our knowledge, utilization of mixed metal oxide/graphene oxide thin films as solar selective surface is yet to be explored. Both CuCoO and graphene oxide (GO) have generated significant research interest and have widespread applications in clean energy devices due to the good combinations of many important properties. Therefore, in this work we focus on the introduction of GO to the 3d transition metal-based CuCoO coatings and develop the new types optical thin films via dip-coating sol-gel technology to be used as solar selective surfaces. It is believed that use of graphene oxide in wet chemistry based sol-gel derived thin films will explore the new platform of producing highly efficient selective solar surfaces. Generally, 3d transition metal nitride based thin film coatings are studied for structural, mechanical, and electrical applications. However, a very limited number of investigations are directed in search of their optical and solar selective behaviors. With the increasing demand for clean energy alternatives, and economically viable energy devices our endeavor might bring some fruitful breakthroughs in development of 3d transition metal oxide and metal nitride based thin film coatings.

Due to its flexibility and numerous technical advantages, the soft chemical sol-gel approach has been adopted to synthesize the metal oxides based thin film coatings. Unbalanced magnetron sputtered technique has been used for the development of transition metal nitride based thin film coatings for their spectral selective and local electronic structure studies. Sol-gel derived cobalt-copper oxide based coatings, transition metal nitride based sputtered Ti$_x$M$_y$N$_z$ ($M = \text{Al or AlSi}$) and Cr$_{1-x}$M$_x$N ($M = \text{Al, Si and/or Ni}$, with doping concentration, $x$ varying from 14.3 to 28.5 at.%) coatings were extensively studied in search of their spectrally selective behavior, mechanical properties, thermal stability, surface morphology and surface electronic properties. We discuss the spectral selective features of these coatings with their crystal structure,
electronic and chemical bonding states. In order to realize the correlation between crystal structure and surface morphology, bonding states, local bonding structures and structure-property relationships of these nanostructured coatings for their solar selective and local electronic behaviors, characterizations were carried out using XRD, synchrotron radiation X-ray powder diffraction, SEM, EDX, XPS, NEXAFS, UV-Vis and FTIR tests, and nanoindentation measurements.

In the case of CuCoO coatings, a high solar absorptance of 83.40% and a low thermal emittance of 5.70% were recorded which gives a solar selectivity of 14.63 (the ratio of the maximum absorption in visible and the minimum emission in infra-red to far infra-red region; $\alpha/\epsilon$). With the incorporation of 1.5 wt.% of graphene oxide to the copper-cobalt oxide coatings, a high solar selectivity of 29.01 was achieved. Optical studies showed that the solar absorptance, in the visible range, of the TiN coatings improved significantly from 51% to 81% with AlSi-doping. However, an increase of solar absorptance of up to 66% was recorded from coatings doped with Al-content. Meanwhile, the Al doping can reduce the thermal emittance in the infrared range from 6.06% to 5.11%, whereas doping with AlSi reduces the emittance to ca 3.58%. The highest solar selectivity of 22.63 was achieved with TiAlSiN coatings. The high temperature investigations of the sputtered TiAlSiN coatings show the highest solar selectivity of 24.63 at 600 °C. Sputtered Cr$_{1-x}$M$_x$N coatings were investigated to realize the surface and inner structural properties of the materials through the structural evolution of CrN$_x$ matrix with addition of doping (Al, Si or Ni) elements. Investigations on the local bonding states and grain boundaries of these coatings, using NEXAFS technique, provide significant information which facilitates understanding of the local electronic structure of the atoms and shed light on the origins of the high mechanical strength and oxidation resistance of these technologically important coatings. These findings help improve our understanding of local bonding structures, which could potentially lead to improved coating designs for mechanical applications.
DEDICATION

This noble work has been dedicated to the memory of my departed parents Mrs Rabya Khatun, and Mr M Motiur Rahman, to my wife Fatima Begum and to the part of my heart- my daughter Tasfia Humayrah Rafa, the four most loving people in this planet. I love you all dearly.
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SYMBOLS AND ABBREVIATIONS

\( \alpha \)  
Solar absorptance

\( \varepsilon \)  
Thermal emittance

\( s \)  
Solar selectivity

\( c \)  
Speed of light \( (3 \times 10^8 \text{ m/s}) \)

\( h \)  
Planck’s constant \( (6.63 \times 10^{-34} \text{ J.s}) \)

\( k_B \)  
Boltzmann constant \( (1.38 \times 10^{-23} \text{ m}^2\text{kg.s}^{-2}\text{K}^{-1}) \)

\( \sigma \)  
Stefan’s constant \( (5.56 \times 10^{-8} \text{ W/m}^2\text{K}^4) \)

\( \lambda \)  
Wavelength

\( \omega \)  
Angular frequency

\( \mu \)  
Cosine of the polar angle

\( k \)  
Extinction coefficient

\( n \)  
Refractive index

\( \phi \)  
Work function

\( \text{kW} \)  
Kilowatt

\( I \)  
Intensity distribution of the solar radiation

\( I_p \)  
Intensity distribution of the Planck’s black-body

\( E_g \)  
Energy band-gap

\( P \)  
Pressure

\( T \)  
Temperature

\( A \)  
Area

\( D_g \)  
Grain size

\( R \)  
Reflectance

\( H \)  
Hardness

\( E \)  
Young’s modulus

\( F \)  
Structure factor

\( \text{DC} \)  
Direct current

\( \text{BE} \)  
Binding energy

\( \text{VL} \)  
Vacuum level

\( \text{EM} \)  
Electromagnetic radiation

\( \text{PV} \)  
Photovoltaic

\( \text{PVT} \)  
Photovoltaic thermal

\( \text{XRD} \)  
X-ray diffraction

\( \text{PD} \)  
Powder diffraction
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>SR-XRD</td>
<td>Synchrotron radiation X-ray diffraction</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>XTEM</td>
<td>Cross-sectional transmission electron microscopy</td>
</tr>
<tr>
<td>AM</td>
<td>Air mass</td>
</tr>
<tr>
<td>AR</td>
<td>Antireflection</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-rays</td>
</tr>
<tr>
<td>UV-Vis-NIR</td>
<td>Ultraviolet visible near infra-red</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>FIR</td>
<td>Far infrared</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron spectroscopy chemical analysis</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XES</td>
<td>X-ray emission spectroscopy</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption fine structure microscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near-edge X-ray absorption fine structure</td>
</tr>
<tr>
<td>SXR</td>
<td>Soft X-ray</td>
</tr>
<tr>
<td>AEY</td>
<td>Auger electron yield</td>
</tr>
<tr>
<td>TFY</td>
<td>Total fluorescence yield</td>
</tr>
<tr>
<td>TEY</td>
<td>Total electron yield</td>
</tr>
<tr>
<td>PEY</td>
<td>Partial electron yield</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>HRXPS</td>
<td>High resolution X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>SR-XPS</td>
<td>Synchrotron radiation X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>PDOS</td>
<td>Partial density of states</td>
</tr>
<tr>
<td>DMS</td>
<td>Diluted magnetic semiconductor</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>SPD</td>
<td>Spray pyrolysis deposition</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>-------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga pascal</td>
</tr>
<tr>
<td>TPa</td>
<td>Tera pascal</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>PMT</td>
<td>Photo multiplier tube</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>TCF</td>
<td>Transparent conductive films</td>
</tr>
<tr>
<td>DSSCs</td>
<td>Dye sensitized solar cells</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulse laser deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>HIL</td>
<td>Hole injection layer</td>
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</table>
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M Mahbubur Rahman
Murdoch University
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JOURNAL PAPERS


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CHAPTER ONE: INTRODUCTION

1.1 General Introduction

This thesis is a study of transition metal oxides and metal nitrides based thin film coatings for solar selective surface and mechanical applications. In the following sections, we present some background on the present study, literature reviews from previously published articles, an outline of the objectives of the present study and lay out of the dissertation.

1.2 Background of the Present Study

Due to rapid industrialization and very high population growth across the globe, there has been an increase in world energy demand. Around 85% of the world’s power requirements come from fossil fuels such as oil, gas and coal. The use of these fossil fuels has led to potentially disastrous environmental impacts caused by the release of greenhouse gases and is a matter of serious concern which needs to be urgently addressed for the sustainable development of our planet energy sources [1]. Mankind’s dependence on fossil fuels not only results in climate change and global warming, but also in the rapid exhaustion of natural energy sources. It is anticipated that by 2050, world annual energy consumption will increase to nearly 30 TWyr (Tera Watt-years) which is almost double current needs. The lifeblood of modern civilizations is dependent upon the availability of an economical supply of energy. Therefore, unless suitable energy alternatives are found, mankind is heading towards an energy crisis. Research is now underway to allay global concerns over the issue of climate change and to find alternative, sustainable, renewable, and clean energy sources. In this context, solar energy is an environmentally friendly, alternative and renewable energy source that does not cause pollution or noise disturbance. However, one of the major challenges in implementing large scale solar power is its low efficiency and the high production cost of solar power devices. Solar radiation can be converted into a usable form of energy such as heat or electricity via photothermal conversion or photovoltaic (PV) conversion.

Photovoltaics are one of the most effective methods of the direct conversion of solar energy to electricity which have been studied since the 1950s. It is now considered to be one of the most promising and simplest methods of providing sustainable energy needs. When
Photovoltaics create energy, a semiconductor having an appropriate band-gap absorbs sunlight and generates electrons and holes. Such a semiconductor diode junction is used to separate the respective charge carriers and thus allow the flow of electricity. Photovoltaic conversion of solar radiation into electrical power is, generally associated with three major processes: (i) absorption of solar radiation to form locally confined excitons, (ii) transportation of the excitons towards the donor-acceptor interface and subsequent dissociation to form free electrons and holes, and (iii) transfer of charges to the electrodes to produce electrical power [2]. In a PV device, depending on the type of PV panels used, only 5–30% of the incident solar radiation is transformed into electricity and the remaining energy is converted into heat and wasted. This large amount of excessive heat might lead to some undesirable consequences such as a drop in cell efficiency by increasing the operating temperature of the PV panel, and permanent structural damage of the solar device [3]. Since more than 50% of the incoming solar energy has been found to be wasted in the form of heat, it is possible for PV panels to be integrated into another energy converter to form a hybrid system to use the incident radiation and improving the cell’s efficiency [3-6]. If a thermal collector with a suitable fluid circulation was used, power conversion efficiency could be kept at an acceptable level. Hybrid photovoltaic thermal devices (PVTs) are usually a combination of a photovoltaic (PV) and a solar thermal device which gives out electricity and heat from one integrated device and which can efficiently use the wasted heat produced by a PV module [3]. This approach is focused on PV panels of varying bandgap from the highest to the lowest in order to get good efficiency with the absorption of a major portion of the incident solar spectrum [7]. A PVT device can also be termed as a PV which is used as a thermal absorber [8]. This hybrid PVT system provides electricity and heat, significantly increasing the energy output from the PV cell and reducing the system’s operating temperatures. The heat produced can be utilized for various purposes such as domestic and industrial hot water supply, and the heating and cooling of buildings.

Photothermal use of solar energy typically involves a solar heating system that supplies hot water or hot air for domestic and industrial uses. The photothermal collector is one of the most important components of the solar heating system [9]. In order to increase the effectiveness of a solar thermal energy system, the absorption of incident solar radiation should be maximized and thermal losses from the collector minimized. The solar selective surface is a key component of a solar collector and determines the efficiency in solar–thermal energy conversion [10]. Selective surfaces consist of solar absorbing thin
films which are made of novel metallic nanoparticles, embedded in metallic oxides/metallic nitrides. They are used as thermal solar collectors that absorb and convert solar radiation into heat. In recent years, transition metal oxides and metal nitrides have been commonly used in mid and high temperature applications [9, 11-25]. A spectrally selective surface is normally used to improve photothermal conversion performance in cases where there is high absorptance, $\alpha$ (in the solar spectrum region (0.3 to 2.5 µm)) and low emittance, $\varepsilon$ (i.e., high reflection in the infra-red (IR) region ($\geq$ 2.5 µm) at the operating temperatures [14, 26].

An ideal selective surface absorbs all of the incoming solar energy in the visible range while 100% of the IR energy is reflected back from the absorbing surface indicating that no heat is lost through thermal radiation. However, in practice, an ideal selective surface does not exist in nature, nor is it possible to fabricate a material that exhibits ideal behavior in the reflectance transition wavelength range [27]. The practical use of selective surfaces was introduced in 1955 at the Solar Energy Conference held in Tucson, Arizona [28]. Since then, many studies have been undertaken on the design and fabrication of selective solar absorbing coatings by various research groups around the world. Readers more interested in about the detail overview of the selective solar surfaces are referred to the available literature [27, 29-32]. Well-developed selective solar surfaces such as intrinsic absorbers, coating/metal tandems, optical trapping absorbers, particulate coatings, semiconductor/metal tandems, multilayer thin films, transparent heat reflector/absorber tandems and transparent, heat reflecting and conducting coatings are very popular [33]. In the next few decades, selectively solar-absorbing coatings will be studied in great detail and improved using various methods [34, 35].

It has been reported that a single absorption coating attains a solar absorption of 0.85 along with a thermal emittance of 0.03 while a multi-layer coating e.g., two absorbing and one anti-reflecting layers significantly improves the absorptance and emittance to 0.93 and 0.05 respectively [36]. Single layers of Si$_3$N$_4$, SiO$_2$ or Al$_2$O$_3$ etc. are generally used as anti-reflection (AR) coatings [25]. Due to the discontinuous changes in the refractive index, single layer coatings result in a high reflection of the incoming solar radiation [37]. A patented selective absorber is capable of achieving a very high efficiency with a solar absorptance of 0.97 and a normal thermal emittance of 0.05 [38]. A two-layer absorber could be successfully improved by adding an antireflecting (AR) third layer [39]. It has been reported in an earlier study that a 120 nm film shows a normal solar absorptance of 0.80 and a normal thermal emittance of 0.03 [40]. Once an
AR had been added, the solar absorptance was reported to increase to 0.91 while the thermal emittance remained constant. Such an assembly consists of three layers: highly absorbing base of the film, the middle layer containing a medium absorbing film and an AR layer on the top [39, 41]. AR enhances the solar absorptance and it also works as a protective layer [40]. In practice, a good solar selective absorber possesses an absorptance of \(\alpha > 0.90\) and an emittance, \(\varepsilon \leq 0.2\). Better selectivity can be achieved by using multilayer selective absorbers consisting of an absorber placed between the anti-reflecting layers in a metallic substrate. This type of multi-layer coating allows solar radiation to easily pass through the surface material and it creates a destructive interference in the coating, resulting in a high absorption. The optical performance of the absorbers depends upon the composition of the thin film, its design, surface roughness, surface morphology and nanostructure, film thickness and optical constants of the constituent materials. The reflecting behavior of the metal substrate and porosity of the AR coatings also plays a significant role in controlling the selectivity of the coatings [32]. To achieve higher selectivity, thin solar absorbing coatings on suitable highly reflective metallic substrates is essential [42]. A good selective absorbing surface can be designed by an absorber-reflector assembly. In such an approach, the reflector is coated with a highly absorbing layer over the visible solar spectrum while the infrared region is made transparent. Absorption of the selective surfaces can be also increased by using graded selective surfaces [43] i.e., decreasing the refractive index from substrate to the surface. The multilayer absorber-reflector tandem concept has been used widely to obtain high selectivity [44]. Many studies have been done on multilayer absorber-reflector based selective surface coatings [30, 37, 43-47]. Studies of selective surface coatings of carbon nanoparticles embedded in SiO\(_2\), ZnO and NiO matrices grown on Al substrates using sol-gel method have also been reported [42]. CuO\(_x\) thin films prepared by a one-step chemical conversion have been found to exhibit high performance as solar selective absorbers [25]. In other reports, Ni [48], Co [49], or Cr [50] pigmented porous alumina has been suggested as being good solar selective surfaces due to their high absorption and low emittance at low temperatures (T <100 °C), and other groups have investigated various types of metal oxides and metal nitrides based selective solar surfaces such as CuCoO, MnCoO, NiCoO, PtAl\(_2\)O\(_3\), MoAl\(_2\)O\(_3\), CuAl\(_2\)O\(_3\), NiAl\(_2\)O\(_3\), TiAlN, TiAlN/AION, TiAlN/TiAlON/Si\(_3\)N\(_4\), HfO\(_x/Mo/HfO\(_2\), MoAlN, and WAlN [13, 20-23, 25, 51-58].

In recent years, scientists and technologists around the world have shown increasing interest in the study of 3d transition metallic nitrides and metallic oxides based selective
surfaces (in pure state and with various dopants) due to their many favorable properties such as having a large band-gap, high surface acoustic velocity, corrosion resistance, wear resistance, erosion resistance, oxidation resistance, excellent chemical and thermal stability and physical robustness [59-70]. In addition to solar selective surfaces, these materials have found wide range of applications in the following areas:

- spintronics and non-volatile storage [65-67],
- microelectronic devices [70],
- in many optical devices such as active and passive optical planar waveguides,
- antireflecting coatings [71-75],
- ultraviolet and visible light emitters and detectors,
- optical storage devices [61],
- semiconductor industry for optoelectronic devices at high power and temperatures [60],
- high temperature structural materials,
- gate dielectrics in microstructural devices [76, 77],
- electronic and spin-dependent photonic devices [61, 62],
- microelectronics devices, and
- diffusion barriers [57, 78].

Because of these many favorable properties, scientific interest in transition metal nitrides and oxides has been accelerated and dedicated to the development of new species of coatings with superior properties.

1.3 Review of Earlier Work

Mixed metal oxides based thin films with general composition \( AB_2O_4 \), where \( A \) is a divalent metal ion occupying the tetrahedral \( A \)-sites while \( B \) is a trivalent ion occupying at octahedral \( B \)-sites \( e.g., CuFe_2O_4, CuCo_2O_4, \) and \( CuMn_2O_4 \) are studied by different groups [79-82]. Mixed metal oxide based thin films have been extensively studied by different groups around the world [83-87] because of their widespread applications in,

- catalysts for volatile organic compounds [88],
- gas sensors [89],
- electrocatalysts for the oxygen electrode [90],
- electrocatalytic cells [91],
- oxidation-reduction reaction electrocatalyst [92].
- pollution controls [93],
- photovoltaics and photocatalysis [94],
- selective solar absorbers [95, 96],
- dye sensitized solar cells [97],
- batteries and memory devices [98, 99], and
- for absorption optimizations and industrial applications [21].

Cobalt based metal oxides are used in a wide variety of high-tech applications [98-101]. Pure copper oxide [6], cobalt-copper oxide, manganese-cobalt oxide, nickel-cobalt oxide [20, 21], copper-aluminum oxide [102] have been reported in studies of spectrally selective solar absorbers, high absorption optical coatings and industrial applications. Manganese-cobalt oxides have been studied with a focus on the influence of synthesis conditions on the oxidation states and cationic distribution in the tetragonal and cubic phases [103].

Optical characterization of industrial roll-coating sputtered nickel-nickel oxide solar selective surface has been reported by Adsten et al. [45]. Structural and optical properties of pulsed sputter deposited Cr_{x}O_{y}/Cr/Cr_{2}O_{3} solar selective coatings on Cu substrates were found to demonstrate high selectivity after being annealed at 300 °C for 2h in air [54]. However, at higher temperatures the selectivity was decreased significantly which might be due to the increased surface roughness, oxidation of Cr crystallites and the formation of CuO. The formation of CuO and the increase in Cr^{3+} vacancies due to the outward diffusion of Cr and creation of CuO at higher sintering temperatures was supported by XPS studies. In another study, Shaklee et al. [104] examined the spectral selectivity of composite enamel coatings consisting of spinel-type transition-metal-oxide pigments embedded in a borosilicate-glass matrix deposited on stainless steel substrate. The optimization of solar selective coatings based on the NiO thin films on copper substrate using an inexpensive and up-scalable spray pyrolysis deposition (SPD) has been reported by Voinea et al. [105]. The deposition parameters were varied in order to maximize the solar absorbance and minimize the thermal emittance. By varying the deposition parameters, a good solar selectivity (α/ε = 0.95/0.05) was recorded by the Cu/CuO_{x}/NiO solar absorber compared with the ones obtained by other methods shown in studies. In their work, the authors also recommended new additives for tailoring the surface of solar selective coatings. Solar thermal flat-plate collectors based selective coatings comprised of crystalline CuO and amorphous NiO composites prepared by robotic spray pyrolyzed
deposition show high selectivity values (>30) [106]. Sol-gel derived spin coated C/NiO nanocomposite solar energy absorbing surfaces deposited on aluminum substrates were found to show a selectivity of 17.2 [107]. The cobalt oxide (Co$_3$O$_4$) films containing 1-D interlinked nanowires synthesized via spray pyrolysis technique showed better values of absorptance (0.94), emittance (0.17) compared to the data reported studies. The selectivity of coatings was reported to be 5.529. These coatings have the potential of being good selective absorbers. Their optical properties indicate the red shift of absorption peaks, thereby showing a quantum-confined effect and semiconducting nature [108]. Copper oxide (CuO) thin film coatings made of 1D nanostructures prepared through a facile chemical oxidation of copper (Cu) substrate at different pH conditions possess high solar-selectivity value of 13.8 and are suitable for selective solar absorbers in solar collectors for thermal energy conversion [109]. In Amun’s study [110], the combined CuCoO thin films showed a selectivity of just over 14. The Al$_x$O$_y$/Pt/Al$_x$O$_y$ multilayer coatings deposited by an electron beam vacuum evaporator onto copper substrate at room temperature were found to be thermally stable with good spectral selectivity of $\alpha/\varepsilon = 0.951/0.09$ at 500 °C. However, at 600 °C and 700 °C the solar selectivity decreased to 0.92/0.10 and 0.846/0.11 respectively, and might be due to the diffusion of Cu and creation of CuO and Cu$_2$O phases [111]. There have been numerous investigations available in studies on metal oxide thin films for the improvement and optimization of physicochemical, optical, thermal, electro-chemical, photo-chemical, magnetic, dielectric and electro-magnetic properties focusing on their practical applications such as clean energy devices, solar cells, photovoltaics, thermal collectors, selective solar surfaces and smart windows.

Graphene is a 2D carbon allotrope with a one-atom-thick planar sheet of $sp^2$-hybridized carbon atoms, densely packed in a honeycomb lattice structure. Graphene is the thinnest known material with numerous application potential. The band gap properties of graphene (for semiconductor applications) is relatively well-known, whereas pristine graphene has a zero band gap and graphene oxide (GO) is essentially a wide band gap semiconductor [112]. Graphene has unique properties such as extraordinary thermal and mechanical stability, chemical inertness against oxygen and water, high current density [113], ballistic transport and nanoscale super hydrophobicity [114-116], high specific surface area (2630 m$^2$/g) [117], exceptionally high thermal conductivity (5000 W/m/K) [118], very high intrinsic electron mobility (250,000 cm$^2$/Vs) [119], a high Young’s modulus (1TPa) [120] and high optical transparency (97.7%). As a result of having so
many beneficial properties, graphene has gained appreciable research attention in recent years. At room temperature graphene possesses the lowest resistivity ($\sim 10^{-6}$ ohm-cm) among all known metals [116]. A single layer of graphene produces exceptionally high optical transparency under white light [112]. High optical transparency and high conductivity of graphene also makes it ideal for various other technological applications such as organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), liquid crystal displays (LCDs), touch screens, composite materials, optoelectronics, and sensors [112]. An exceptionally high Young’s modulus of 1 TPa and ultimate strength of 130 GPa make graphene the strongest of all known materials [121]. Graphene shows remarkable transport phenomena and a broad electrochemical window [122]. The use of graphene in energy harvesting and storage devices is also very interesting because of its potential for the development of practical applications [116]. These features make graphene advantageous for applications in energy technologies. Furthermore, graphene based materials are very important from the fundamental and technological point of view because they are non-toxic, chemically and thermally tolerant, and mechanically robust.

Optical applications of graphene oxide are also well known [123]. Because of its large surface area, graphene offers very high optical absorptivity. The high optical absorption and tunable optical bandgap are the most favorable characteristics of graphene and makes it an ideal material for effective light harnessing [124]. Light absorbing photovoltaic applications of graphene based materials have been reported in an earlier research [125]. Optical absorption and power conversion efficiency (PCE) of layer-transferred graphene in organic hybrid solar cells have been reported in earlier studies [126]. Application of graphene in organic photovoltaic devices has been realized by several other groups [127, 128]. In order to achieve improved efficiency, graphene is a promising candidate for many practical applications in energy related areas and light harvesting devices such as inorganic [129], organic [130, 131], hybrid [132], and dye sensitized solar cells [133]. A series of comprehensive reviews are focused on investigating the manufacturing, properties, and towards the applications of graphene and graphene-based materials in energy related areas [114, 134, 135]. Optimization of optical properties of graphene oxide by mixing with inorganic compounds to form a hybrid system is also feasible in the development of GO based selective surfaces. Since GO offers good solubility in aqueous and polar solvents, the sol-gel method is a feasible technique to prepare GO based thin films.
Over the years many strategies have been adopted to design metal oxide thin films based light harvesting assemblies with improved properties such as photovoltaics [136, 137], thermal collectors [138, 139], photovoltaic thermal solar panels [140, 141], and solar selective absorbers [142]. Some of the most popular processes are the sputtering method [143], the sol-gel technique [21], the thermal evaporation technique [144], the glass crystallization process [145], spray pyrolysis [146] and the organometallic precursor method [147]. Among the existing methods, some of them require high material consumption and are detrimental to the environment while others are costly and inefficient. For example, sol-gel derived mixed metal oxides based thin film selective solar surfaces attract much attention because of their flexibility and beneficial characteristics. They are inexpensive, physically, chemically and thermally stable, are easy to prepare, have a shorter processing time, are non-toxic, require less equipment, have a compatible band gap, and high electron mobility [21].

The soft chemical sol-gel synthesis of inorganic materials has been found to show superior properties such as low formation and crystallization temperatures, better compositional uniformity at low temperatures and conformational coverage in the case of films over the solid state synthesis routes [148]. The easy synthesis, low-cost and facile approach of this technique is highly recommended for a wide range of applications in the development of selective solar surfaces. For these reasons, the development of superior high performance, low cost and environmentally friendly solar selective surfaces is always being in the hot spot.

Over the past few decades scientists and technologists around the world are showing significant interest in the investigation of metallic nitride based thin film coatings with various dopants because of their remarkable properties such as large band-gap, high surface acoustic velocity, corrosion resistance, oxidation resistance, excellent chemical and thermal stability and physical robustness [59-70, 149]. These materials are extensively used:
- in spintronics and non-volatile storage [65-67],
- in microelectronic devices [70],
- in optical devices such as active and passive optical planar waveguides, and antireflecting coatings [71-75],
- in the semiconductor industry for optoelectronic devices at high power and temperatures [60],
- as high temperature structural materials and gate dielectrics in microstructural devices [76, 77],
- in electronic and spin-dependent photonic devices [61, 62],
- in ultraviolet and visible light emitters and detectors, and
- in optical storage devices [61].

The introduction of a suitable amount of dopant can remarkably enhance the various properties (as mentioned in the above sections) by inducing defects such as vacancy, atom substitution, cluster formation and deformation [64].

Historically, transition metal nitride based sputtered coatings are well known as hard protective coatings which are extensively used in high-speed/dry cutting and metal forming tools. They are well suited for this purpose as they are hard materials, have superior oxidation-, wear-, and corrosion resistant and have high thermal and chemical stability. Hardness, oxidation-, wear-, and corrosion resistance, and tribiological behaviors of these coatings are also dependent on the microstructure and chemical compositions. Currently researchers around the world are using new dopants to initiate defects in order to develop new phenomena, improve their qualities and utilize them to new applications. With this in mind, it has been observed that transition metal nitride based coatings have also been extensively discussed in relation to their applications as solar selective absorbers in an invited review [150]. In Ref. [151], magnetron sputtered TiAlN/TiAlON coatings synthesized onto a metal substrate exhibited high absorptance and low emittance. The absorptance of the coatings was substantially enhanced to 0.95 by adding Si$_3$N$_4$ antireflection coating on the top of films. A higher thermal stability and high solar selectivity of 0.95/0.07 = 13.57 was achieved by this tandem selective surface.

Until now, the main hurdle in using these alternative and clean energy devices as opposed to using conventional energy sources has been their high cost. Over the past few years, 3d transition metal nitride based thin films have gained a lot of research interest as selective solar surfaces in solar thermal conversion devices. 3d transition metal nitrides and oxynitrides based selective surfaces constitute a new technical approach to maximize the efficiency of power conversion at a reasonable cost. Various types of metal nitrides and oxynitrides based selective solar surfaces such as TiN, ZrN, HfN, TiAIN, TiAION, NbAIN, NbAION, MoAIN, and WAIN have been investigated by many groups [12-15, 24, 51, 53, 57, 150, 152, 153]. Generally, power conversion performance of a selective solar surface depends upon the coating materials and coating design. Transition metal nitride based tandem
coatings *e.g.*, TiAlN/AlON, and TiAl/TiAlN/TiAlON/TiAlO have been explored for the potential commercial development of selective solar surfaces [13, 154]. In Ref. [55], TiAlN/TiAlON/Si₃N₄ selective absorbers were produced on various substrates such as copper, nickel, stainless steel, glass and nimonic. Some of the substrates were preferred for high temperature applications because at high temperature exposure the diffusion of copper can damage the optical properties of the absorbing coatings. Among all the substrates, Cu was found to offer the lowest emittance owing to its superior free electron density [155].

1.4 Objectives of the Present Study

Despite the availability of many research studies on metal oxide thin films and GO thin films for their optical and light harvesting purposes, it appears that the utilization of mixed metal oxide/GO thin films as solar selective surface is yet to be explored. Both CuCoO and GO have generated tremendous research interest and have received widespread applications in clean energy devices, therefore, in the present study the strategy is to introduce a controlled amount of GO to the 3d transition metal based CuCoO coatings and develop new types of optical thin films via dip-coating sol-gel technology which is used as solar selective surfaces. With this in mind, the use of carbon materials in wet chemistry based sol-gel derived thin films has the potential to be useful in developing highly efficient selective solar surfaces. Taking into account all of their favorable characteristics, the use of graphene and graphene oxide based materials might bring about revolutionary changes in renewable energy and advance the production of high-tech commercial materials beyond the silicon age [156]. With the increasing demand for clean energy alternatives, and economically viable energy devices, it is submitted that this study may bring some fruitful breakthroughs in the development of graphene oxide added mixed metal oxide thin films based solar energy conversion devices to be used as solar selective surfaces.

Regardless of so many developments in transition metal nitrides based selective solar surfaces, these materials are yet to be commercialized for solar energy conversion applications [13, 58, 153]. Keeping these facts in mind, researchers over the world are trying to identify suitable product materials, analytical tools, fabricating techniques, testing and training requirements, potential customers, and market strength for the potential development of the most efficient and cost-effective selective solar surface. Furthermore, at this stage, research and development work on the material and coating
selection, thermal absorber design and manufacturing, power conversion efficiency and effectiveness, performance testing, system optimization, control and reliability, product quality and ease of delivery and installation must be focused. Thus, for a successful market introduction of selective surface based solar panels, optimal concepts, challenging broadly based research and development efforts are important. Until now, a very limited number of investigations have been conducted in respect of the optical behaviors of transition metal nitride based coatings, and studies on the solar selective behavior of these materials are even rare [71-75, 151]. In view of above, the second part of this thesis has an emphasis on inspecting the transition metal nitride based sputtered Ti$MN_x$ ($M = \text{Al or AlSi}$) and Cr$_{1-x}N_x$N ($N = \text{Al, Si and/or Ni, with doping concentration varying from 14.3 to 28.5 at.\%}$) coatings were extensively studied in search of their spectrally selective behavior, mechanical properties, thermal stability, surface morphology and surface electronic properties. In addition to the UV-Vis and FTIR tests; XRD, synchrotron radiation XRD, SEM, XPS and nanoindentation measurements were also implemented in order to understand the correlation of the crystal structure and surface morphology of these nanostructured coatings to their solar selectivity values.

Synchrotron radiation facilities are widely used to characterize the electronic structure of homogeneous alloys in pure and doped states. NEXAFS is a popular and powerful spectroscopic method for the probing the surface unoccupied electronic structure of transition metal nitride based thin films because: NEXAFS data provide with the density of states (DOS) of the unoccupied molecular orbitals directly related to their structural and electronic properties, and the AEY and TFY modes of NEXAFS work by different detection limits that clearly differentiate the bulk and surface properties of the coatings. Due to numerous unique advantages such as polarization control, coherence, high brightness and photon-energy tunability, synchrotron radiation facilities are widely used in the identification of the atoms, molecules and compounds [157]. NEXAFS is used to comprehend complex systems and detecting the co-existence of various phases either in crystalline or in amorphous form. NEXAFS spectroscopy essentially provides a unique opportunity to probe differences in the electronic structure as the composition of transition metal nitride (CrN) changes as seen in shifts in the Al $K$-, Cr $L$-, and Si $K$-edge absorption energies. The bonding structural evolution and the spectral changes were correlated in the X-ray absorption near-edge structure (XANES) studies of the aluminum incorporated titanium nitride [158] which afforded a comprehensive treatment on the local atomic structure of TiN. Further, the addition of Al and Si was found to play
significant roles in tailoring the structure of the grain boundary within CrN coatings as well as the surface chemistry of the oxide layer, allowing the development of highly oxidation and corrosion resistant superhard coatings [157]. The appearance of direct \( d \)-bonds and an increase in peak intensities within the Cr \( L \)-edge spectra confirmed the possible variations in valence and a reduction in crystalline domains [159]. Similarly, an increase in Ni \( L \)-absorption edges intensity showed an improvement in the coordination and effective charge of the nickel atoms [159]. Understanding the electronic and surface structure of transition metal nitride-based thin film coatings is therefore crucial from both an experimental and theoretical perspective. However, there has been very limited effort toward elucidating the effects of dopant elements on the electronic and surface structural evolution, and on the tailoring of the grain boundaries. In view of these facts, in this study, we have carried out NEXAFS measurements on the \( \text{Cr}_{1-x}M_x\text{N} \) (where \( M = \text{Al}, \text{Si} \) and Ni) films both in AEY and TFY modes. In the present work, the main objectives are concerned,

- incorporation of graphene oxide to synthesize sol-gel wet chemistry derived 3d transition metal oxide based thin film coatings for solar selective surface applications,
- to examine the systematic variation of the process parameters such as concentration of the solution, dip coating speed, and sintering temperature,
- to investigate the effect of graphene oxide onto the solar absorptance characteristics of the CuCoO coatings in the visible range of the solar spectrum,
- to observe the effect of the graphene oxide onto the thermal emittance of the synthesized films in the infrared range of solar spectrum
- to see the structural, mechanical, optical behaviors and thermal stability of graphene oxide doped \( \text{Cu}_x\text{Co}_y\text{O}_z \) composites in order to achieve better solar selective performance
- to focus the potential development of 3d transition metal nitride based \( \text{Ti}_xM_{1-x}y\text{N} \) (where \( M = \text{Al}, \text{and AlSi}; x = 0.50, 0.25 \) and \( y = 0.50 \) ) coatings to be used as a solar selective surface in solar thermal collectors,
- to address the high temperature physical and morphological stability, surface bonding states, and solar selective behaviors of magnetron sputtered \( \text{TiAlSiN} \) coatings,
- to establish the bonding structural evolution in \( \text{Cr}_{1-x}M_x\text{N} \) (where \( M = \text{Al}, \text{and Si} \) ) coatings upon the subsequent doping of Al and Si, by measuring the Al \( K^- \), Cr \( L^- \), and Si \( K \)-edge NEXAFS spectra using the synchrotron radiation,
- to gain novel insights into the roles of dopants in tailoring the structure of the grain boundary within \( \text{Cr}_{1-x}M_x\text{N} \) coatings through NEXAFS experiments, as well as elucidating their effects on the electronic and surface structural evolution,
- to investigate the effect of dopant elements (Al, and Si) on the crystalline phase, surface structural evolution and local electronic bonding states of the Cr$_{1-z}$(Al/Si)$_z$N films around the nitrogen K absorption edges (N K-edge) via surface sensitive Auger electron yield (AEY) and bulk sensitive total fluorescence yield (TFY) modes of NEXAFS experiments,
- to understand the effects of Ni, Al and Si doping elements on the local electronic properties and surface bonding structural evolution and their subsequent roles in modifying the grain boundaries of Cr$_{1-z}$Ni$_z$N coatings, the NEXAFS measurements were carried out at Cr L-, Ni L-, N K-edges both in surface sensitive AEY and bulk sensitive TFY modes.

1.5 Layout of the Thesis

There are twelve chapters in this thesis. Background information of the present study together with a review of previously published works and objectives are presented in Chapter 1. Chapter 2 includes the theoretical features associated with the interaction between the thin-film coatings and solar radiation and the designs for solar selective absorbers. The structural stability, mechanical properties, and thermal stability phenomena of these coatings are also discussed in this chapter. Recent advances in the sol-gel derived transition metal oxides and transition metal nitride based thin film coatings are presented in Chapter 3. A major portion of Chapter 1 and Chapter 3 has been published in two review papers in two journals: Journal of Advanced Physics (Journal article 12) and International Journal of Chemical Engineering (Journal Article 9).

Chapter 4 deals with the fabrication of sol-gel derived dip-coated and unbalanced magnetron sputtered coated thin films. The experimental approaches, the equipment used and the film characterisation techniques are described in Chapter 5. Chapters 6 to 11 comprise the major findings made from the characterisation of the coatings prepared and further commentary. Chapter 6 deals with the structural thermal stability of graphene oxide-doped copper-cobalt oxide coatings as a solar selective surface. It has been published to Journal of Materials Science and Technology for publication (Journal article 2).

Chapters 7 and 8 deal with the impact of composition and annealing temperatures on structural, surface morphological, mechanical, surface chemical bonding states and the solar selectivity properties of TiN, TiAlN, TiAlSiN sputtered coatings. The major results
of Chapter 7 have been published in *RSC Advances* (Journal article 1) while the contents of Chapter 8 have been published in *Journal of Alloys and Compounds* (Journal article 7).

The results presented in Chapter 9 cover the mechanical properties and novel insights into the roles of dopants (Al and Si) in tailoring the structure of the grain boundary within Cr$_{1-x}$M$_x$N coatings through NEXAFS experiments. They have been published in the *Journal of Alloys and Compounds* (Journal article 14). Understanding the local bonding structures of Ni-doped chromium nitride coatings through synchrotron radiation NEXAFS spectroscopy is dealt with is designed as Chapter 10. The contents of this chapter have also been published in *The Journal of Physical Chemistry C* (Journal article 10). The research results from Chapter 11 describes the local bonding structure of Cr$_{1-x}$(Al/Si)$_x$N thin film coatings at N K-edge and probed using synchrotron radiation NEXAFS spectroscopy. This has been published in the *Journal of Alloys and Compounds* (Journal Article 8). A brief summary of the present study, need for future development, and scopes of further investigations been discussed in the last Chapter as Conclusions.
CHAPTER TWO: THEORETICAL FORMULATION

2.1 General Introduction

This chapter deals with the underlying theory and principles of thin film based photovoltaic thermal solar panels for selective surface applications. Detailed descriptions of the relevant theoretical formulations of various measurements undertaken in this work have been provided. The theoretical formulation forms the platform of research techniques which are based on physical phenomena, thermodynamic principles and available mathematical models.

2.2 History and Utilization of Solar Energy

Solar energy generated by nuclear fusion in the core of the sun travels to the Earth’s surface through space in the form of electromagnetic energy called photons or quanta. Every 20 minutes the sun produces enough energy to provide all of mankind’s energy requirements for a year. However, only 30% of the actual solar energy emitted by the sun reaches the Earth’s surface. A large portion of the solar radiation is absorbed by the clouds and surrounding atmosphere. The amount of solar radiation received at any point on the Earth’s surface is dependent upon the time, the amount of cloud and the latitude at that point.

The use of solar technology can be recorded as far back as the 7th century B.C. when it was discovered that fire could be created by concentrating the sun’s heat with glass and mirrors. In the 3rd century B.C. the Ancient Greeks began to construct their houses in such a way to harness the sun to provide light and heat for indoor spaces. In the 1st to 4th century A.D. the Romans had built many south facing houses with glass windows and doors, in order to sustain the heat during winter. Until the discovery of the photovoltaic effect by Edmond Becquerel in 1839 [160], the use of solar energy was relatively common the world over by means such as solar collectors, solar thermal technology and solar cooking. In 1861 August Mouchet constructed the first solar-powered steam engines for a number of practical applications. In 1883 Charles Fritts from the United States of America developed the first solar cell from selenium wafers [161]. The first commercial solar water heater was patented by Clarence Kemp in 1891 [162].
In 1954, the Bell laboratories produced the first silicon photovoltaic (PV) solar cell with a 4% efficiency to run domestic electrical equipment. Later, these silicon solar cells were improved to achieve an 11% efficiency. Up until 1969, the commercial PV solar cells were very expensive and electricity from solar cells cost in the vicinity of $100 to $300 per watt. In 1970, the Exxon Corporation designed a remarkably low cost solar cell, pulling the price down from $100/watt to $20/watt such that eventually solar cells would become competitive with fossil fuels [163]. Since the 1990s, due to the large growth of the PV solar industry around the world, production costs have been reduced significantly thus making solar energy more affordable than ever before. Furthermore, the development and marketing of solar water heaters have resulted in a lowering demand for gas and electricity, thereby reducing the costs of solar cells [164].

A typical solar power generator is comprised of two major components: a collector that receives the solar radiation and converts it to electricity, heat or both, and a storage unit in order to store energy for the future use. The storage unit can retain the power generated during the periods of maximum incoming sunlight and supply it when it is needed. There are different types of collectors e.g., flat-plate collectors, focusing collectors, passive collectors and various other forms of storage units. Collecting methods and storing systems can vary from one device to the other.

2.3 Sources of Renewable Energy

In order to resolve the approaching energy crisis which has been primarily caused by the exhaustion of natural resources for power production, search for an alternative, clean, sustainable and renewable energy sources has received a great degree of attention from scientists and technologists around the world. To ensure the most effective and fruitful use of renewable energy, scientists are trying to develop cost-effective, highly efficient and environmentally friendly power conversion and storage devices [165]. There are various sources of energies such as biomass, nuclear power plant, wind energy, and fossil fuels, each source having some negative characteristics. Biomass offers low efficiency [166], nuclear power has major inherent risks, wind turbines have low energy density and intermittency and burning of fossil fuels results in the increase of greenhouse gases which leads to global warming [167]. Even though all energy sources must be considered when making decisions to deal with the energy crisis, among the existing sources, the solar energy is arguably the best carbon-free, renewable, sustainable, environmental
friendly, noise-free and pollution free, source capable of supplying a large amount of energy to satisfy the world’s multifold energy needs.

2.4 Solar Energy and Thermal Radiative Energy

The sun is at the centre of the solar system situated at a distance of about $1.496 \times 10^{11}$ m from the earth, with an estimated diameter of $1.39196 \times 10^{9}$ m. The spectrum of the solar energy varies from long infrared wavelengths to very short wavelengths of $\gamma$-rays. The sun is generating energy as a continuous fusion reactor with an estimated total electromagnetic radiative power of about $3.8 \times 10^{27}$ W. Outside the Earth's atmosphere, the extra-terrestrial solar radiation ($G_{sc}$) is $\sim1367 \pm 3\%$ W/m$^2$ which is almost steady, [168] being divided into ultraviolet (8% of total), visible (46%) and near infrared (46%). About 30% of the solar radiation received by the Earth is directly reflected into space and the rest is converted to heat which is absorbed in the air, the earth and oceans (47% of total), to become potential energy in the hydrological cycle (23%), mechanical energy in winds and waves (<1%) and chemical energy in photosynthesis (<1%). Overall, this accounts for 15,000 times the amount of energy used by humans in the form of fossil, nuclear power and hydro-electric [169].

The sun is considered to be a black body with an effective blackbody temperature of $\sim5800$ K. The blackbody spectrum and the extraterrestrial spectrum of the sun differ slightly from each other due to the absorption and scattering of solar radiation in the ozone layer, ionosphere, and the atmosphere by O$_2$, O$_3$, H$_2$O and CO$_2$. Absorption holes are created in the terrestrial solar spectrum due to the absorption of certain wavelengths by the atmospheric compounds as shown in Fig. 1. Rayleigh scattering is the scattering of light by the air molecules, which is extended to scattering from particles up to about a tenth of the wavelength of the light. Rayleigh scattering is symmetric both in the forward and backward directions, and is more effective at short wavelengths ($\propto \frac{1}{\lambda^4}$).
Absorption and scattering occur when electromagnetic radiation is incident on a particle, and depends on the size, shape and optical properties of the material’s surface. Scattering can occur with either small or large particles and also by multiplying reflected radiation and it is favoured at shorter wavelengths. For any sufficiently small particle as compared to the incoming wavelength, a strong symmetric Rayleigh scattering occurs [171]. The intensity and spectral distribution of the terrestrial solar spectral varies with the change of the atmospheric absorption components, scattering components and air mass [170]. The use of solar energy which is a sustainable source of energy which is abundantly available throughout the world can significantly contribute to mankind’s everyday power requirements. Due to the low power density and large seasonal variation at high latitudes, special technical and economic requirements are needed for solar energy applications around the world.

2.5 Heat Transfer and Its Modes

The transfer of heat is the thermal energy exchange between objects due to a difference in temperature between them. Generally, the heat is transferred from a higher temperature object to a lower temperature object. According to the thermodynamic principles the heat transfer changes the internal energy of both objects involved in the process. The flow of
heat between two objects continues until they reach a point at which a thermal equilibrium is achieved. Temperature is a measure of how hot or cold an object is or it is the amount of energy of the molecules that a body holds. The rate of heat transfer is measured in watts (W) i.e., joules per second (J/s). The rate of heat transfer per unit area is expressed in watts per area (W/m²). Various mechanisms are involved in heat transfer processes e.g., thermal conduction, thermal convection and thermal radiation.

Conduction of heat is also known as heat diffusion, and it is the direct transfer of heat energy between two systems. Conduction takes place due to molecular agitation within the material without any motion of the material as a whole. Conduction is a kind of energy transfer across a system due to the interactions of the randomly moving neighbouring molecules and atoms. Generally, in conduction heat transfer takes place within a solid or between solids in thermal contact with each other.

The convection process is used by the fluids (e.g., gas and liquid etc) to transfer heat. In convection, the heat energy is transferred by the mass or macroscopic motion of the fluid, when a cool fluid flows through a warm body. Convection can be of two types: natural convection, where the fluid motion is created by the warm fluid itself, and forced convection, where the flow is caused by some external means e.g., pumps. In natural convection, the density of the fluid reduces as it is heated and becomes lighter than the cold fluid. When heat is supplied to a fluid, it gives rise to a volumetric expansion which in turn creates a gravity-induced pressure gradient. The expanded fluid is displaced and thereby heat is transferred. The warm fluid is replaced by a cooler one, which can then extract more heat away from the surface. In natural convection, bulk fluid motions are caused by buoyancy forces resulting from the change in density of the fluid stimulated by the change in temperature, whereas in the case of forced convection, artificial fluid motions are created by some external means.

In the radiation process, the transmission of heat energy is achieved without any intervening medium. All objects with a temperature above 0K emit radiation that travels at the speed of light. The electromagnetic radiation emitted by a material is known as thermal radiation. This type of heat transfer takes place when a certain specific radiation is incident upon a material and it is absorbed. For example, an object which absorbed solar radiation under the exposure of the sun is warmer than it would be in the shade. Thermal radiation is caused by the rapid movements of atoms and molecules in materials which are composed of charged particles e.g., electrons and protons. The movement of
these charged particles results in the emission of em-radiation which carries energy away from the surface.

### 2.6 Electromagnetic Radiation

According to the Maxwell’s classical electromagnetic theory, light is a form of electromagnetic radiation which possesses both electric and magnetic fields. EM radiation can be classified into ranges of wavelengths according to the different criteria. The solar electromagnetic spectrum covers the ultraviolet-visible-near infrared (UV-Vis-NIR) and thermal region regions in the wavelength range of \( \lambda = 300-2500 \) nm and \( \lambda = 2500-5500 \) nm respectively. The UV-Vis-NIR and thermal regions of the solar spectrum are the most important for the application of solar devices. The entire spectrum distribution has been displayed in Fig. 2 (below). The total electromagnetic radiation power of the Sun which is the ultimate energy source, consists of \(~8\%\) in the UV range, \(~46\%\) in the visible range and \(46\%\) in the near-infrared range [168, 171]. Most of the solar radiation is absorbed or scattered by the cloud, oxygen, nitrogen, water vapour, ozone, carbon-dioxide and by various other particles present in the atmosphere. In addition to scattering and absorption, the solar spectral distribution and intensity are also influenced by the air mass (\(i.e.,\) the ratio of optical mass at a slant path to the vertical path) of the ray that covers the atmosphere [172]. For example, air mass has a value of 1 when the sun is overhead \(i.e.,\) solar rays are perpendicular to the horizontal surface of the Earth. When the Sun is about \(41.8^\circ\) above the horizon, the air mass value becomes 1.5 (AM1.5) [173]. Even though a very small deviation on the optical properties of the solar selective absorber is observed to occur with the variation of air mass value, in the present work we have used AM1.5 to investigate the absorptance of our thin film coatings deposited on the aluminum substrates. This method has been suggested by Duffie and Beckman [168].

All objects emit thermal radiation in the form of electromagnetic waves at all temperatures above the absolute zero, and they absorb such radiation from the surrounding atmosphere. A warmer object emits more radiation than it absorbs, while a cooler one absorbs more radiation than it emits. Inevitably, the object arrives at a state at which the rate of heat absorption and emission are equal, generally, known as thermal equilibrium. Thermal radiation is a kind of em-radiation which is emitted from a light or heat source as a consequence of its temperature. It comprises of ultra-violet, visible and infrared radiations. It is produced by the thermal motion of charged particles in a
material. Above absolute zero, the kinetic energies of the atoms or molecules of any material is changing and thereby causing charge/dipole oscillations which in turn results in the creation of thermal radiation. Sunlight is a very common source that gives out thermal radiation generated by the hot plasma.

\[ E(\lambda, T) = \frac{2\pi c^2}{\lambda^5} \left( \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \right) \] (2.1)

where \( k = 1.38 \times 10^{-23} \text{ J/K} \) is the Boltzmann’s constant, \( c = 3 \times 10^8 \text{ m/s} \) is the speed of light and \( h = 6.63 \times 10^{-34} \text{ J.s} \) is the well-known Planck’s radiation constant, and \( T \) is the blackbody temperature in Kelvin. Planck’s law is applicable where the intensity of radiation emitted by a unit surface area into a fixed direction from a blackbody as a function of wavelength at a fixed temperature.

**Figure 2.** The solar spectrum distribution [174].

The wavelengths and the intensity of thermal radiation are dependent on the temperature and optical properties of the material. Thermal radiation is also known as blackbody radiation. Its surface absorbs all the incoming radiation and reemits the heat energy according to Planck’s phenomenon of blackbody radiation [175]. According to Planck’s theory, the spectrum emitted by a black body, \( E(\lambda, T) \) depends on the object’s temperature and is expressed by the following equation:
The total radiated power per unit area *i.e.*, the total radiant intensity of an ideal blackbody, is given by Stefan-Boltzmann’s law:

\[ E(T) = \sigma T^4 \]  

(2.2)

where \( \sigma \) is the Stefan-Bolzmann constant (\( \sigma = 5.6696 \times 10^{-8} \text{ W/m}^2\cdot\text{K}^4 \)) independent of material, surface and temperature. A hot object will always emit less efficiently than that of a cavity radiator, therefore, we can introduce an additional positive parameter, \( \varepsilon \), known as the emissivity. This emissivity is always less than 1 and its value will depend on the material, the surface, and the temperature. Thus, for a real material, Stefan's-Boltzmann law will take the following form:

\[ E(T) = \varepsilon \sigma T^4 \]  

(2.3)

Since the solar spectrum incident at the Earth’s surface falls in the wavelength range of 300 nm and 2500 nm (UV/Vis/NIR regions) with the maximum solar intensity is around 5500 nm, the optical characteristics of a practical object in the IR region can be characterised by its thermal emission compared to the radiation emitted by a blackbody. Following Fig. 3 shows the emission spectra of solar hemispherical irradiance for an air mass of 1.5 and blackbody-like object at various temperatures. Below 200 °C, no overlap between the solar energy confined in wavelength range of 0.3-2.5 μm and the thermal radiation emitted in wavelengths range of 2-30 μm was observed. With the increase in blackbody temperature, the emission also increases. At the same time, the power density peaks were also shifted towards shorter wavelengths. Thus, a thin film based device can be designed which absorbs the higher solar energy and emits a lower portion of the absorbed energy that is termed as a selective solar surface.
Figure 3. Hemispherical solar irradiance for air mass 1.5 (ISO standard 9845-1, 1992) and blackbody-like spectral emittance at 100 °C, 200 °C and 300 °C. Reflection curves for an ideal and real selective solar absorber are included. This picture is extracted from Ref. [172, 176].

It is to be noted that all the curves look quite similar. The total area under each curve represents the radiant intensity which is found to be increased as the temperature increases. The curves begin at zero intensity at zero wavelength, near γ-rays and X-rays, rise up to a peak value and then fall back slowly to zero as the wavelength increases. These measurements were recorded in the nineteenth century. In 1893, German Physicist Wilhelm Wien successfully interpreted the data. In his interpretation, Wien postulated that the wavelength at which the maximum of the curve occurred is inversely proportional to the absolute temperature of that material. This has been referred to as Wien's displacement law. The frequency of the radiation emitted by a black body can be computed from Wien’s displacement law. Wien was awarded the Nobel prize in Physics in 1911 for his revolutionary discovery. As an equation, Wien's law is expressed as follows:

\[ \lambda_m T = 2.8977685 \times 10^{-3} \text{ m} \cdot \text{K} \]  

(2.4)

where \( \lambda_{\text{max}} \) is the maximum wavelength and \( T \) is the absolute temperature of the black body. According to Wien's displacement law, the hotter an object is, the shorter the
wavelength at which it will emit most of its radiation. It also implies that the wavelength for maximum radiation power can be obtained by dividing Wien's constant by the temperature of the black body in kelvin. Therefore, Wien’s displacement law governs the shift of the peak to shorter wavelengths as the temperature rises, while the Stefan-Boltzmann law interprets the growth in the height of the curve with the increase in temperature of the blackbody. However, this growth is not continuous; rather, it is very abrupt since it varies with the fourth power of the temperature of the object.

2.7 Absorption of Electromagnetic Radiation by Thin Film Coatings

Electromagnetic waves are generated by the vibration of an electric charge and contain both the electric and magnetic field components. Light waves are electromagnetic waves that can travel, i.e., can transport energy from one location to another through the vacuum at a speed of $3.00 \times 10^8$ m/s. The transport of energy through a medium is related with the absorption and re-emission of energy by the atoms and molecules of the material. When EM waves are incident upon a material, energy is absorbed which causes the electrons to undergo vibrations. After passing through the medium, the intensity of the em-radiation is attenuated. The radiant energy is transformed into heat or some other form of molecular energy. The amount of energy absorption depends on a few factors such as the thickness of the absorbing medium, the electronic and nuclear constituents of the medium, wavelength of the incident radiation, temperature of the absorbing medium and the concentration of the absorbing material. In certain specific cases, electric and magnetic fields might also affect the absorption. If $I$ is the intensity of an electromagnetic wave after traversing a thickness $x$ of a medium and $I_0$ is the incident intensity of the beam at the surface, then the change of intensity throughout the medium can be expressed by Lambert’s law:

$$ I = I_0 e^{-\beta x} \quad (2.5) $$

where $\beta$ is a constant known as the absorption coefficient. In logarithmic form this exponential relation can be expressed as,

$$ \log \left( \frac{I}{I_0} \right) = -\beta x \quad (2.6) $$

The quantity ‘$\beta x$’ is also referred as the absorbance of the medium or, the optical density.
Absorption from the electromagnetic waves (visible or ultraviolet radiation) by a material always involves the loss of energy by the radiation, and a gain in energy by the atoms or molecules of the material. The energy absorbed from the electromagnetic waves is primarily used to excite electrons to higher energy states, and ultimately appears as increased kinetic energy of the molecules and released as heat.

The absorption coefficient, $\beta$, is defined as,

$$\beta = \frac{2\omega k}{c}$$  \hspace{1cm} (2.7)

The angular frequency $\omega$ can be defined as,

$$\omega = \frac{2\pi c}{\lambda}$$  \hspace{1cm} (2.8)

Combining Eqs. (2.7) and (2.8), Eq. (2.6) can be expressed as,

$$\log\left(\frac{I}{I_0}\right) = -\beta x = -\frac{4\pi kx}{\lambda}$$  \hspace{1cm} (2.9)

The factor, $kx/\lambda$ in Eq. (2.9) plays an important role in designing a thin coating which is a spectrally selective absorber. When $\lambda >> kx$, the film behaves as a transparent one. From Fig. 3 it is seen that the transition area from low to high reflectance at wavelength range ~2-3 μm can be estimated by choosing proper $k$ and $x$ values. At a certain specific wavelength, an intrinsic selective absorber has a constant $k$ value and $x$ is the only parameter which can be varied.

### Optical Properties of Thin Film Coatings

The optical properties of a material are defined as its response after being exposed to the electromagnetic spectrum of solar radiation. When a solar radiation is incident upon a material’s surface, part of it may be reflected back to the source, refracted through the material, absorbed by the material, transmitted through the materials or scattered by atoms and molecules depending on the transparency of the material. How light interacts with matter mainly depends upon the frequency of the incident radiation and the characteristics of the atoms of the matter. In the following sections we introduce some basic optical parameters, principles and concepts associated with the behaviors of electromagnetic radiation and their interactions with materials.
2.8.1 Optical Parameters

When solar radiation interacts with the surface of an object, a number of different reactions could occur, the result being dependent on the wavelength of the incident photon and the nature of the atoms of the material. In most cases, optical properties of solar absorber surfaces are expressed by two surface’s quantities: the solar absorptance, $\alpha$ and the infrared thermal emittance, $\epsilon$. These two parameters are expressed in several ways: monochromatic directional absorptance $\alpha(\mu, \varphi)$, the directional absorptance $\alpha(\mu, \varphi)$, the monochromatic hemispherical absorptance $\alpha_{\lambda}$, and the hemispherical absorptance $\alpha$, which differ from each other significantly, where $\mu$ is the cosine of the polar angle $\theta$ and $\varphi$ is the azimuthal angle. For example, monochromatic directional absorptance $\alpha(\mu, \varphi)$ is a surface property, whereas the directional absorptance $\alpha(\mu, \varphi)$ depends upon the wavelength distribution of the incoming radiation. Definitions and explanations of these four parameters are described by Duffie and Beckman [168]. In the following sections we discuss some of the specific optical parameters within the scope of this study.

2.8.1.1 Optical Reflection

As the light is incident on a surface at a certain specific angle, it changes the direction at the interface of two media and returns back into the medium from which it has originated. Reflection of light depends on the nature of the interface. Generally, reflection of light arises whenever light passes through the interface of two media having two different refractive indices and surface roughness. It is to be noted that a small fraction of the incident light is reflected from the interface while the rest is refracted through the surface. Reflection of light obeys the following rules:

a. The incident beam, reflected beam and the normal to the reflection surface all lie in the plane of incidence.

b. The angle of incidence must be equal to the angle of reflection.

Reflectivity or reflectance is also defined as the fraction of the incident light that is reflected at the interface. In mathematical form it is expressed as,

$$R = \frac{I_R}{I_0}$$  \hspace{1cm} (2.10)

where $I_R$ and $I_0$ are the intensities of the incident and reflected light respectively. In the case of normal incidence the reflectivity is measured by Fresnel’s equation

$$R = \frac{(n_2-n_1)^2}{(n_2+n_1)^2}$$  \hspace{1cm} (2.11)
where \( n_1 \) and \( n_2 \) are the indices of refraction of two media. However, if the incident beam is not perpendicular to the interface, \( R \) will be a function of the angle of incidence. Since the index of reflection of air is near about unity, hence when light travels from air into a solid medium the reflectivity is given as,

\[
R = \frac{(n_1 - 1)^2}{(n_1 + 1)^2}
\]  

(2.12)

Accordingly, the higher the index of refraction of the solid medium, the lower the reflectivity is. The refractive index of a solid material depends on the incident beam’s wavelength, thereby the reflectivity also varies with the wavelength.

### 2.8.1.2 Optical Refraction and Refractive Index

Two optical constants: refractive index (\( n \)) and the extinction coefficient (\( k \)) are conveniently used to represent the propagation of electromagnetic waves and the dissipation of energy in the medium of propagation. Assuming the material to extend indefinitely, the complex refractive index can be defined by the following function,

\[
\tilde{N} = n + ik = \left( \varepsilon \mu + i \frac{4 \pi \sigma}{\omega} \right)^{1/2}
\]

\[
= \left[ \mu (\varepsilon + i \frac{4 \pi \sigma}{\omega}) \right]^{1/2}
\]

\[
= \left[ \mu \varepsilon \right]^{1/2}
\]

(2.13)

Complex wave vector,

\[
\tilde{q} = \frac{\omega}{c} \tilde{N}
\]

\[
= \frac{n \omega}{c} + i \frac{k \omega}{c}
\]

where the refractive index \( n \) and the extinction coefficient \( k \) are defined in terms of by the conductivity \( (\sigma_1) \), the permeability \( (\mu_1) \), and the dielectric constant \( (\varepsilon_1) \):

\[
n^2 = \frac{\mu}{2} \left[ \left( \varepsilon^2 + \left( \frac{4 \pi \sigma}{\omega} \right)^2 \right)^{1/2} + \varepsilon \right]
\]

(2.15)

\[
k^2 = \frac{\mu}{2} \left[ \left( \varepsilon^2 + \left( \frac{4 \pi \sigma}{\omega} \right)^2 \right)^{1/2} - \varepsilon \right]
\]

(2.16)

Equations (2.15) and (2.16) relate to the propagation of the electromagnetic waves in the matter. The quantities \( \varepsilon, \sigma \) and \( \mu \) are defined only when \( \omega = 0 \). Thus, in terms of \( n \) and \( k \) the dielectric constant, permeability and conductivity are expressed:

\[
n^2 - k^2 = \varepsilon \mu
\]

(2.17)

\[
2nk = \frac{4 \pi \mu \sigma}{\omega}
\]

(2.18)
Thus, Eq. (2.13) can be rearranged as,

\[ \hat{N}^2 = \mu(\varepsilon + i \frac{4\pi\sigma}{\omega}) = \mu \varepsilon \approx \frac{4\pi \mu \varepsilon}{\omega} \quad (2.19) \]

The absolute value of \( \hat{N} \) and the phase difference \( \phi \) between the magnetic and dielectric field vectors are given by,

\[ |\hat{N}| = \left( n^2 + k^2 \right)^{\frac{1}{2}} \quad (2.20) \]

\[ \tan \phi = \frac{k}{n} \quad (2.21) \]

In an ideal insulator or in free space, the electric and magnetic fields are in phase because \( k = 0 \). However in a metal at low frequencies, \( n \approx k \) and phase difference \( \phi = 45^\circ \).

### 2.8.1.3 Optical Scattering

Scattering is a physical process where various types of waves (light, sound etc) or particles are deviated from their straight trajectory due to some localized irregularities in the medium which they pass through or at the interface between two media. Scattering may arise as a result of the physical collision between electrons, protons, atoms, molecules, photon or other kinds of particles. Absorption and scattering are two major physical processes that contribute to the visible appearance of most objects. The visual appearance of an object which is described as white is caused by the multiple scattering of light by internal or surface inhomogeneity. A highly scattering surface of an object appears dusty or dull whereas in the absence of scattering the object exhibits a refined and glossy appearance. Scattering in light can be caused via two mechanisms: surface scattering and volume scattering. Surface scattering emerges from the interaction of photons of light with the surface of a material, while volume scattering occurs only in the bulk of the material and is completely independent of the surfaces of the material. Surface scattering of light is a consequence of the interaction of light photons with the electric field of a particle or molecule of a material. The incident photons induce oscillating dipoles around the electron cloud and radiate energy in all possible directions. This radiated energy is known as the scattering of light. Scattering of light by individual particles depends on the particle’s size, refractive index and wavelength of the incident light.
2.8.1.4 Solar Absorptance and Thermal Emittance

The incidence of solar radiation on a non-metallic material can be absorbed via two mechanisms: electronic polarization and valence band-conduction band electron transitions. The first kind of absorption is important only at light frequencies around the relaxation frequency of the constituent atoms, while the second mechanism involves valence band-conduction, band electron transitions that depend on band-gap, and band structures. When solar radiation impinges upon the surface of a material, it is absorbed by the excitation of an electron from the nearly filled valence band travels across the band gap, and into an empty state within the conduction band. This phenomenon has been described in the following Fig. 4. As a result, a free electron is created in the conduction band leaving a hole behind the valence band. Absorption of light photon satisfies the following relationship,

\[ h\nu \geq E_g \]  

(2.22)

![Diagram showing photon absorption in a material](image)

Figure 4. Phenomenon of photon absorption in a material.

In terms of wavelength, Eq. (2.22) can be written as,

\[ \frac{hc}{\lambda} \geq E_g \]  

(2.23)

Maximum and minimum band-gap energy at which light is absorbed in a material can be computed using the following two Eqs.:

\[ E_g(\text{max}) = \frac{hc}{\lambda_{\text{min}}} \]  

(2.24)
\[ E_g'(\text{min}) = \frac{hc}{\lambda_{\text{max}}} \]  

However, the intensity of the absorbed solar radiation depends on the nature of the medium and exponentially decreases with the distance traversed by the light according to the Eq. (2.5). In Eq. (2.5), \( I_0 \) is the intensity of the incident radiation and \( \beta \) is the absorption coefficient, characteristic of the particular material. Materials that possess large \( \beta \) are highly absorptive. Upon the incidence of solar radiation on the surface of a material, some part of the light is absorbed, some portion is reflected back to the medium while the rest is transmitted through the material. This is demonstrated in the following Fig. 5.

![Diagram of solar radiation absorption, reflection, and transmission](image)

**Figure 5.** Phenomenon of absorption, reflection and transmission of solar radiation.

For certain incoming solar radiation, according to the principle of conservation of energy, the summation of the solar absorptance, reflectance and transmittance is unity and can be expressed by the following relationship,

\[ \alpha(\lambda) + \rho(\lambda) + t(\lambda) = 1 \]  

Generally for a highly reflecting metal or opaque surface, the transmission coefficient is zero \( i.e., \ t(\lambda) = 0 \) and energy is absorbed or reflected from all directions. In thermodynamic equilibrium, for a certain specific wavelength the absorptance of an object is equal to the emittance. Combinations of these phenomena give out the following relationship:

\[ \alpha(\lambda) = \epsilon(\lambda) = 1 - \rho(\lambda) \]  

(2.27)
The solar absorptance of a material’s surface is defined as a fraction of the solar radiation incident on the surface of the material that is absorbed. The solar absorptance is a function of both the incident spectrum and the reflection function of the material. From Eq. (2.27), the solar absorptance of a material can be conveniently computed via Duffie and Beckman method using the following relationship [168],

\[
\alpha = \frac{\int_0^\infty I_s(\lambda)(1-\rho(\lambda))d\lambda}{\int_0^\infty I_s(\lambda)d\lambda} \quad (2.28)
\]

Here (1- \( \rho(\lambda) \)) is the absorbed light, where \( \rho(\lambda) \) is the measured reflection as a function of the wavelength \( \lambda \) and \( I_s \) is the intensity distribution of the incoming solar radiation. The solar spectrum has an air mass of AM1.5 in accordance with the ISO standard 9845-1 (1992).

The spectrum of a blackbody is temperature dependent. The solar emittance is defined as the weighted fraction (by total power density) of the emitted radiation and can be calculated using the intensity distribution of a blackbody spectrum within the operating temperature of the absorbing medium. For high temperature applications, this is generally regarded to be greater than 400 °C. The operating temperature is estimated as the temperature at which the solar absorptance becomes equal to the solar emittance and temperature reaches static equilibrium. Thus, the equilibrium temperature can be computed according to the Stefan-Boltzmann law,

\[
T = 4 \sqrt{\frac{S\alpha}{4\epsilon \sigma}} \quad (2.29)
\]

where \( S \) is the solar constant and \( \sigma \) is the Stefan-Boltzmann’s constant. From Eq. (2.27), the thermal emittance of any material can be estimated via Duffie and Beckman method [168],

\[
\varepsilon = \frac{\int_0^\infty I_p(\lambda)(1-\rho(\lambda))d\lambda}{\int_0^\infty I_p(\lambda)d\lambda} \quad (2.30)
\]

where \( I_p \) is the intensity distribution of the Planck black-body.

The solar absorptance and thermal emittance are material-dependent parameters which can be estimated from optical measurements. The solar absorptance and thermal emittance can be also measured following the tables of spectral distribution versus equal energy increments [168].
2.8.1.5 Solar Selectivity

Generally, an ideal solar selective surface would have zero reflectance in the visible range of the solar spectrum and 100% reflectance in the infrared region of the solar spectrum. This corresponds to the thermal radiation spectrum of a blackbody at the operating temperature of the absorbing surface. In real life, no such ideally selective surface exists which absorbs 100% of the incident solar radiation in the visible range and reflects 100% of the incident solar radiation in the IR range, however in the laboratory we can fabricate solar selective materials that can maximize the solar absorption in the visible range and minimize the energy lost via thermal emittance. A very common way of preparing a solar selective surface is to apply a highly solar absorptive thin film onto a non-selective highly reflective metal substrate. This is known as an absorber–reflector tandem system. Absorption, transmission and emission from such an absorber–reflector tandem system are depicted in Fig. 5. The spectral features of an ideal solar selective surface and the basis of a real solar selective surface are demonstrated in Fig. 3. At earth’s surface, the incident solar flux is limited to the range between 0.3 and 2.5 μm (in the UV-Vis-NIR wavelength range) with a maximum solar intensity at 0.55 μm. In the infrared and far-infrared (IR-FIR) range of the solar spectrum, the optical response of a real material is, generally, characterized by its thermal emission compared to an ideal blackbody at 100, 200 and 300 °C. From Fig. 3, it is seen that as the temperature of the blackbody increases, energy emission is increased and the peak position is shifted towards shorter wavelength sides. These features indicate the potential of patterning a material that absorbs the maximum amount of incident solar radiation and reemits a minimum amount of the absorbed radiation, thereby forming the basis of an ideal solar selective surface. The performance criterion of a solar selective surface is generally evaluated by the ratio of the solar absorptance ($\alpha$) to the thermal emittance ($\varepsilon$) via following relation,

$$s = \frac{\alpha}{\varepsilon}$$  \hspace{1cm} (2.32)

This important parameter, $s$ is known as the solar selectivity of the solar selective surface.
2.9 Selective Solar Surfaces

In order to understand the behaviour of the absorbing surfaces, knowledge of the blackbody spectrum at a given temperature and the distribution of the solar spectrum are essential. The solar spectrum incident at the surface of the earth is limited in the wavelength range of 0.3 to 2.5 μm \textit{i.e.}, UV-Vis/NIR wavelength ranges. The solar reflectance measurements are conducted in the wavelength range 0.3-2.5 μm at near normal (\(\theta \approx 0\)) angle of incidence \textit{i.e.}, the solar absorptance is characterized at which the sun is at the zenith angle relative to the absorbing surface. In the case of oblique incidence, the near normal solar absorptance must be modified for the characterization of solar thermal collector devices. The optical properties of an object in the IR region can be estimated by its thermal emittance compared to the ideal blackbody. As is observed in Fig. 3, the blackbody spectrum for temperatures between 50 to 100 °C and the solar spectrum do not overlap each other, hence, one can design a surface which absorbs the maximum possible of the incident solar radiation and which emits the least energy. Such a material with high absorptance and low reflectance in the visible region, and low emittance and high reflectance in the infrared wavelength range is called a selective solar surface. A spectrally selective solar surface has different spectral reflectance at different wavelengths. An ideal selective solar absorbing surface should have a zero reflectance in the visible range (between 0.3 and 3 μm) and unity in the IR region (between 3 and 50 μm) which does not exist in nature, and it is not possible to fabricate such a device either.

Historically, the selective solar surfaces have been studied in detail since the 1950’s, when the idea of using wavelength separation was introduced by Tabor [177]. A very large number literature is available on the detailed overview, design and fabrication of selective solar surfaces such as intrinsic absorbers, coating/metal tandems, optical trapping absorbers, particulate coatings, semiconductor/metal tandems, multilayer thin films, transparent heat reflector/absorber tandems and transparent and heat reflecting and conducting coatings [31, 32, 178-180]. Fig. 6 shows a few examples of some selective solar surfaces which are available. The most common type of spectrally selective solar absorber is an absorber-reflector tandem composed of a combination of two surfaces: a highly absorbing surface in the solar spectrum and a highly reflective surface in the infrared regions. They are the most common types of commercially available selective absorbers [178, 179]. Cermet or ceramic surfaces consist of small particles embedded in a dielectric matrix deposited on a highly infrared reflecting metal substrate [35]. A high degree of flexibility together with design optimization in the choice of constituents,
particle concentration, coating thickness, shape and orientation of particles are offered by metal particle/dielectric selective solar surfaces [179].

Figure 6. Configurations of different types of selective solar surfaces for the absorption of solar energy.

A significant amount of effort has been devoted to the development of absorber-reflector metal tandem selective absorbers by many research groups [30, 47, 181, 182]. In the 1970’s, multilayer coatings were prepared and utilized for the control of satellite
temperature within the space programmes in the USA and the Soviet Union via vacuum deposition techniques [29]. These types of coatings were also useful for terrestrial applications. In the past few decades selectively solar-absorbing coatings have been studied and developed using various methods [35].

Metal–aluminium nitride (M–AlN) cermet selective solar coatings were deposited by a novel direct current, magnetron sputtering system in which AlN worked as the ceramic component in the cermets and stainless steel [183]. An electrochemical deposition method was employed for the development of black chromium or black nickel thin film based selective surface for the efficient conversion of solar thermal energy with good selective properties [184]. There are several ways of designing a selective surface ranging from simple black painted surfaces to sophisticated optical systems. The optical characteristics of various types of selective surfaces are elaborately described in Ref. [26, 185]. High absorptance in the visible range and low emittance in the infrared range, together with a low manufacturing cost, large production volumes, high thermal and mechanical stability and long-term durability are the key factors for the industrial development of selective solar surfaces. In following sections we discuss the designs of various types of selective solar absorbing surfaces.

2.10 Selective Solar Absorber Designs

Various types of designing routes are followed to develop the selective solar surfaces on substrates with different optical properties [30, 47, 168, 179, 186-188]. It has been reported in earlier investigations that some of the transition metal compounds and semiconductors were found to work well as intrinsic selective materials [47, 189]. Among them, the most common absorber type is the absorber-reflector tandem. In the following sections we discuss some of the widely applied selective solar absorber designs. A common absorber-reflector tandem type selective absorber consists of two layers, the bottom layer which is highly absorbent in the visible wavelengths range and another highly reflecting top layer in the infrared region [190, 191]. Most of the commercially manufactured selective absorbing surfaces are of this type. Some of the designs are discussed below.
2.10.1 Semiconductor Coatings

Semiconductor based low band gap spectrally selective solar coatings can be deposited on a highly infrared reflecting metal substrate so that it absorbs the solar radiation. When the light energy is incident upon the semiconductor coatings, photons having energy greater than the band gap are absorbed while the photons with energy less than the band gap energy are transmitted through the coatings. To achieve high solar absorptance, the refractive index of the semiconductor should be kept to a minimum; however, semiconductor coatings have a high refractive index. Minimum refractive index can be accomplished by controlling the thickness of the coatings or by applying an antireflection layer to obtain a destructive interference effect. SiO$_2$, Si$_3$N$_4$, and Si etc can be used as an anti-reflection coating on top of the multilayer stack [192].

2.10.2 Textured Surface Coatings

Spectrally selective surfaces can be successfully deposited by creating texture of a suitable scale on metal substrates. The textured surface absorbs energy by capturing the solar radiation by multiple reflections and absorptions processes. In the case of larger wavelengths, surfaces behave as fairly smooth ones and thereby working as a poor radiator i.e., emits low thermal energy. Textured copper, nickel, and stainless steel prepared by sputter etching are common examples of textured metal surfaces [193, 194]. Microstructural morphology of the textured coatings can be shown as a top absorbing layer of air filled metal i.e., rough surface backed by a highly reflecting metal substrate. Optical characterizations of such coatings can be performed using the effective medium theories as reported in Refs. [195, 196].

2.10.3 Composite Coatings

Composite based selective solar coatings are usually transition metals embedded in an oxide matrix. They are also called cermets. Composite coatings are usually deposited on a highly infrared reflecting metal substrate. Composite coatings absorb solar radiation strongly and are almost transparent in the IR region and exhibit good optical properties appropriate for selective solar absorbing surfaces [188, 197]. By controlling the thickness of the composite coatings the wavelength of the transmittance-absorption transition can be controlled, thus providing a high degree of flexibility to solar selectivity. Composite coatings with thickness 0.5 to 1.0 μm, and volume fraction of 0.3 to 0.4, have a solar absorptance of between 0.94 to 0.97 and a thermal emittance of ~0.10 to 0.20 [188, 197-
The optical properties of composite based coatings can be also considered in light of effective medium theory [195, 196, 200, 201]. Size dependent selectivity of composite coatings can be predicted with the application of effective medium theory. Nowadays, metal-dielectric based selective solar surfaces e.g., molybdenum-aluminium oxide (Mo-Al₂O₃), nickel/nickel oxide (Ni-NiOₓ), both produced by sputtering, nickel pigmented anodic aluminium oxide (Ni-Al₂O₃), and electroplated black chrome (Cr-Cr₂O₃) are commercially available for flat plate solar collectors [188]. Ceramic-metal absorber with an AR coating could attain a solar absorptance in the range of 0.91 to 0.97 and a thermal emittance of 0.02–0.07 [202]. Fig. 7 shows examples of different types of composite coating solar selective absorbers. Nickel pigmented anodic aluminium oxide (Ni-Al₂O₃) and sputtered nickel/nickel oxide (Ni-NiOₓ) composite coatings are available in Refs. [48, 198, 203]. In Ni-Al₂O₃ composite coatings, the particles are uniformly distributed in the matrix, while in Ni-NiOₓ the particles are arranged with graded index composition. In cermet coatings, the absorption is due to the light scattering by the boundaries between the metallic phase and the dielectric phase [204, 205]. In cermets, the metallic particles work as a modifier for the optical response of the ceramic phase [29, 96]. Metal/dielectric film based graded composite selective absorber exhibit very high solar absorptance [32]. The graded composition is designed with a continuously decreasing refractive index and an extinction coefficient from the substrate to the AR coating surface [32]. An ideal selective absorber has a refractive index, \( n = 1 \) and extinction coefficient, \( k = 0 \), in order to avoid refraction mismatch between air and the top coating. The small particle composites in graded surfaces have large \( n \) values, and high metal fraction composites are needed to permit the utilization of the interference effect and to obtain a sharp absorptance edge [178]. Therefore, an AR coating is required to reduce the reflection from the front surface. A real AR coating should have a refractive index approximately midway between air (\( n = 1 \)) and the underlying metallic selective absorber (\( n \approx 2.3 \)) which can be accomplished by common dielectrics. Thus, an AR material compatible with any particular selective absorber can be chosen [178]. For example, 80 nm thick Al₂O₃ coatings can serve the purpose regarding this matter [32, 178]. Comprehensive descriptions about the designs and use of AR coatings are found in earlier reports [206-208].
Different types of composite coatings for the absorption of solar energy.

2.10.4 Painted Coatings

Selective solar absorbing paints are tandem types of absorbing particles which are uniformly distributed in a matrix which can be produced on a metal substrate. These types of selective coatings are simple and cost-effective [209-217]. This type of absorber falls in the category of the tandem type, with absorbing particles uniformly distributed in a matrix deposited on a metal substrate [218]. Optical performances of the SSA paints are governed by intrinsic optical constants, particle size-dependent scattering and absorption. Selective paints usually contain various types of polymers as binders that absorb IR radiation and hence the thermal emittance of such paints become higher and thereby results in a low selectivity.
Furthermore, it is not feasible to make paint coatings thinner than 1–2 μm because the thickness of the paint layer is limited by the size of the ground pigment particles [219]. The particles usually agglomerate and their size becomes comparable to or larger than the incident wavelength of light, thereby reducing the optical performance of the paints. Fumed silica is usually added to the paints to reduce the particle agglomerations. Experimental studies on iron-manganese-copper oxide pigment with a silicone binder offer a solar absorptance of 0.92 and a thermal emittance of 0.13 [220]. The spectral selectivity of such pigment coatings depends on the dispersion of the particle size in the matrix, particle volume fraction and thickness. The Solarect-Z, and the SolkoteHI/SORB-II™ are the examples of two commercially developed selective solar absorbing paints. In order to reduce the thermal emittance of selective paint coatings, a spinel-type CuCoMnO₄ pigment coating without binder have been suggested following a simple method via the sol-gel synthesis [219, 221]. In other investigations, spinel or metal oxide type solar absorbers of less than three components of transition metal are reported [10, 222, 223]. The CuMn spinel oxide coating has been found to show smart performance for industrial applications [223].

### 2.11 Antireflection Layer

Anti-reflection coating is a kind of optical layer forming part of an optical device to minimize the reflection of the incident radiation and thereby enhancing the optical performances of the system by utilizing the maximum amount of incoming energy. In the case of an antireflection layer, the reflected waves from different optical interfaces partially or totally cancel each other out by means of destructive interference. If the thickness of the coating is a quarter wavelength and refractive index is less than the substrate, then the two reflections are 180 degrees out of phase. The thicknesses of the layers are selected to create destructive interference in the reflected beams, and constructive interference in the transmitted beams. A suitable wavelength range must be chosen for the design of such coatings. For spectrally selective absorbing surfaces, the incident solar energy should be absorbed to the maximum possible level without reflection from the surface. This can be achieved by putting an antireflection (AR) layer on top of the selective solar surface [208]. The best refractive index value of the AR layer is when its refractive index is equal to the square root of the refractive index of the material on which it is deposited. This is only valid for non-absorbing dielectric materials. The AR layer will increase solar absorptance without increasing the emittance.
value for a sufficiently thin (<100 nm) AR layer [224]. Silica or titania normally provides suitable refractive indexes as AR thin films.
CHAPTER THREE: RECENT ADVANCES ON SOL-GEL AND SPUTTERED COATINGS AS SOLAR SELECTIVE SURFACES AND MECHANICAL APPLICATIONS

3.1 General Introduction

This chapter includes comprehensive literature reviews, fundamental theories and principles, and recently published results on the importance of including graphene, graphene oxide with sol-gel derived 3d transition metal oxides-based thin film coatings for their energy related, solar selective surface and mechanical applications. In addition to the mixed metal oxide based thin film coatings, a few binary, ternary and quaternary 3d transition metal nitride based sputtered coatings are also discussed for the aforementioned purposes.

3.2 Recent Advances in Mixed Metal Oxide-based Coatings

Due to their impressive structural diversity and their wide range of physical, mechanical, chemical and electrical properties, thin film coatings based on transition metal oxides are found in a wide variety of technological applications including photothermal conversions. Wide-spread applications and steadily increasing scientific interest in metal oxide based films have been dedicated to the development of new species of solar selective coatings with superior properties. As solar selective surfaces are the easiest and most direct way of harvesting solar energy, in recent years, transition metal oxide based thin film coatings have received significant attention for mid and high temperature applications [15, 17, 225-228]. It is well known that an ideal selective solar surface absorbs all of the incoming radiation, while the reflection is kept at a minimum in the visible range of the solar spectrum. Ideally, the reflection should be zero. In this instance the reflector is coated with a highly absorbing layer over the visible solar spectrum while the infrared region is made transparent. Various types of mixed metal oxide with thin film based selective solar surfaces such as Ni$_x$Co$_y$O$_z$, Mn$_x$Co$_y$O$_z$, Cu$_x$Co$_y$O$_z$, PtAl$_2$O$_3$, MoAl$_2$O$_3$, CuAl$_2$O$_3$, NiAl$_2$O$_3$, CuFe$_2$O$_4$, CuCo$_2$O$_4$, and CuMn$_2$O$_4$ are thoroughly investigated by many groups [51, 53, 225-229]. These mixed metal oxides based coatings have found wide-spread applications such as selective solar absorbers, dye sensitized solar cells, batteries and memory devices, absorption optimization and industrial purposes [85, 86]. Optical and other properties of these materials can be modified by selecting the elements and controlling the process...
parameters which alter the density of free electrons in their $d$-bands. In light of the importance of solar selective materials for the photothermal applications, detailed knowledge of the synthesis process and its recent developments would be very useful for material scientists who wish to optimize its favorable physicochemical properties.

Due to their many beneficial properties, graphene-based materials have been widely explored in the area of photovoltaic research. Although graphene oxide is a relatively new material, from current literature regarding its practical applications, it is now seen as a smart candidate and has already made a widespread research impact across many disciplines including a cleaner alternative for the energy generation processes. Graphene has a large surface area and therefore offers very high optical absorbity and has many applications such as in energy conversion. The high optical absorption and tunable optical bandgap are the most appealing characteristics of graphene that make it an ideal material for effective light harnessing [124]. Due to its exceptionally high carrier mobility and superior electron transfer properties, graphene has great potential to be used for making flexible, cost-effective and high performance photovoltaic devices [230]. Light absorbing photovoltaic applications of graphene based materials have been reported in earlier research [125]. The characteristics of graphene such as surface affinity, electrical conductivity, work function, oxide-group defects, surface free energy, and bandgap (an important aspect in the future of graphene-based), offer a potentially viable route for engineering better product performance [231]. Meanwhile, research on the real life applications of graphene based materials in the field of energy generation, conversion and storage are emerging as highly appealing e.g., solar cells, supercapacitors, fuel cells and lithium ion batteries [134]. There are many reports which substantiate the importance and outstanding potential of graphene-based composites being used in the manufacture of high-performance energy-storage devices [232-234]. In an extensive review, Brownson et al. [235] present their findings on the electrochemical applications of graphene in energy storage and energy generation devices e.g., super-capacitor, lithium ion batteries and fuel cells. Optical absorption and power conversion efficiency of layer-transferred graphene in organic hybrid solar cells have been reported in earlier studies [126]. In organic photovoltaics (OPVs), graphene oxide (GO) was used as a hole injection layer (HIL) in conventional OPVs and a power conversion efficiency of 3.5% was achieved [236]. Another study used reduced graphene oxide (rGO) as an anode buffer layer in OPVs and found that with the introduction of rGO, the final PCE was 4.8%. However, with a GO buffer layer the PCE was found to be 5.6%, whereas without a GO buffer layer, the
reported PCE was only 4.1% [237]. In a more recent report, reduced GO based organic PV devices achieved an overall power-conversion efficiency of 1.1% [238]. Application of graphene in organic photovoltaic devices has been realized by several other groups [127, 128]. In order to achieve improved efficiency, graphene is a promising candidate for many practical applications in energy related areas and light harvesting devices e.g., inorganic [129], organic [130, 131], hybrid [132], and dye sensitized solar cells [133].

There have been a series of comprehensive reviews focused on investigating the properties, manufacturing processes and application of graphene and graphene-based materials in energy related areas [114, 134, 135]. Optimization of optical properties of graphene oxide by mixing with inorganic compounds to form a hybrid system is also feasible in the development of GO based selective surface. Since GO offers good solubility in aqueous and polar solvents, hence the sol-gel method is a feasible technique to prepare GO based thin films. In the earlier literature, it has been shown that the hybrid film of GO and CNTs worked well as a buffer layer in polymer type tandem solar cells [239].

Ultra-thin graphene films fabricated from exfoliated graphite oxide has been demonstrated as transparent, conductive electrodes for solid-state dye-sensitized solar cells [133]. Superior electrical behaviors have been reported in graphene based composite materials [240]. Due to its higher electrical conductivity, high carrier mobility and high optical transmittance in the visible light, graphene oxide has been established as a promising precursor to the synthesis of transparent conductive films (TCFs) [241]. Detailed descriptions about the recent advances in the improvement of physicochemical behaviors of reduced graphene oxide and its applications as energy storage electrode materials have been reported in Ref. [242]. In their comprehensive review work, Chen et al. [243] reported that graphene oxides have potential applications in the field of electrochemistry. Graphene and graphene based materials such as GO have become promising subjects of research due to their ultra-sensitive sensor response and the lowest detection capability. Detailed descriptions of the latest advancement and new perspectives of graphene based gas and vapor sensors have been discussed in another review [244]. Because of its potential as electrode materials and having a capability of electron or hole transfer along its 2D surface area, graphene and graphene based materials are commonly used as clean energy devices in rechargeable lithium ion batteries and electrochemical double layer capacitors [241]. Further studies also show that graphene and graphene-based materials have a remarkable impact on the electronic
and optoelectronic devices, nanocomposites, chemical sensors, energy conversion and energy storage devices [245, 246]. Quantum dots based graphene oxide solar panels show benchmark efficiencies in range of 4.4–5.4% [247]. Fabrication technology, properties and applications of graphene and graphene derived materials in energy related areas are reported in a series of extensive reviews [114, 134, 135, 248]. A superior power conversion efficiency was attained by integrating graphene into titanium oxide based DSSCs [249]. In another report, organic photovoltaic cells manufactured with a graphene oxide doped single-walled carbon nanotube has been achieved a PCE value of 2.7% whereas the PCE value of pristine single walled carbon nanotube anodes was reported to be 0.44% [250]. Wet chemistry processed fullerene, single-walled CNTs, and GO derived thin film based PV solar cells with good power conversion efficiency and higher environmental stability have been reported [251].

3.3 Recent Advances on Mixed Metal Nitride-based Thin Films

Over the years research interests on metallic nitride based thin film coatings in pure states and with various dopants have received substantial attention because of their large band-gap, high hardness, good electrical and thermal conductivity, high melting points, high surface acoustic velocity, are corrosion resistant, oxidation resistant, have excellent chemical and thermal stability and physical robustness [59-70, 149, 252]. Due to this unique combination of numerous properties, these materials are thoroughly investigated both theoretically and experimentally for a large variety of applications as outlined in Chapter 1 under the Section 1.3.

X-ray absorption near-edge structure (XANES) has been used to study the Al-incorporated titanium nitride [253]. In their study, the authors discussed the bonding and structural evolution of the TiN thin films with the increase in Al-addition, and the spectral changes were correlated. Their study gave a complete report on the local atomic structure. Meanwhile, attempts to produce new doping materials and efforts to improve their novel properties have never ceased [254]. In recent years, the interest of researchers in studying large band-gap semiconductors with various dopants have been accelerated because of their potential applications to spintronics and nonvolatile storage [65-67]. Wide band gap binary nitrides such as AlN, GaN and InN have been popular wide range applications in ultraviolet and visible light emitters and detectors, and optical storage devices [149]. Due to the excellent chemical and thermal stability and mechanical hardness, GaN and AlN are also suitable for microelectronic devices [18]. Structural,
optical and electrical properties of Mn and Cr-doped GaN diluted magnetic semiconductors (DMSs) are widely investigated due to their potential applications in electronic and spin-dependent photonic devices [8-10]. In Ref. [11] structural properties and growth mechanisms of Cr-added AlN, GaN and InN are discussed. Electronic structure of plasma assisted pulse laser deposited AlN, CrN and Cr-doped AlN thin films were studied by X-ray absorption (XPS) and soft X-ray emission spectroscopy at the near K-edge [6] and results were compared with that of density function models. Due to the large band-gap (6.2 eV), high surface acoustic velocity, thermal and physical robustness AlN is used in the semiconductor industry for optoelectronic devices at high power and temperatures [6]. Ti-Ni alloys are widely used in the design of instruments, aerospace technologies and medicine [255-257] because of their improved functional and mechanical properties such as superelasticity and shape memory effects. There are many publications available which explain the correlation between electronic structure and phase stability of these materials [258-261].

Hard coating materials can be synthesized via reactive magnetron sputtering [262-264], cathodic arc ion plating [265-267], and beam plasma-assisted physical vapor deposition [268]. The hard coating materials can be also produced by a combination of a hard, and relatively brittle nitride with a soft metal in order to attain a better fracture toughness [269-272]. This concept was primarily used for the production of cemented carbide (WC–Co) where WC delivers the high hardness while cobalt metal refines the fracture toughness [273]. In another report, superhard nanocomposite coatings are designed with the combination of a hard transition metal-nitride (TiN, W2N, VN and others) and a covalent nitride (Si3N4, BN, etc.) [274-276]. These types of coatings show a thermodynamically driven, strong spinodal segregation [275] which results in high thermal stability of the nanostructure along with the superhardness (hardness >40 GPa) at high annealing temperatures [274]. Various methods have been suggested to harden and toughen some materials, however; at this point in time no single specific test procedure or unique system is available to measure the toughness of such coatings [277]. The toughening and hardening mechanisms of various nanostructured coatings and toughness measuring methodology have been described in a comprehensive review [277].

The superhardness which is observed in CrN coatings is mainly governed by grain size and grain boundary structures [278, 279]. Generally, the hardness of a material is increased with the decrease in its grain size [280]. If Si, Al or Ti are introduced into CrN, it has been found that the grain size within the material is reduced to tens of nanometres
which results in coating hardening [281]. At nano-scale grains, the formation of dislocations becomes tough and the hardness of the Cr_{1-x}M_{x}N coatings is thus controlled by its grain boundary [277]. Generally, nanostructured coatings are formed by two different nanocrystalline phases or a combination of a nanocrystalline and an amorphous structure, exhibit extraordinary physical and mechanical properties. The mechanical properties of nanostructured composite materials are dependent on the grain boundary angle, grain boundary structure, boundary sliding and movement of dislocations. Because of the very small grain sizes (~410 nm) and the important role of their grain boundaries, nanocomposite materials exhibit quite exceptional properties than that of their bulk states. The primary reason for the superior hardness of these nanocomposites is plastic deformation and the leading cause of dislocations. It is also believed that the cohesive forces appearing between atoms and compression macrostresses initiated during the period of the film synthesis process might also cause the hardening of the films [282]. Macrostresses are undesirable and can be avoided by close control over the film deposition process. Until now, only a few studies have been carried out which have investigated the role of these doping elements in modifying the grain boundaries of Cr_{1-x}M_{x}N coatings. More recently, a study of high resolution transmission electron microscopy (HRTEM) showed that Cr_{1-x}M_{x}N coatings consist of nanocrystalline grains surrounded by amorphous boundaries [283]. The impact of these amorphous boundaries on the material hardness is yet to be studied. Thus, there are enormous opportunities to tailor and carry out an investigation of the structure of the amorphous boundary for enhanced coating properties. Moreover, the oxidation resistance of materials at high temperatures is typically controlled by surface chemistry and the construction of grain boundaries [284]. In transition metal nitrides, native oxide layers are generally formed on the surface of the coatings [285], leading to a substantial increase in their heat-resistance. Addition of Si, Al or Ti hinders the penetration of oxygen along the grain boundaries and accordingly, the hardness of the coatings might be significantly reduced. Therefore, a study of structural and compositional characteristics of the oxide layer will provide more useful information about the impact on these coatings. Structural characterizations of CrSiN and CrAlN films [286] have been performed by means of cross-sectional bright field TEM (XTEM), high resolution X-ray photoelectron spectroscopy (HRXPS), XRD and nanoindentation techniques. The authors used the XTEM method to observe the factors influencing the mechanical properties of CrSiN coatings with the progressive addition of Si, while XPS and nanoindentation methods describe the surface chemical composition and physical hardness, elastic modulus and residual stress respectively. It
has been reported that grazing incidence X-ray diffraction (GIXRD) patterns of CrN coatings have been unaffected with the Al-doping [286]. Samples undoped and doped with low, medium and high amount of Al were identified to be cubic structure, however, other studies reported the existence of wurtzite structure of CrN with Al-doping. An XPS study found the existence of amorphous phase of AlN at the grain boundaries. Preferred orientations have been found to be altered by the Al-substitutions. According to the GIXRD data it has been observed that (200) preferred orientation is reduced monotonically with the increase in Al-content while a linear increase in the intensity is observed on (111) and (220) reflection planes [286]. Effect of Si on the TiN and AlCrN thin films were studies by Endrino et al. [59] by means of XRD and NEXAFS techniques. In few earlier investigations [68, 69], it has been observed that the addition of silicon can remarkably improve their physical hardness, toughness and oxidation resistance. As the amount of silicon content is increased the sample has been found to lose its crystallinity which is reflected in the broadening of their intensity peaks. Furthermore, it was observed that with the addition of 9 to 14 at.% of silicon, silicon appears in the form of silicon nitride (Si$_3$N$_4$) [59]. NEXAFS technology is widely used in solving complex systems and to identify the coexistence of various phases either in ordered (crystalline) or in a disordered (amorphous) state.

Superhardness has been also identified in TiN coatings by the addition of appropriate amount of silicon. Suitable amount of doping can promote various defects such as vacancy, interstitial atom, atom substitution, cluster, deformation, etc. Nowadays, researchers around the world are undertaking new dopants to initiate various defects in order to develop new interactions and improve the desired qualities. With the incorporation of silicon to the TiN, the microstructures of the coatings are changed from closely packed columnar grains to nanocrystals. It was also observed that the newly formed nanocrystals were embedded in a Si$_3$N$_4$ amorphous phase [287, 288]. The authors contend that this superhardness is due to the resultant effects of the fine grain size and strong interfacial bonding between the nanograins and amorphous outlooks. Various types of transition metal nitride based materials are commercially utilized as hard coatings, corrosion resistant and decorative coatings among other things [289]. Because of its superior hardness, nontoxicity and high chemical stability, TiN is extensively used as a protective coating material in mechanical equipment, cutting and polishing tools, molds, hard disks, dies, and medical implants [290]. The toughness, oxidation resistant behavior, corrosion resistance and thermal stability of these coatings can be significantly
altered by introducing aluminum Al [291]. The introduction of silicon to the transition metal nitrides substantially affects the grain size and phase formation and thereby enhance hardness, oxidation and corrosion resistance, toughness and other desirable characteristics [292-295]. Elaborate structural investigations of TiSiN coatings have been by means of X-ray diffraction (XRD) and transmission electron microscopy techniques [296, 297]. X-ray absorption spectroscopic (XAS) studies of TiSiN has identified the gradual changes in Si K-edge spectra in terms of the silicon content [294, 298]. Combining the TEM and XAS results, and taking into account the columnar nanodomains of TiN, the authors confirmed the dissolution of silicon in the titanium nitride system.

Silica-titania based thin films are largely used in many optical devices such as active and passive optical planar waveguides, and antireflecting coatings [71-75]. XPS [299], NEXAFS and EXAFS [300, 301], NMR [302, 303] and IR spectroscopy [304-307] are successfully used for the understanding and explanation of Si-based and Si-Ti based thin films. X-ray absorption fine structure (XAFS) spectroscopy analysis reveals that Ti$^{4+}$ ions are four-fold coordinated in Si-Ti based thin films while both 5 and 6-fold coordination have been reported for Na-Ti-Si based glasses [300, 301, 308]. Katsikini et al. [309] performed NEXAFS studies on binary AlN, GaN and InN nitrides and explained that the energy position of the absorption edge ($E_{\text{abs}}$) of these materials are redshifted monotonically with the atomic number of the cation. It is strongly believed that structural, electro-magnetic properties and the distribution of dopants are very closely related with doping content. XPS and NEXAFS investigations discussed how the electronic structure of Ti-Ni binary alloys changes with the atomic concentrations of the constituents of the alloy [310]. Theoretical and experimental NEXAFS study on $\beta$- and spinel types of silicon nitrides have been performed by Tatsumi et al. [311]. The authors in their experimental study noted that the local environments of Al are invariant of the composition while the theoretical prediction reported the chemical shifts of the reference materials. Elastic constants of silicon nitride were found to be decreased with the increase in Al-content [312], thereby causing lattice softening. This lattice softening is very significant with respect to applications and performances [312].

At high temperatures CrN binary coatings are not compatible with hot forming dyes and high speed machining applications [313]. In order to resolve these issues, the introduction of Zr, Si or Al into the CrN matrix has been successfully used [314-317]. CrZrN coatings are useful in high temperature applications [318]. The use of CrAlN as protective
coatings has been accelerated in recent years because of their improved corrosion and oxidation resistance and superior hardness [319, 320]. The thermal stability of CrAlN coatings is improved with the addition of silicon [321, 322]. A good combination of reasonably high hardness and high toughness is very important from an engineering applications view point as opposed to superhard coatings which have high brittleness. High toughness means high recalcitrance to crack generation under stress. In another report it was concluded that the introduction of silicon, aluminum, or yttrium significantly improves the high temperature characteristics of CrZr-based nitrides [323-325]. Very high hardness, high temperature wear resistance and superior oxidation resistance were observed in CrZr(Si/Al)N [323, 325]. The effect of aluminum on the microstructure, coating structure and mechanical characteristics of CrZrN with low and high amount of Zr-content were studied in terms of their hardness, toughness, adhesion, phase structure and particle morphology [313]. The extraordinary oxidation resistance property of chromium nitrides arise from the formation of the solid and preventive Cr₂O₃ layer on the surface of the coatings [326]. The oxidation resistant behavior of many other ternary coatings such as Cr(Ti/B/C/Ta/Nb)N was also explored in the earlier studies [327-335]. It has been established that Ti–Al–N and Cr–Al–N show better mechanical and oxidation resistance performances at higher temperatures in comparison with the conventional binary TiN and CrN thin film coatings [336]. This is due to the replacement of titanium or chromium atoms by aluminum atoms. It can be observed that TiN and CrN start to oxidize readily ~ 770 and ~970 K respectively while oxidation of TiAlN and CrAlN occurs above 970 K and 1170 K respectively [336].

Nanocrystalline titanium nitride thin films have found applications in different areas of semiconductor device technology e.g., gate electrodes in field-effect transistors, Al diffusion barriers and ultra-large scale integrated circuits [152, 337, 338]. Mutual interactions with the electrons in Ti and N atoms and the electronic structure of the stoichiometric titanium nitride affect the optical, electronic, and electrical behaviors of these nanocomposite films [339]. The complex dielectric function of TiN films was analyzed on the basis of intra-band absorption and inter-band transitions in terms of the free electron Drude model and the Lorentz oscillator model [339]. Furthermore, the combined Drude–Lorentz model was utilized to demonstrate the metallic nature of titanium nitride coatings and the origin of band structure modifications. Additionally, the XRD and electron microscopy validated the spectroscopic ellipsometry results and gave insights into the atomistic mechanisms affecting the grains morphology and their
correlation with the electronic and optical properties. In Ref. [151], magnetron sputtered TiAlN/TiAlON coatings synthesized onto a metal substrate exhibited high absorbance and low emittance. The absorbance of the coatings was substantially enhanced to 0.95 by adding Si$_3$N$_4$ antireflection coating on the top of films. A higher thermal stability and high solar selectivity of $0.95/0.07 = 13.57$ was achieved by this tandem selective surface.

In an experimental investigation, metal-like CrN and wide-band gap semiconducting Cr$_2$O$_3$ was combined with a reactive dc magnetron sputtered system in Ar/N$_2$/O$_2$ atmospheres to deposit CrON and modify their band-gap and electronic properties for optical and electronic applications [340]. Photothermal conversion of spectrally selective magnetron sputtered chromium oxynitride has been reported in previous study [18]. Correlations between chemical structure and optical properties [341-343], structural morphology and optical behaviors have been established [341]. Interrelationships among the mechanical properties, chemical composition, optical properties, and crystal structure of dc magnetron sputtered ZrCuN thin film coatings was investigated by Zeman et al. [344]. Microstructural study, the electronic and optical characteristics of various chromium nitride coatings deposited by unbalanced reactive magnetron sputtering was performed by Logothetidis et al. [345]. The influence of nitrogen flow to the phase formation in Cr, Cr$_2$N, CrN coatings was investigated to validate the XRD results. Using Drude-Lorentz model [339, 346] together with the electronic structure of Cr$_2$N, CrN, the experimental results reckoned the metallic character of Cr$_2$N phase and the semiconducting nature of CrN structure [347, 348]. Their study gave a complete outline of the local atomic structure of these materials. Meanwhile, attempts to produce new doping materials and research to improve their novel properties have never stopped [254].

3.4 Results

In the following sections, some significant results from recently published papers aimed at the synthesis of cobalt-based metal oxide thin films on glass and aluminum substrates via sol-gel dip-coating method and transition metal nitride based sputtered coatings deposited on steel substrates, are presented.
3.4.1 XRD Analysis of Metal Oxides-based Coatings

The XRD spectra of the Mn-Co, CuCo, Ni-Co thin film coatings deposited on aluminum substrates (with 2 and 6 dip-heating cycles, in a geometry of $2\theta = 10^\circ$ to $40^\circ$) show a marginal difference from the aluminum substrate patterns. Due to the poor crystallinity of sol-gel derived $M_xCo_yO_z$ (with $M =$ Mn, Cu, or Ni) coatings, the stoichiometric formulation of the metal-oxide phases were hardly detected by XRD analysis [21]. Temperature dependent XRD analysis of sol-gel synthesized Cu-Co coatings on aluminum substrates were carried out in our other report [228]. Bragg peaks observed at $2\theta$ positions of 35.3° (011), 36.9° (310) and 40.2° (301) were identified as orthorhombic CoCu$_2$O$_3$ phase (JCPDS 76-0442, space group = $P_{mmm}$ (59)). The peaks arisen at $2\theta = 31.3^\circ$ and 38.5° were recognized to mixed phases of CoCuO$_2$ (JCPDS 74-1855) and CuCoO$_2$ (JCPDS 21-0256). However, at a higher annealing temperature, the degree of crystallinity of the CoCu$_2$O$_3$ phase was observed to have increased along the (301) direction.

3.4.2 XPS Analysis of Metal Oxide-based Thin Films

Synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) was implemented to determine the surface electronic structure of the thin film coatings. Multiple oxidation states for copper e.g., octahedral and tetrahedral Cu$^+$, octahedral and paramagnetic Cu$^{2+}$ were observed whereas cobalt composed of mixed Co$^{2+,3+}$ oxidation states. The oxygen was from lattice, surface and subsurface oxygen [225]. It was noted that the increase of copper concentration promoted the formation of octahedral Cu$^{2+}$ and reduced the octahedral Cu$^+$ ions [226]. Further investigation showed the octahedral Cu$^{2+}$ ions replace the Co$^{2+}$ site in the cobalt structure host. However, the local coordination of Co, Cu and O were not changed, within experimental errors, by the different concentration ratios of [Cu] and [Co], except for the coating with [Cu]/[Co] = 2 where the local coordination had a small change due to the loss of octahedral Cu$^+$ [226]. The decoupling of O1s spectra indicates that metal-O bonding states dominate in the thin films, and there was a small amount of metal-hydroxyl bonding. The double pair of metal 2p XPS ((i.e., Cu2p (2p$_{3/2}$ and 2p$_{1/2}$), and Co2p (2p$_{3/2}$ and 2p$_{1/2}$)) peaks indicate that metal-O (oxidized metal) and elemental metal coexist in the thin film coatings. The oxidization state of metal from metal 2p XPS is consistent with the decoupling analysis of O1s spectra. The C1s peaks in all the XPS spectra are due to some carbides, C-H from pump oil and/or surface...
contamination due to air exposure of the sample before it was brought into the vacuum chamber for analysis.

### 3.4.3 Optical Properties of Metal Oxide-based Thin Film Coatings

Systematic studies of the optical properties of Cu$_x$Co$_y$O$_z$ thin film coatings with respect to varying [Cu]/[Co] concentration ratio, speed of dip coating, dip heating cycles and sintering temperature are explained in the following sections. Generally the optical performance of a thin film coating is described by two parameters: optical absorptance ($\alpha$), and thermal emittance ($\varepsilon$). In order to increase the effectiveness of a solar thermal energy system, absorption of incident solar radiation should be maximized and thermal losses from the collector minimized. The solar selective absorber surface is the key component of a solar collector and is a significant contributor to the efficiency in solar–thermal energy conversion. The solar absorptance of thin film coatings is strongly dependent on the surface morphology and surface roughness of the deposited layers. A rough surface minimizes the reflection of incoming solar radiation from the film surface, whereas pores contribute to reduce the refractive index. The relaxation mechanisms of the coatings together with the multiple reflections and resonant scattering in the pores around the film surfaces also contribute to enhance the absorptance behavior. The calculated solar absorptance values of Ni$_x$Co$_y$O$_z$, Mn$_x$Co$_y$O$_z$, and Cu$_x$Co$_y$O$_z$ coatings are based on the AM1.5 solar spectrum standard. The reflectance spectra of these coatings were recorded from 250 to 2500 nm using a UV–Vis-NIR Jasco V-670 double beam spectrophotometer with 60 mm integrating sphere. The solar absorptance values of these thin film coatings were calculated based on reflectance ($R\%$) following the Duffie and Beckman method as described in Ref. [349]. The absorptance values at a dip speed of 60 mm/min and various dip heating cycles are presented in Table 1 [21].

**Table 1.** Solar absorptance values of sol-gel derived NiCoO, MnCoO, and CuCoO coatings deposited on aluminum substrates.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Dip-heating cycles</th>
<th>Dip speed (mm/min)</th>
<th>Sintering temperature (°C)</th>
<th>Absorptance, $\alpha$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_x$Co$_y$O$_z$</td>
<td>2</td>
<td>6</td>
<td></td>
<td>24.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>500</td>
<td>32.20</td>
</tr>
<tr>
<td>Mn$_x$Co$_y$O$_z$</td>
<td>2</td>
<td></td>
<td></td>
<td>32.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td></td>
<td>32.60</td>
</tr>
<tr>
<td>Cu$_x$Co$_y$O$_z$</td>
<td>2</td>
<td>6</td>
<td></td>
<td>41.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>71.30</td>
</tr>
</tbody>
</table>
From Table 1, it is clear that the nickel-cobalt coatings exhibit the lowest absorptance. It is also clear that increasing the dip-heating cycles improved the absorptive capability of all the coatings. This improvement in absorptance is due to the increase of the film’s thickness resulting from the increased dip heating cycle. A more pronounced effect is detected in the Cu-Co as compared to the Ni-Co and Mn-Co coatings. As such we will concentrate on the Cu-Co coating outcomes. The reflectance spectra of Cu–Co oxide thin film coatings with various [Cu] and [Co] ratios showed that the absorption edge shifted from shorter wavelengths to longer wavelengths (or from high frequencies to low frequencies) as the dip-speed and concentrations were increased. As the Cu-Co coatings showed the highest absorptance, we investigated the effect of deposition conditions on the absorptance of the 500 °C annealed Cu-Co copper–cobalt oxide thin films. The deposition conditions were varied by: (i) changing the dip coating speed over the range 60-180 mm/min for various [Cu] and [Co] concentration ratios such that [Cu]/[Co] = 1; and (ii) varying the concentration ratio [Cu]/[Co] from 0.5-2.0 for the optimum dip coating speed. The results are displayed in Table 2 and Table 3 [225].

Table 2. The solar absorptance of Cu$_x$Co$_y$O$_z$ coatings, sintered at 500 °C in air for 1 hour using 4 dip-heating cycle, with varying speed of dip coating parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\frac{[Cu]}{[Co]}$ ratio</th>
<th>Dip speed (mm/min)</th>
<th>Absorptance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_x$Co$_y$O$_z$</td>
<td>$\frac{0.15}{0.15} = 1$</td>
<td>60</td>
<td>66.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>77.030</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>77.90</td>
</tr>
<tr>
<td></td>
<td>$\frac{0.20}{0.20} = 1$</td>
<td>60</td>
<td>77.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>79.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>79.80</td>
</tr>
<tr>
<td></td>
<td>$\frac{0.25}{0.25} = 1$</td>
<td>60</td>
<td>80.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>83.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>84.50</td>
</tr>
<tr>
<td></td>
<td>$\frac{0.30}{0.30} = 1$</td>
<td>60</td>
<td>79.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>120</td>
<td>83.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180</td>
<td>84.74</td>
</tr>
</tbody>
</table>
Table 3. The Solar absorptance of Cu$_x$Co$_y$O$_z$ coatings, sintered at 500 °C in air for 1 hour using 4 dip-heating cycle, with varying concentration ratio [Cu]/[Co].

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Cu]</th>
<th>[Co]</th>
<th>Ratio</th>
<th>Absorptance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_x$Co$_y$O$_z$</td>
<td>0.125</td>
<td>0.25</td>
<td>0.5</td>
<td>86.077</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.25</td>
<td>1</td>
<td>83.40</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.125</td>
<td>2</td>
<td>74.13</td>
</tr>
</tbody>
</table>

The results from Table 3 suggest that the sample with the high absorptance value of 86.77% will be suitable for application as a coating for solar selective surfaces in photothermal collectors. Infrared reflectance spectra of the Cu$_x$Co$_y$O$_z$ coatings were acquired in the wavelength range 2.5 to 15.4 µm using a reflected-off type Perkin Elmer Spectrum 100 FTIR spectrophotometer with integrating sphere in the wavelength range of 2.5 to 15.4 µm. The FTIR reflectance spectra were used to compute the thermal emittance, ε value of this coating [349]. Thermal emittance is defined as a weighted fraction between emitted radiation and the Planck black body distribution and is used to appraise the performance of solar selective surfaces in the mid to far-infrared range of the spectrum [227]. Analysis of FTIR reflectance spectra data of sol-gel derived Cu$_x$Co$_y$O$_z$ coatings were reported in Ref. [227]. Using the emittance value of Cu$_x$Co$_y$O$_z$ coatings as reported in Ref. [227], we presented the solar selectivity results of Cu$_x$Co$_y$O$_z$ coatings in the following Table 4 [228]. A thermal emittance value below 10% is, generally, considered to be ideal for a thin film material which is to be used as a solar selective surface.

Table 4. Solar selectivity of sol-gel derived Cu$_x$Co$_y$O$_z$ coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solar absorptance, α (%)</th>
<th>Thermal emittance, ε (%)</th>
<th>Solar selectivity (s = α/ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_x$Co$_y$O$_z$</td>
<td>86.77</td>
<td>5.54</td>
<td>15.66</td>
</tr>
</tbody>
</table>


3.4.4 Mechanical Properties of Metal Oxide-based Coatings

A nanoindentator (Ultra-Micro Indentation System 2000, Australia) equipped with a Berkovich indenter was used to measure the mechanical properties of the coated Cu-Co-oxide films. From the load vs penetration depth plot, Young’s modulus ($E$), hardness ($H$), and wear resistance ($H/E$) were calculated. The mechanical properties of the synthesized coatings at various annealing temperatures are presented in Table 5 [228].

Table 5. Mechanical properties of annealed Cu$_x$Co$_y$O$_z$ coatings.

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Sintering temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Hardness, $H$ (GPa)</td>
<td>3.18</td>
</tr>
<tr>
<td>Elastic modulus, $E$ (GPa)</td>
<td>91.40</td>
</tr>
<tr>
<td>Wear resistance, $H/E$</td>
<td>0.035</td>
</tr>
<tr>
<td>Poisson’s ratio, $\sigma$</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Results from Table 5, reveal that the degree of resistance to deformation increases with increasing annealing temperature reaching up to maximum resistance at 650 °C in this temperature range. Thus, the heat treatment has a positive impact on the mechanical properties of the coating layer.

3.5 Transition Metal Nitride-based Sputtered Coatings as Selective Solar Surface: Recently Published Data

Due to their combination of chemical, corrosion, oxidation, and wear resistance behaviours, their extraordinary thermal stability and tuneable optical properties e.g., refractive index, absorptance, reflectance and transmittance transition metal nitride based coatings are preferred as candidates to be used in solar selective surface applications [11, 12, 350, 351]. Despite their technological importance, there have been a very limited number of investigations on optical selectivity in the presence of various dopants. Optical parameters of transition metal nitride coatings vary from one application to another. For solar selective surface applications, these coatings must possess high solar absorptance of the visible light and low thermal emittance in the infrared region of the light. Widespread applications and steadily increasing scientific interest in metal nitrides have been concerned with the development of new species of coatings possessing superior properties. Properties of nanocomposite transition metal nitrides can be controlled by
selecting the elements and process parameters of the forming films. Nanocrystalline transition metal nitrides, carbides and carbonitrides are investigated due to their unique optical and decorative properties [341-343, 352, 353]. Correlations between chemical structure and optical properties [341-343], and structural morphology and optical behaviours have been reported [341]. Interrelationships among the mechanical properties, chemical composition, optical properties, and crystal structure of dc magnetron sputtered metal nitride thin film coatings was investigated by Zeman et al. [344].

The optical applications of transition metal nitrides based selective solar coatings have been discussed for their optical applications in an invited review [150]. It has been found that nanocrystalline titanium nitride thin films have applications in different areas of semiconductor device technology such as gate electrodes in field-effect transistors, Al diffusion barriers, and ultra-large scale integrated circuits [152, 337, 338]. The electronic properties of titanium nitrides and carbides have been extensively studied under different experimental and theoretical approaches [354-358], however optical studies of these materials did not receive significant concentration either experimentally or theoretically [354, 359, 360] especially the solar selectivity study is even rare [57, 71-75, 151]. In Ref. [151], magnetron sputtered TiAlN/TiAlON coatings synthesized onto a metal substrate exhibited high absorptance and low emittance. The absorptance of the coatings was substantially enhanced to 0.95 by adding Si$_3$N$_4$ antireflection coating on the top of films. A higher thermal stability and high solar selectivity of 0.95/0.07 = 13.57 was achieved by this tandem selective surface. Since solar selective surfaces are the easiest and most direct way of harvesting the solar energy, in recent years, transition metal nitrides have received more interest in mid and high temperature applications [9, 11-19, 153, 361]. Solar selectivity values of few recently published transition metal nitride based thin film coatings are listed in the following Table 6.
<table>
<thead>
<tr>
<th>Sample compositions</th>
<th>Al-concentration or (x)</th>
<th>substrate</th>
<th>Deposition method</th>
<th>Absorptance (α) and emittance (ε) calculation method</th>
<th>Selectivity (s = α/ε) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAIN</td>
<td>-</td>
<td>Copper</td>
<td>Sputtering</td>
<td>Solar spectrum reflectometer and emissometer</td>
<td>12.9 [55]</td>
</tr>
<tr>
<td>TiAIN/TiAlION</td>
<td>-</td>
<td>Copper</td>
<td>Sputtering</td>
<td>Solar spectrum reflectometer and emissometer</td>
<td>15.2 [55]</td>
</tr>
<tr>
<td>Ti_{1-x}Al_{x}N</td>
<td>0.21</td>
<td>Copper</td>
<td>Sputtering</td>
<td>UV-Vis and FTIR reflectivity</td>
<td>5.4 [362]</td>
</tr>
<tr>
<td></td>
<td>0.58</td>
<td>Copper</td>
<td>Sputtering</td>
<td>UV-Vis and FTIR reflectivity</td>
<td>5.0 [362]</td>
</tr>
<tr>
<td>TiAIN/TiAlION</td>
<td>-</td>
<td>Copper</td>
<td>Sputtering</td>
<td>Solar spectrum reflectometer and emissometer</td>
<td>13.6 [55, 363]</td>
</tr>
<tr>
<td>/Si_{3}N_{4}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiAIN/TiAlION</td>
<td>-</td>
<td>Glass</td>
<td>Sputtering</td>
<td>Solar spectrum reflectometer and emissometer</td>
<td>13.3 [55]</td>
</tr>
<tr>
<td>/Si_{3}N_{4}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiAIN/TiAlION</td>
<td>-</td>
<td>Stainless steel</td>
<td>Sputtering</td>
<td>Solar spectrum reflectometer and emissometer</td>
<td>7.4 [55]</td>
</tr>
<tr>
<td>/Si_{3}N_{4}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiAIN/TiAlION</td>
<td>-</td>
<td>Nickel</td>
<td>Sputtering</td>
<td>Solar spectrum reflectometer and emissometer</td>
<td>6.7 [55]</td>
</tr>
<tr>
<td>/Si_{3}N_{4}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti_{1-x}Al_{x}N/Ag/Ti_{1-x}Al_{x}N</td>
<td>-</td>
<td>Glass</td>
<td>Sputtering</td>
<td>UV-Vis and FTIR reflectivity</td>
<td>18.1 [364]</td>
</tr>
<tr>
<td>Ti_{0.5}Al_{0.5}N/Ti_{0.25}Al_{0.75}N/AlN</td>
<td>-</td>
<td>Stainless steel</td>
<td>Sputtering</td>
<td>Spectroscopic phase modulated ellipsometer</td>
<td>23.5 [365]</td>
</tr>
<tr>
<td>TiAl/TiAIN/TiAlION/TiAIO</td>
<td>-</td>
<td>Stainless steel and Copper</td>
<td>Sputtering</td>
<td>UV-Vis-NIR and emissometer</td>
<td>11.8 [366]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Spectral selectivity values of TiN-based sputtered coatings.
Transition metal nitrides have a wide variety of applications across a broad range of practical fields due to their structural diversity and their range of useful mechanical, chemical, and electrical properties. Generally nitride materials fall into two main classes: transition-metal nitrides and ionic-covalent nitrides [367]. In transition-metal nitrides, the metal-metal bonds are predominant whereas nitrogen-(non)metal bonds are superior in ionic covalent nitrides. According to their crystal symmetry and behaviors, transition-metal nitrides are very similar to carbides while the ionic-covalent nitrides are closer to oxides. The optical properties of transition-metals and ionic-covalent oxynitride materials, and the influences of synthesis conditions and chemical structures on their optical properties were reviewed by Xie et al. [367]. Optical properties of such materials can be modified by controlling the compositions that alters the density of free electrons in their *d*-bands [57, 351]. Optical properties can be also regulated by integrating another metal component into the transition metal nitride systems which transforms the bonding nature from metallic to covalent one [57]. For example, Ti$_{1-x}$Al$_x$N coatings exhibit metallic nature with low Ti-content ($x \leq 0.48$) and dielectric behavior with high titanium amount up to $x = 0.77$ [57]. Gradual improvement in the optical transmittance was observed with the subsequent increase in aluminum content to the Ti$_{1-x}$Al$_x$N coatings. Furthermore, coatings with $x < 0.5$ showed a maximum transmission and a maximum reflection in the visible region together with a high reflectance and low absorptance in the infrared region. The applications of transition metal nitride and carbide class materials in low temperature fuel cell technology have been investigated by various research groups [368, 369]. Extensive investigations on a range of optical parameters such as band-gap, refractive index, reflectance, absorptance, emittance, transmittance and photoluminescence of different oxynitride materials and their applications as selective solar surfaces, antireflection coatings, visible-light-driven photocatalysts, phosphors for light-emitting diodes, ecological pigments, and smart windows have also been undertaken [11, 12, 350, 351, 367]. Optical parameters of transition metal nitride coatings vary from one application to another. In order to understand the property-structure relationship and improving the efficiency of the materials, the chemistry of metal nitrides and their corresponding crystal structures has been studied extensively [370-373].

The correlation between the mechanical properties, optical properties, and crystal structure of dc magnetron sputtered ZrCuN thin film coatings is reported earlier [344]. Microstructural, electronic and optical characteristics of various chromium nitride
coatings deposited by unbalanced reactive magnetron sputtering system were studied by Logothetidis et al. [345]. The influence of nitrogen flow on formation of Cr, Cr$_2$N, CrN phases in the coatings was investigated in order to validate the XRD results. Using the Drude-Lorentz model [339, 346] and taking into account the electronic structure of Cr$_2$N, CrN, the experimental results revealed the metallic character of Cr$_2$N phase and the semiconducting nature of CrN structure [347, 348]. Nanocrystalline TiN based thin film coatings have found applications in different areas of semiconductor device technology such as gate electrodes in field-effect transistors, Al diffusion barriers, and ultra-large scale integrated circuits and many more [152, 337, 338].
CHAPTER FOUR: SPECIMEN SYNTHESIS TECHNIQUES

4.1 General Overview

This study has utilized two different specimen synthesis techniques. The first approach deals with the fabrication of CuCoO thin film coatings using sol-gel dip-coating technique while the second involves the fabrication of transition metal nitride (e.g., CrN, TiN etc) based thin film coating via an unbalanced magnetron sputtering system. Detailed descriptions of the solution preparation, dip-coating method and magnetron sputtering technology for the thin film synthesis have been presented in the following sections.

4.2 Sol-gel Process

The development of new materials is an important aspect in the research and development of new energy generation systems and mechanical applications. Over the past few decades many processing methods have been proposed for the successful preparation of optical thin films of high quality by different research groups around the world. The processing methods studied include the magnetic the sputtering technique, the electrochemical method, painting, vacuum deposition, electrochemical process, and mechanical grinding [40, 55, 176, 374-377]. Among the currently used methods, some require high material consumption and are detrimental to the environment, while others are costly and inefficient [40, 55, 176, 374, 377]. There are a some types of Al₂O₃ based coatings e.g., Co-Al₂O₃ [49, 200], Mo-Al₂O₃ [378, 379] and Ni-Al₂O₃ [44, 48, 380-382] which have been used widely as a selective surface due to their outstanding optical properties and thermal stability. Sputtering technique and solution-chemical methods are mainly employed to synthesize these types of coatings [36, 40, 382, 383]. Recently, a simple approach to synthesize CuMn-spinel thin film by dip-coating followed by air sintering was reported by Bayón et al. [10, 222, 223]. Botröm et al. [39, 40, 384, 385] and Nejati [386] reported that they had synthesized NiAl₂O₃ thin film solar selective absorber by the sol-gel method. This method is simple, cost effective and easy to operate. For these reasons, the development of low cost, easy to operate, environmentally friendly, high quality, high stability and high performance solar selective surfaces has always found a lot of interest. Even though sol-gel technology was first proposed more than a century ago, it has only gained popularity in the last two decades. It has been seen as a method offering a way to prepare samples in days rather than the months required by
other conventional methods. In the case of thin films it is even possible to prepare samples in a matter of hours following the sol-gel technique.

The sol-gel process is a wet-chemical process commonly used for the synthesis of ceramic and glassy materials. The sol-gel dip-coating is a straightforward process of producing thin film coatings with well-defined doping levels and with homogeneous distributions of dopants. This solution’s chemical process is used in fundamental research as well as in direct industrial applications for the fabrication of various thin films, nanomaterials, ceramics, nanopowders, nanofibers and homogeneous nano-crystallite layers. Furthermore, the sol-gel dip-coating method has also been widely adopted for the fabrication of crystalline mixed metal oxide thin films. The sol-gel dip-coating process starts with the conversion of suitable precursors into a colloidal solution after dip-coating which evolves into a gel of either discrete particles or network polymers. The final state of the thin films is formed by a heat-treatment depending on the material’s state. The sol-gel dip-coating film deposition technique has some advantages compared to other conventional ones such as the low number of apparatus needed, low costs, high chemical stability and high homogeneity, easy waste disposal and versatility of formation of the thin films, especially in the case of nanocrystalline structure and amorphous structure. Furthermore, one of the greatest advantages of the sol-gel technique is that in the case of sol-gel derived materials, densification can be often achieved at a much lower temperature compared to the other traditional deposition methods. Additionally, this approach is a cost effective, easily operated and low-temperature system that confirms the fine control of the surface morphology along with the fine chemical composition. The sol-gel derived materials have wide range of practical applications in many important technological devices such as electronics, solar cells, energy generation, energy conversion, energy storage, optics, space, sensors, protective coatings and medicines. The details overview of the dip-coating machine, precursors and reagents needed for film deposition, sol-gel preparation and dip-coating technique will be described in the following sections.

4.3 The Dip-coating Machine

The view of the dip-coating machine used for samples deposition has been shown in the following Fig. 8. The substrate is mounted on a metal clip at the end a metal rod. The substrate was dipped into the sol which is contained in a small beaker. During the dip-coating process, the vertical movement starts towards the downwards and stops when the
substrate is dipped properly within the sol. After dipping for 1 minute in the solutions, the substrate was withdrawn in the upward direction slowly and steadily. A dipping rate of 180 mm/min and a withdrawal rate of 120 mm/min were maintained for the entire series of the films studied in this investigation. After the dip-coating the sample was kept in the air for a period of time and then dried at ~250 °C for few seconds. The same coating procedure has been repeated for several times as needed. The film formed in this way is an amorphous and nano-porous state. Finally, the coated samples were put into a furnace and annealed at a temperature of 500 °C for 1 hour. This way, an amorphous film is converted into a crystallographically arranged nano-film. The properties of the films are strongly influenced by the chemical compositions, the deposition parameters e.g., withdrawal rate, sintering temperature, sintering time and cooling down conditions. Fig. 9 shows the annealing furnace.

Figure 8. Dip-coating machine.
4.4 Chemicals, Reagents and Precursors

All chemicals were used as received from the manufacturer and without any further purification. MilliQ water was used throughout the solution preparation. Table 7 summarizes all the raw materials and chemicals used in the thin film synthesis together with their purity level and manufacturers.

Figure 9. Sintering furnace.
Table 7. Precursors, reagents, and raw materials used for the synthesis of mixed metal oxide thin film coatings.

<table>
<thead>
<tr>
<th>Name of the chemicals/reagents/precursors</th>
<th>Symbol/Chemical formula</th>
<th>Manufacturer</th>
<th>Grade</th>
<th>Purpose of Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen gas</td>
<td>N₂</td>
<td>BOC Limited, Australia</td>
<td>Highly pure</td>
<td>Drying the Al substrates</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>Anofol</td>
<td>-</td>
<td>Substrate</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>Rowe Scientific</td>
<td>85%</td>
<td>Precursor to clean the Al substrate</td>
</tr>
<tr>
<td>Chromium (VI) oxide</td>
<td>CrO₃</td>
<td>Sigma-Aldrich</td>
<td>99.99%</td>
<td>Precursor to clean the Al substrate</td>
</tr>
<tr>
<td>Cobalt (II) chloride dihydrate</td>
<td>CoCl₂. 6H₂O</td>
<td>APS Chemical</td>
<td>&gt;99%</td>
<td>Precursor of the thin films</td>
</tr>
<tr>
<td>Copper (II) acetate monohydrate</td>
<td>(Cu(OOCCH₃)₂.H₂O</td>
<td>Alfa Aesar</td>
<td>&gt;98%</td>
<td>Precursor of the thin films</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>C₃H₆COOH</td>
<td>Chem Supply</td>
<td>&gt;99%</td>
<td>Complexing agent for the thin film sols</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>GO</td>
<td>-</td>
<td>-</td>
<td>Precursor of the thin films</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅O</td>
<td>Merck</td>
<td>&gt;99.5%</td>
<td>Solvent of the thin films</td>
</tr>
<tr>
<td>Propanal</td>
<td>C₃H₈O</td>
<td>Fisher Chem</td>
<td>99.96%</td>
<td>Solvent of the thin films</td>
</tr>
<tr>
<td>Acetone</td>
<td>(CH₃)₂CO</td>
<td>Ajax Finechem</td>
<td>99.5%</td>
<td>solvent for cleaning and storage of various lab items</td>
</tr>
</tbody>
</table>

4.5 Brief Description of the Sol-gel Dip Coating Technique

Sol-gel dip coating is a popular and simple way of producing thin film coated materials. Dip-coating refers to the immersing a substrate into a beaker containing a coating solution and removing it from the solution and subsequently dried. Generally, the sol-gel dip coating process can be segmented into six major stages: substrate preparation, sol preparation, immersion, dwell time, withdrawal the substrate and sintering. In the following sections, all the major steps involved in the thin film coating mechanisms are outlined.
4.5.1 Substrate Preparation

Highly reflective commercial flat plate aluminum sourced from Anofol in Italy was used for the preparation of the substrates. The dimensions of the substrates used for the thin film depositions are $2 \times 4 \text{ cm}^2$. The substrates were cleaned with an etching solution to make them optically smooth and to reduce the alumina layer before the film deposition. The etching solution was made by mixing 35 grams of chromium (VI) oxide 20 ml of 85% phosphoric acid in one litre of milliQ water. An appropriate amount of etching solution was put into a beaker and heated up to 80 °C. The substrates were then placed in the hot solution and heated for about 10 minutes. The substrates were then washed out in hot water followed by a flash of distilled water. Finally, the substrates were dried by a blowing nitrogen stream. Using this cleaning method an optically clean, pure and smooth aluminum substrate was achieved as shown in Fig. 10.

4.5.2 Sol Preparation

The copper-cobalt oxide thin film coatings were prepared in a pure state and with the doping of a controlled amount of GO. 0.1, 0.5, 1.0, 1.5 wt.% GO were used for this purpose. In order to prepare these types of thin films, the raw materials used were: cobalt (II) chloride (CoCl$_2$.6H$_2$O, APS Chemical, >99%), copper (II) acetate monohydrate (Cu(OOCCH$_3$)$_2$.H$_2$O, Alfa Aesar, 98%), propionate acid (C$_2$H$_5$COOH, Chem Supply, 99%), graphene oxide, milliQ water, and absolute ethanol (Merck). All the precursors were used as received without any further purification. The pure CuCoO coatings were synthesized by mixing certain concentrations of (Cu(OOCCH$_3$)$_2$.H$_2$O and CoCl$_2$.6H$_2$O of 0.25 M at a copper to cobalt ratio ([Cu]/[Co] = 1. The absolute ethanol was used as the solvent while the propionate acid (C$_2$H$_5$COOH) was used as a complexing agent. The solution was stirred for 2 hours in a sealed glass container at room temperature.

4.5.3 Immersion

The final solution was used for thin film preparation on aluminum substrates using a dip-coater. The aluminum substrates were immersed in the solutions at a constant speed of 180 mm/min. During the entire period of dip-coating process a relative humidity and temperature of ~50% and 20 °C respectively have been maintained.
4.5.4 Dwell Time

The substrates were fully immersed and motionless for two minutes to permit the coating solution to attach itself to the substrate.

4.5.5 Withdrawal Rate

A withdrawal rate of 120 mm/min has been used to ensure the production of relatively smooth and even films. The adhesion of the film on the substrate was immediate (ca 10 s) during the dipping process. The coated film was then dried at 150 °C for ~10 seconds on the hot plate. Thin films with different thicknesses could be successfully prepared by repeating the dipping and drying cycles and changing the withdrawal rates. The faster the substrate is withdrawn from the tank, the thicker the coating material that will be applied to the substrate. Generally, the coating thickness is mainly dependent on the withdrawal speed, the solid content and the viscosity of the liquid.

4.5.6 Sintering

In order to enhance the mechanical characteristics, structural stability, grain growth and to improve the polycondensation, the subsequent thermal treatment of the films is essential. Thus, the deposited coatings were sintered in an oven furnace at 500 °C for 1 hour to remove volatiles. A heating rate of 50 °C /min was maintained throughout the sintering process. If the final temperature was set too low, residual organic groups would not be completely removed, resulting in a poor optical coating quality. Sintering is a kind of heat treatment of powder compacts at elevated temperatures where diffusional mass transport is appreciable. In sintering, a dense, tough object is obtained by heating a compacted powder for a certain time at a temperature high enough to significantly promote diffusion, but which is lower than the melting point of the composition. The driving force for sintering is the reduction in the surface free energy of the powder. It is traditionally used for manufacturing ceramic objects. At the end of the sintering, a dense polycrystalline sample is formed without any appreciable change in the average overall density of a powder compact. Sintering is extensively used for the synthesis of polycrystalline materials for the following purposes:

- to bind the particles together so as to contribute sufficient strength to the thin film coatings,
- to densify the coatings by eliminating the pores,
- to homogenize the materials by completing the reactions left behind during the solution preparation and stirring process,
- to improve the mechanical properties \(i.e.,\) strengthen the elastic modulus,
- to harden and fracture toughen the coatings,
- to ensure homogenous distribution of grain number, grain size and shape by improving the microstructure of films, and
- to get a stable chemical composition and crystal structure.

Figs. 10 display the CuCoO thin film coatings in pure state and with the doping contents. The entire thin film preparation methodology can be summarized by the flow chart shown as Fig. 11.

**Figure 10.** (a) Clean aluminum substrate (b) copper-cobalt oxide thin film coating without GO (c) Copper-cobalt oxide thin film coating with the addition of GO.
Figure 11. The block diagram for the thin film deposition using the sol-gel dip coating method.

4.6 Magnetron Sputtering Technique

A magnetron consists of a target of which the coating is to be made with magnets arranged behind it which generate a magnetic trap for the charged particles (e.g., Ar ions) in front of the target. When power is supplied to the magnetrons, they put the target at a negative voltage typically -300 V or better. In the sputtering method, a cathode (target material) is bombarded by energetic ions produced in a glow discharge plasma which is placed in front of the cathode plate. This bombardment leads to the removal (sputtering) of target atoms that are headed towards the substrate region and which condense to produce a thin film. At the same time, the secondary electrons released from the target
surface play an important role in sustaining the plasma. This is the basic principle of a conventional sputtering system which has its own limitations such as low deposition rates, high substrate heating effects and low ionization efficiencies in the plasma. Nowadays, an unbalanced magnetron sputtering system is utilized to overcome these limitations.

An unbalanced magnetron sputtering system is a physical vapor deposition coating technology that uses extra magnetic coils to intensify the plasma close to the product. In an unbalanced magnetron, the outer ring of magnets is strengthened relative to the central pole. The magnets within the magnetrons are arranged in such a way that alternating poles are next to each other resulting in the linkage of field lines (see Fig. 12). Some of the field lines are closed between the central and outer poles in the magnetron while the rest are directed towards the substrate and some secondary electrons are able to follow these field lines. The effect of the unbalanced magnetic field is to trap fast moving secondary electrons that escape from the target surface. These electrons undergo ionizing collisions with neutral gas atoms away from the target surface and produce a greater number of ions and more electrons in the region of the substrate, considerably increasing the substrate ion bombardment. As a result, plasma is no longer restrained to the target surface, but it also flows out towards the substrate region. In other words, a secondary dense plasma is produced in the target region which, in turn, leads to enhanced ion bombardment of the target and thereby gives higher sputtering rates and higher deposition rates of the films at the substrate. Furthermore, the increased ionization efficiency attained in the magnetron permits the discharge to be preserved at lower operating pressures (typically, $10^{-3}$ mbar) and lower operating voltages (typically, -500V) than the conventional sputtering technique. The negative bias and higher degree of ion bombardment into the substrate region ensures a more densely sputtered coating and is successfully used to control many properties of the growing films. For a given set of deposition conditions, the ion current supplied to the growing film depends on the strength and design of the magnetic array in the magnetron. However in newly designed magnetrons, the magnetic arrays can be adjusted in situ without the use of electromagnets.
Figure 12. The unbalanced magnetron sputtering system.

The following Fig. 13 represents the schematic diagram of magnetron sputtering method for the fabrication of Cr$_x$M$_{1-x}$N coatings where M = Al, Si and Ni.

Figure 13. The magnetron sputtering method for the fabrication of Cr$_x$M$_{1-x}$N coatings where M = Al, Si and Ni.
A schematic diagram of magnetron sputtering method to synthesize TiAlSiN thin film coatings are shown in Fig. 14.

![Diagram of magnetron sputtering](image)

**Figure 14.** The magnetron sputtering method to synthesize TiAlSiN thin film coatings

The magnetron sputter coating system is a stainless steel chamber equipped with the pumps necessary to create a high quality vacuum, sample support and rotation equipment. The sources of coating materials are known as magnetrons. A typical diagram of the magnetron sputtering chamber and its control unit is shown in Fig. 15.
Figure 15. The unbalanced magnetron sputtering system (UDP650, Teer Coating Limited, Droitwich, Worcestershire, UK) installed at The City University of Hong Kong.

Generally, it takes 30 minutes of pumping to attain a vacuum adequate to begin the coating process (a pressure of > 1.013×10⁻⁴ Pa) A closely controlled flow of argon gas is introduced whilst the pumps are still running, and this helps to increase the pressure in the system to the levels desired to operate the magnetrons. The simultaneous operation of pumping down to the high vacuum level and the continual throughput of Ar gas confirms that coating atmospheres are both clean and reproducible. Sputtering also leads to the heating of the target, so the magnetron incorporates channels for water cooling during operation. The unbalanced magnetron sputtering system generates substantial impacts in application areas including hard and superhard coatings, low friction coatings, wear-resistant coatings, corrosion-resistant coatings, decorative coatings and coatings with specific optical, electrical and mechanical properties. Magnetron sputtering is used at Teer Coatings Ltd in the UK have excellent adhesion to the workpiece and a wide range of properties which have been tailored to suit engineering applications. It is a powerful and flexible system which can be used to coat solid metal or alloys and a variety of compounds.
4.7 Sputtering Conditions for the Synthesis of Metal Nitride Coatings

Thin film coatings of Cr$_{1-x}$M$_x$N, (where $M$ is Al, Si, or Ni and $x$ was varied from 0 to 28.5 at.% to produce films with low, medium and high concentration of the dopants) TiN, TiAlN, and TiAlSiN were deposited onto AISI M2 tool steel substrates at the City University of Hong Kong via closed field unbalanced magnetron sputtering system (UDP650, Teer Coating Ltd, Droitwich, Worcestershire, UK). In addition to the above samples, the reference samples of AlN, and Si$_3$N$_4$ were also prepared to compare the results. Following Table 8 represents the at.% of Al/Si/Ni contents as of low, medium and high doping elements in CrN coatings.

**Table 8.** Chemical compositions of Cr$_{1-x}$M$_x$N, where $M$ = Al, Si, and Ni, with different Al/Si/Ni contents.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Amount of Al/Si/Ni</th>
<th>Al/Si/Ni content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_{1-x}$M$_x$N</td>
<td>Low</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>28.5</td>
</tr>
</tbody>
</table>

The magnetron sputtered system is equipped with a four-target configuration. The steel substrates were subsequently ultrasonically cleaned in an acetone and methanol solution. Before putting it into the vacuum chamber, the substrates were dried with nitrogen gas. A background pressure of 2.67×10$^{-4}$ Pa was obtained in the chamber before the deposition process. The substrates were sputter cleaned with Ar plasma at a bias of -450 V for 30 minutes. In order to achieve a homogeneous film thickness, the substrate was rotated at a speed of 10 rpm throughout the synthesis process. A Ti$_{0.5}$N$_{0.5}$ film was produced at a Ti target current of 8 A, while the Al target current was varied between 0 and 7 A for the synthesis of the TiAlN, and TiAlSiN coatings. However, for the TiAlSiN coating, a Si target current of 1.5 A was also applied. The nitride coatings were prepared in Ar+N$_2$ mixed gas atmosphere. Prior to the taking of measurements, all the samples were mechanically cleaned in an ultra-high vacuum via a diamond needle file and tungsten-wire brush. The details of the deposition parameters for the sputtered TiN, TiAlN and TiAlSiN coatings are displayed in Table 9.
Table 9. Details of the deposition conditions of the TiN, TiAlN and TiAlSiN unbalanced magnetron sputtered coatings.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Ti$<em>{0.5}$N$</em>{0.5}$ coating</th>
<th>Ti$<em>{0.25}$Al$</em>{0.25}$N$_{0.5}$ coating</th>
<th>Ti$<em>{0.5}$Al$</em>{0.25}$Si$<em>{0.05}$N$</em>{0.5}$ coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Ti$<em>{0.5}$N$</em>{0.5}$</td>
<td>Ti$<em>{0.25}$Al$</em>{0.25}$N$_{0.5}$</td>
<td>Ti$<em>{0.5}$Al$</em>{0.25}$Si$<em>{0.05}$N$</em>{0.5}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>30.947 g/mol</td>
<td>25.721 g/mol</td>
<td>25.776 g/mol</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Fm$^3$m(225)</td>
<td>Fm$^3$m(225)</td>
<td>Fm$^3$m(225)</td>
</tr>
<tr>
<td>Substrate</td>
<td>M42 Steel (HRC60)</td>
<td>M42 Steel (HRC60)</td>
<td>M42 Steel (HRC60)</td>
</tr>
<tr>
<td>Target materials</td>
<td>Ti target only</td>
<td>Ti + Al targets</td>
<td>Ti + Al + Si targets</td>
</tr>
<tr>
<td>Reaction gas</td>
<td>Ar is working gas, N$_2$ is reactive gas</td>
<td>Ar is working gas, N$_2$ is reactive gas</td>
<td>Ar is working gas, N$_2$ is reactive gas</td>
</tr>
<tr>
<td>Substrate thickness</td>
<td>3 mm</td>
<td>3 mm</td>
<td>3 mm</td>
</tr>
<tr>
<td>Target to substrate distance</td>
<td>170 mm</td>
<td>170 mm</td>
<td>170 mm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>500 °C</td>
<td>500 °C</td>
<td>500 °C</td>
</tr>
<tr>
<td>Substrate DC bias voltage</td>
<td>-50 V</td>
<td>-60 V</td>
<td>-55 V</td>
</tr>
<tr>
<td>Substrate holder rotation frequency</td>
<td>10 rpm</td>
<td>10 rpm</td>
<td>10 rpm</td>
</tr>
<tr>
<td>Ar flow rate</td>
<td>50 sccm</td>
<td>20 sccm</td>
<td>20 sccm</td>
</tr>
<tr>
<td>N$_2$ flow rate</td>
<td>Controlled by optical emission monitor (OEM)</td>
<td>Controlled by optical emission monitor (OEM)</td>
<td>Controlled by optical emission monitor (OEM)</td>
</tr>
<tr>
<td>Ar partial pressure</td>
<td>0.133 Pa</td>
<td>0.133 Pa</td>
<td>0.133 Pa</td>
</tr>
<tr>
<td>N$_2$ partial pressure</td>
<td>0.04 Pa</td>
<td>0.106 Pa</td>
<td>0.106 Pa</td>
</tr>
<tr>
<td>(Ar + N$_2$) pressure</td>
<td>0.17 Pa</td>
<td>0.24 Pa</td>
<td>0.24 Pa</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>0.17 Pa</td>
<td>0.24 Pa</td>
<td>0.24 Pa</td>
</tr>
<tr>
<td>Base/ultimate pressure</td>
<td>4 ×10^{-4} Pa</td>
<td>4 ×10^{-4} Pa</td>
<td>4 ×10^{-4} Pa</td>
</tr>
<tr>
<td>Ti target power</td>
<td>2 kW</td>
<td>2.2 kW</td>
<td>2 kW</td>
</tr>
<tr>
<td>Ti target current</td>
<td>8.0 A (DC)</td>
<td>6.0 A (DC)</td>
<td>6.0 A (DC)</td>
</tr>
<tr>
<td>Al target power</td>
<td>-</td>
<td>1.6 kW</td>
<td>1.2 kW</td>
</tr>
<tr>
<td>Al target current</td>
<td>-</td>
<td>6.0 A (DC)</td>
<td>4.5 A (DC)</td>
</tr>
<tr>
<td>Si target power</td>
<td>-</td>
<td>-</td>
<td>460 kW</td>
</tr>
<tr>
<td>Si target current</td>
<td>-</td>
<td>-</td>
<td>1.5 A (DC)</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>~1.3 nm/min</td>
<td>~2.2 nm/min</td>
<td>~2.2 nm/min</td>
</tr>
<tr>
<td>Deposition time</td>
<td>150 min</td>
<td>90 min</td>
<td>90 min</td>
</tr>
<tr>
<td>Thickness of the coating</td>
<td>~0.2 µm</td>
<td>~0.2 µm</td>
<td>~0.2 µm</td>
</tr>
</tbody>
</table>

sccm = standard cubic centimeter per minute (a unit of flow measurements)
CHAPTER FIVE: EXPERIMENTAL TECHNIQUES

5.1 General Introduction

The experimental work carried out in the present study can be broadly classified into two major components: (a) the fabrication of 3d transition metal oxide based thin film coatings using the sol-gel dip–coating technique and unbalanced magnetron sputtered based metal nitride based coatings; and (b) the characterizations of the coated films for their structural morphologies and other properties to analyze the surface and interface chemistries via scanning electron microscopy (SEM), EDX, XRD, ultraviolet visible (UV-Vis) spectroscopy, Fourier transform infra-red (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), nanoindentation technique, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

Detailed description of the preparation of solutions, the sol-gel dip-coating method and unbalanced magnetron sputtering technique for the thin film synthesis mechanism have been presented separately in Chapter four. Thus, this chapter deals with the instrumentations and brief theoretical insights of various experimental techniques used for the structural, morphological, optical, mechanical and chemical characterizations of the coated films.

5.2 Instrumentations and Characterization Methods

High precision instruments are needed to study, characterize and quantify nanoscale materials because these materials differ greatly from their bulk counterparts. Investigations of the surface structure of these materials are essential because the chemistries at the surface and interface regions are quite different from their bulk structure. In the present study, CuCoO thin film coatings in pure states with the doping of controlled amounts of graphene oxide (GO) are conducted by means of several experimental methods. Complementary methods were used to overcome the limitations of a single characterization technique. The phase identification and quantitative determination of the thin film coatings were performed by the non-destructive XRD technique. The XRD method was supported by the EDX and XPS, while the surface morphology and topography were imaged by the SEM technique. Further interfacial studies regarding the various surface oxidation states and surface electronic structure were conducted using the synchrotron radiation near-edge X-ray absorption fine structure
(NEXAFS) spectroscopic technique. The optical properties leading to the solar selectivity in the visible and infrared spectrum were carried out by UV-Vis-NIR and FTIR methods. The mechanical properties were studied to observe the hardness and elasticity of the thin films by the nanoindentation technique, finite element modeling and the accelerated thermal durability test. A brief theoretical background of the different techniques, an overview of the instruments, characterization techniques, and experimental methods used in this work have been furnished in the following sections of this chapter.

5.3 XRD Measurements

5.3.1 X-Ray Diffraction (XRD)

Since the wavelength of X-rays (~1Å) is of the same order of magnitude as the lattice constant of crystals, they provide useful information about the crystal structure. It is also one of the oldest and most effective tools for determining the atomic arrangement in a crystal. In contrast to a liquid, Bragg diffraction of crystalline solids produces surprising patterns of reflected X-rays. For certain specific wavelengths and incident angles, intense peaks of reflected radiation, generally known as Bragg peaks, are produced. The concept of Bragg diffraction applies equally to neutron diffraction and also to electron diffraction processes. Bragg formulated this result by modeling the crystal as a set of discrete parallel planes separated by a constant parameter $d$. It was proposed that the incident X-rays produce a Bragg peak if their reflections off the various planes interfered constructively. These reflections abide by the famous Bragg’s law which is stated by the following relation,

$$2d \sin \theta = n\lambda$$

where $d$ is the distance between crystal planes, $\theta$ is the angle between the incident rays and the surface of the crystal, $\lambda$ is the wavelength of the X-ray and $n$ is a positive integer.

Bragg’s law also suggested that the diffraction is only possible when $\lambda<2d$ [387]. A single crystal with a particular set of atomic planes oriented toward the X-ray beam will diffract an X-ray at an angle $\theta$ determined by the Bragg’s relation. Most materials are not single crystals but are composed of billions of very small crystallites. This type of material is referred to as a powder or polycrystalline aggregate. In these materials, there are a great number of crystalline in many orientations. Thus, when a powder is placed in an X-ray beam many inter atomic planes will be seen by the beam but diffraction from each
different type of plane will only occur at its characteristic diffraction angle $\theta$. Thus, instead of a dot pattern, a powder pattern formed in a series of concentric rings.

5.3.2 Analysis of XRD Data

After a pattern emerges, the value of $2\theta$ is calculated for each diffraction line. The interplanar distance $d_{hkl}$ was calculated from $2\theta$ values of the diffraction peaks using the Bragg’s relation. The XRD data consisting of $2\theta$ and $d_{hkl}$ values corresponding to the different crystallographic planes are used to extract the crystallographic and structural parameters of the thin film coatings *viz.*, identification of phases, lattice parameter determination, grain size calculation, etc.

5.3.2.1 Identification of Phases

It is well known that the XRD is one of the most popular and powerful tools to identify crystalline phases of materials and can provide information on unit cell dimensions. In a crystalline material, the scattering of X-rays by the electrons results in maxima and minima in the XRD pattern. The peaks with maximum intensity were found to follow Bragg’s law, that is, for each $d_{hkl}$-spacing. Bragg’s law indicates a maxima at a characteristic diffraction angle $\theta$. The XRD intensity data are plotted as a function of angle $\theta$ and the corresponding XRD pattern is obtained. Since the positions and intensity of the maxima of XRD peaks are characteristics of the crystallographic structure and the atomic composition of a material, the phase identification can be accomplished by comparing the positions and intensities of the Bragg peaks’ standard crystalline materials and the corresponding target material can then be identified. The presence of multiple phases in a compound can be also determined and quantified. XRD technique can also be used to distinguish the amorphous states of materials. Furthermore, quantitative information on single phase and multi-phase materials can be obtained from XRD data. In combination with the use of common materials, the XRD approach can provide precise measures of the constituents of the samples, lattice parameters, site-occupancy factors, unit cell volume, crystal symmetry, atom positions, etc.
5.3.2.2 Lattice Parameter Determination

The lattice parameters of a crystal system can be determined from the relationship between the inter-planar spacing $d_{hkl}$, lattice parameters and Miller indices. Let us consider a cubic crystal having a reflection of (110) in an XRD pattern. We can, therefore, determine the lattice parameter for this particular reflection using the Bragg’s law $2d \sin \theta = \lambda$ and $d_{hkl} = \left( \frac{1}{a_0} \left( h^2 + k^2 + l^2 \right) \right)^{1/2}$, where $\lambda = 0.154 \pm 10^{-5}$ nm for $Cu-K_{\alpha}$ radiation. Simplifying these relationships give, $a_0 = d \sqrt{2}$, and $a_0$ is the determined lattice parameter within an error estimated to be $\pm 0.00001$ nm.

5.3.2.3 Grain Size Determination from XRD Data

Since thin film coatings are crystalline in nature, they exhibit Bragg peaks in XRD measurements. However, due to their small size, significant fine particle broadening is observed in the Bragg peaks. The X-ray scattering from a crystalline solid is given by Bragg’s relation which relates the path difference of X-rays scattered from inter atomic planes spaced as $d = d_{hkl}$ to an integral number $n$ of X-rays wavelength $\lambda$. Simplifying the Bragg’s law, the XRD data can be used to compute the grain size, $D_g$ of a crystal via Debye-Scherrer equation,

$$D_g = \frac{K \lambda}{\delta \cos \theta} \quad (5.2)$$

Here, the constant of proportionality, $K$ (Scherrer constant) depends on how the width is determined, the shape of the crystal and the size distribution of the crystal and $\delta$ is the width of the diffraction patterns. The value of $K$ actually varies from 0.62 to 2.08, for integral breadth of spherical crystals the most common value of $K$ is 0.89. Thus, a more exact empirical treatment of Debye-Scherrer relationship yields,

$$D_g = \frac{0.89 \lambda}{\delta \cos \theta} \quad (5.3)$$

which is used to estimate the crystallite size of very small crystals based on the width of their diffraction patterns.
5.3.3 X-Ray Diffraction (XRD) Measurements Technique

The diffraction data can be collected using either transmission or reflection geometry as shown in the following Fig. 16. In the present investigation, the XRD data was taken using a Bruker Advance D8 X-Ray Diffractometer which measures data in reflection mode and is used mostly with solid samples. A Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector, installed at The University of Queensland, Australia was used for the XRD measurements of our thin film coatings. Fig. 17 shows the view of the Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector system. The Bruker X-ray diffraction system utilizes a modular system approach to provide performance for application ranging from routine characterizations to in-depth research investigations. The XRD measurements were conducted at room temperature. The diffraction technique was used with a primary beam power of 40 kV and 30 mA for Cu radiation. A nickel filter was used to reduce Cu-K\_\beta radiation and Cu-K\_\alpha radiation was only used as the primary beam. Cu-K\_\alpha radiation has a wavelength of 1.54 Å. A (\(\theta\)- 2\(\theta\)) scan was taken from 30° to 60° to get possible fundamental peaks of the sample with the sampling pitch of 0.02° and the time for each step data collection was 1.0 sec. Both the programmable divergence and receiving slits were used to control the irradiated beam area and output intensity from the sample. An anti-scatter slit was used to reduce air scattering. Two solar slits were used to adjust after the tube and in front of the detector to get parallel beam only. The data was recorded in the computer memory.

![Reflection and Transmission](image)

**Figure 16.** Reflection and transmission geometry of X-ray diffraction [388].
Figure 17. Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector installed at The University of Queensland, Australia.

5.3.4 Synchrotron Radiation X-Ray Diffraction (SR-XRD) Measurements Technique

The synchrotron radiation X-ray diffraction (SR-XRD) technique is used as a fingerprint technique for the detection of phase transitions and for finding unexpected and unknown structural forms during the synthesis processes of the coatings. The synchrotron radiation X-ray diffraction technique offers a few advantages over the conventional laboratory based XRD techniques such as highly collimated and intense photon beams, exceptional photon wavelength resolution ($\Delta \lambda / \lambda \approx 2 \times 10^{-4}$), higher angular resolution, ultrafast data acquisition, very high signal-to-noise and signal-to-background ratio. The powder diffraction (PD) beamline is composed of three hutches and a user cabin. These three hutches accommodate the optics, mirrors, double crystal monochromator, the primary end station and a large optical station. The majority of powder diffraction experiments are performed in the primary end station while the large optical table supports a variety of alternative configurations for engineering applications. The PD beamline has three detectors namely, MYTHEN (microstrip detector), PhotonicScience VHR detector, and MarCCD 165 (area detector). The typical beam size of the sample for the focused and unfocussed beam arrangements are 0.5 mm × 0.5 mm and 5 mm × 2 mm respectively.
The SR-XRD tests of TiN, TiAlN and TiAlSiN coatings were carried out with a powder diffraction (PD) beamline 10-BM-1 at the Australian Synchrotron Melbourne. The high resolution XRD data of these coatings was acquired at room temperature, 100, 200 and 300°C for the metal oxides based coatings while the sputtered coatings were tested at room temperature, 500, 600, 700, and 800 °C respectively. The PD beamline operated at 2.5 GeV used a bending magnet source. A continuous spectrum of photons were generated in the range 5–30 keV with a maximum flux of about $10^{13}$ photons/sec. The X-ray wavelength was measured at 0.8265 Å using a LaB6 standard NIST 660a. A beam size of 7 mm in width and 1 mm in height was exposed for 145 mins. The high temperature of the system was attained using an Anton Parr HTK20 furnace that was monitored by a thermocouple. The heating and cooling cycles of the furnace were remotely controlled via a computer interface. A base pressure of $10^{-1}$ mbar was maintained in the analysis chamber. The samples were loaded in a 0.3 mm diameter quartz capillary with diamond powders that were rotated during the experiments. A MYTHEN II microstrip detector system was used to record the high resolution XRD data in the range of $2\theta = 10^\circ$ to $40^\circ$ in steps of 0.2°. At each detector setting SR-XRD data were acquired for 5 minutes. Data collection was commenced after a 3 min thermal equilibration period when the control sensor had reached the set temperature. The acquired data was processed with PDViPeR software in order to obtain the XRD patterns.

5.4 Microstructural Study of Thin Film Coatings

Some properties of thin film coatings are strongly dependent upon the sensitive control of the microstructure. Mechanical properties of the samples are also influenced with the trapped intra-granular pores. Thus, the microstructural studies are very important for making predictions about the mechanical characteristics e.g., elastic modulus.

5.4.1 Scanning Electron Microscopy

The scanning electron microscopy (SEM) analysis is one of the micro-analytical techniques which can be used to image materials that are not generally observed with the resolution offered by visible techniques. Using this technology, materials can be photographed with much more detail than an optical microscope can provide, and it can identify the constituent elements of material. The SEM technique belongs to a broad category of particle beam instruments. In this technique, a specimen is scanned with a focused beam of high energy electrons. The resulting micrographs carry significant
information about the microstructure and surface morphology of the sample. In SEM, materials are bombarded with electrons which have high energies as a result of their mass and having been accelerated with thousands of volts. They generate a number of signals including secondary electrons with low, medium and high energies, X-rays, and back-scattered electrons [389]. The secondary electrons with low energy and back-scattered electrons are of great interest because they carry information about particle morphology. The secondary electrons are recorded in a detector for the imaging of the sample of interest and displayed on a screen. A high secondary electron emission results in a bright photograph while the primary emission offers an image of the surface structure of the sample. The end result is a brightness associated with surface characteristics i.e., an image which looks very much like an ordinary illuminated object. Quantifying elemental compositions is invaluable in many branches of scientific research. In materials research, applications are quite diverse from thin films to thin film semi-conductors to photonics materials and super conductors. In the case of thin-films, by measuring various X-ray intensities at different accelerating voltages, both the composition and thickness of various films deposited on a substrate may be determined with great accuracy.

Since the energy released by X-rays relies on the atomic structure i.e., every atom exhibits a characteristic X-ray emission spectrum, the X-rays produced from the interaction of the electrons with atoms in a sample are characteristic of the elements present in the sample. These X-rays can be differentiated in an energy spectrum in order to calculate the elemental composition of a sample. This is known as EDX. In EDX, a spectrum starting from very low to high voltage (say, from 0.1 to 20 keV) can be recorded in a relatively short time (10-100 s) for a quick analysis of the elemental compositions of the specimen.

5.4.2 Experimental Technique of Scanning Electron Microscopy

Historically SEM has been used in the morphological and elemental analysis of materials. Generally, SEMs are used as cameras for photographing specimens which are beyond the capabilities of ordinary microscopes. The images obtained are similar to those being photographed by ordinary means. The apparent illumination is a function of particle emission rather than normal radiation. In the present work, images of the morphological structures of the film coatings were made using a JCM-6000 scanning electron microscope connected with an EDX analysis column with a maximum EHT (extra high
tension) voltage field emission gun of 30 kV. A JCM-6000 scanning electron microscope is shown in Fig. 18.

Figure 18. JCM-6000 scanning electron microscope, JEOL, Japan.

5.5 Band Structure of Materials

The band structure associated with electrons in crystals is a consequence of their wave nature. The electron wavelength is of the same order as the lattice spacing and the consequence is an interference phenomenon that is related to the electron wavelengths and hence their energies. The principal effect is a forbidden energy zone, called the band gap, between the energy possessed by bound valence electrons and free electrons, and this gap has an enormous influence on the optical properties of the crystal. For example, an interaction between an optical photon and a bound electron is not possible if the electron acquires energy that would place it in the forbidden zone. In such a case, the photon would simply be transmitted by the crystal. If the photons were to have higher energy being sufficient to shift the electron energy into the allowed band beyond the band gap, then it would be absorbed. This explains the high infrared transmittance and high visible absorptance of the semiconductors. The light, however, has a very large wavelength compared with the lattice spacing and so the lattice has no direct effect. The interaction with the light is indirect. The lattice influences the electrons and the electrons
then affect the photons. All of this involves three dimensions, and it is normal to assume that the crystal medium is infinite in extent.

For the lattice directly to affect the photons, its spacing should be comparable with the wavelength of light. Thus, the scale has to be several orders of magnitude greater than that of a crystal. Assume a regular 3D assembly of blocks of one refractive index in a matrix of a different one, with spacing chosen to induce the effects of interference from light propagating through it. As we would expect, such an assembly exhibits a pattern of regions where propagation is forbidden and the regions where it is permitted. By analogy with normal crystals and their electronic properties, this much larger structure is called a photonic crystal and the forbidden propagation regions are photonic band gaps. There are two major problems associated with 3D photonic crystals. The first is the calculation of the properties, and the second, fabrication. Both problems can be mitigated by reducing the number of dimensions.

Two-dimensional photonic crystals can be constructed by the pulling process which is used for the construction of optical fibres. Here the matrix is the normal dielectric glass material used for the fibre while the scattering features are cylindrical holes running parallel to the axis. This can effectively convert the crystals into a fibre by removing the central hole so that the light propagates along its path and is contained by the reflection from the surrounding photonic crystal structure. Since the process effectively removes an “atom” from the lattice, this absence of the hole is called a defect even though it is an intentional feature of the structure. The word ‘defect’ is used in this sense frequently in photonic crystal terminology. The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered: transitions involving $\pi$, $\sigma$ and $n$ electrons; transitions related to the charge-transfer of electrons; and transitions associated with the $d$ and $f$ electrons.

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level. In solid state physics and related areas, the band structure of a material defines the ranges of energy that an electron in the material may have (allowed bands) or may not have (forbidden bands or band gaps). Thus, the band-gap is a region where an electron is forbidden to propagate further. For insulators and semiconductors, the band-gap, generally, refers to the energy
difference between the top of the valence band and the bottom of the conduction band. Band theory is successfully used to investigate electrical characteristics and optical absorption of solids. Fundamental absorption refers to the annihilation or absorption of photons by the excitation of an electron from the valence band up into the conduction band, leaving a hole in the valence band. Both energy and momentum are conserved in such a transition.

5.5.1 Energy Band-gap Calculations

In the case of an indirect-band gap semiconductor, the minimum energy in the conduction band and the maximum energy in the valence band occur at different values of crystal momentum. Photon energies much larger than the forbidden gap are required to give direct transitions of electrons from the valence to the conduction band. However, transitions can occur at lower energies by a two-step process involving not only photons and electrons but also a third particle, a phonon. To estimate the nature of absorption, a random phase model is used where the $k$ momentum selection rate is completely relaxed.

The integrated density of states $N(E)$ has been used and defined by the following relation,

$$N(E) = \int_{-\infty}^{+\infty} g(E) dE$$

The density of states per unit energy interval is expressed as,

$$g(E) = \frac{1}{V} \sum \delta (E - E_n)$$

where $V$ is the volume, $E$ is the energy at which $g(E)$ is to be evaluated and $E_n$ is the energy of the $n$-th state.

If $g_v \propto E^n$ and $g_c \propto (E - E_{opt})$, where energies are measured from the valence band mobility edge in the conduction band (mobility gap), and substituting these values into an expression for the random phase approximation, the relationship obtained $v^2 I_2 (v) \propto (h\nu - E_0)^{p+q+1}$, where $I_2(v)$ is the imaginary part of the complex permittivity. If the density of states of both band edges is parabolic, then the photon energy dependence of the absorption becomes,

$$a\nu \propto v^2 I_2(v) \propto (h\nu - E_{opt})^2$$

So for higher photon energies the simplified general equation which is known as Tauc relation is,

$$a\nu = A(h\nu - E_{opt})^2$$
where $h\nu$ is the energy of absorbed light, $n$ is the parameter connected with distribution of the density of states and $A$ is a constant or Tauc parameter. Here $n = 1/2$ and 2 for direct, indirect allowed transitions, and $n = 3/2$ and 3 for direct, indirect forbidden transitions, respectively. When finding the $n$, the type of transition can be obtained from the absorption spectrum. Thus from the straight-line plots of $(ah\nu)^2$ versus $h\nu$ and $(ah\nu)^{1/2}$ versus $h\nu$ the direct and indirect energy gaps of a material can be determined.

### 5.6 X-ray Photoelectron Spectroscopy (XPS)

EDS, XRF, and FTIR techniques are often known as surface analysis tools. However, generally, they yield signals averaging over depths of 1 to 2 μm. Since, XPS offers a 6 – 8 nm probing depth which is 0.003 to 0.008 times that of EDS, XRF, and FTIR, XPS is a far more accurate surface analysis technique. For example, the XPS technique can provide detection limits of 0.001 to 0.005 at.% for heavy metals, 0.03 at.% for lighter transition metals, 0.2-0.4 at.% for oxygen, nitrogen, and carbon, and about 0.4-1.0 at.% for lithium, beryllium, and boron. The XPS phenomenon is based on the photoelectric effect which was developed by K. Siegbahn and his research group in the mid 1960s. The fundamental concept of XPS is the discharge of electrons from a surface when photons of suitable energy and wavelength are allowed to impinge upon a material. The XPS method is highly surface specific due to the short range of the photoelectrons that are ejected out of the materials. X-ray photoelectron spectroscopy (XPS) is also known as electron spectroscopy for chemical analysis (ESCA). It is the most widely used surface analysis technique to measure the quantitative elemental composition, chemical and electronic states of materials and their chemistry. This approach can be extended from the surface to a depth of ~50 to 100 Å. Traditionally, XPS has been used for surface studies using soft X-rays *i.e.*, monochromatic sources of radiation (photons of fixed energy ~200-2000 eV) to investigate the core-level (inner shell) electrons. The most commonly used X-ray sources are: Mg $K_a$ radiation: $h\nu = 1253.6$ eV and Al $K_a$ radiation: $h\nu = 1486.6$ eV. Thus, the photoelectrons will have kinetic energies in the range of *ca.* 0 - 1250 eV or 0 - 1480 eV. When an atom in the surface of a material is irradiated by a monochromatic soft X-ray photon in an ultrahigh vacuum chamber, an electron is emitted from an inner shell. The kinetic energy ($E_k$) of the ejected photoelectron can be expressed by the following relation:

$$E_k = E_x - E_b - \phi$$ (5.8)
where $E_x$ is the kinetic energy of the X-ray photon, $E_b$ is the binding energy of the atomic orbital from which the electron arises and $\phi$ is the work function of the sample that also depends on the spectrometer [390]. The photoelectrons are guided through the hemispherical photoelectron energy analyzer and energy is chosen by electrostatic fields before heading to the detector. Each element has a characteristic binding energy associated with each core atomic orbital, yielding a set of discrete peaks in the photoelectron spectrum. An XPS spectrum is the plot of the electron counting rate as a function of binding energy. A peak at a particular energy indicates the presence of a certain element and the intensity of the peak corresponds to the concentration of the element in the sample. XPS also analyses the binding energy distribution of the emitted photoelectrons including the composition, elemental identity, chemical state and electronic state of the surface region of a sample in terms of the intensity of the photoelectron peaks. Changes in the structural configuration or chemical states of a chemical element at the surface layers can be identified by examining the shifts in the binding energies of a particular core level. The spectrum not only carries information about the atoms from which the characteristic photoelectrons were emitted, but it also carries information about the chemistry of the atoms from which they came. At the same time, many other chemical bonds have been found to change because of the binding energies of the electrons. The atoms which give rise to the photoelectrons in the sharp peaks are those which are very near to and in the surface of the irradiated material. Low energy X-rays also penetrate the solid materials much more deeply than the thin surface layer from which the photoelectron peaks in the spectrum results.

5.6.1 Applications of XPS Technique in Materials Characterizations

The XPS technique can be successfully used for the following purposes in material characterizations:
- The detection and identification of surface contamination and optical resistant surface coatings,
- The identification of material degradation and causes of corrosion,
- Surface and near-surface characterizations of process-dependent material compositions,
- The identification of stoichiometry of deposited films,
- Variations of the surface compositions of materials due to chemical heating, radiation, and absorption,
- The identification of inter-diffusion and reactions at interfaces,
- The identification of surface and interface characterizations of nanomaterials,
- Multilayer thin film structures e.g., highly absorbing layer with anti-reflective coatings,
- Protective coating problems due to mixing problems, segregation of component materials, and
- Determination of the bulk chemistry of ceramics, minerals, and glasses by examining fractured surfaces.

5.6.2 Synchrotron Radiation XPS

The performance of XPS measurements is influenced by the power of its source and its focusing ability. High resolution XPS results can be found from a synchrotron radiation source. The synchrotron radiation soft X-ray spectroscopy (SXR-XPS) beam-line at the Australian Synchrotron in Melbourne provides a continuous energy distribution over a large energy region with high intensity and tuneability giving an optimal excitation energy instead of a fixed excitation energy source, whereas the standard XPS system uses either Al-Kα or Mg-Kα source for X-rays [391, 392]. Compared to the traditional X-ray sources, the beam size of the synchrotron source is much smaller and this helps to reduce the effects of the non-uniformity of the sample surfaces [393]. Furthermore, the X-ray energies of the synchrotron radiation can be set to various escape depths of out-coming photon electrons and having a better photon ionization cross-section [393]. The information provided by the XPS method in relation to thin film structures plays a significant role in many industrial applications such as corrosion, adhesion, semiconductor and dielectric materials, sensors, magnetic media, and thin film coatings used in a number of industrial applications.

5.6.3 Experimental Technique of X-ray Photoelectron Spectroscopy (XPS) Study

The samples were mounted horizontally on the sample holder by double-sided sticky copper tape. The sample surfaces were normal at the entrance of the electrostatic lens and a charge neutralizer was used to counterbalance the electron deficit on the sample surface during data collection. The electrostatic lens mode and analyzer entrance were set to hybrid and slot mode (\(I_{rs} = 0.6\) and Aperture = 49) respectively. A background pressure of less than 10-9 Torr was maintained at the analyzer chamber throughout the measurements. The X-ray source was held at a primary beam power of 12 kV and 12 mA respectively. Initial survey scans used pass energy of 80 eV. High resolution and good sensitive core level spectra were acquired with pass energy of 10 eV and step size of 0.1
eV. The charging effects were corrected by using the C1s of saturated carbon (C-C/C–H) peak as reference for all samples at a binding energy (BE) of 284.8 eV. The XPS measurements were taken using a Kratos axis ultra-X-ray photoelectron spectrometer (see Fig. 19) installed at the University of Queensland. The collected data was analyzed using CASA XPS (version 2.3.15) software with Shirley background subtraction.

Figure 19. The Kratos Axis Ultra photoelectron spectrometer installed at The University of Queensland, Australia.

The synchrotron radiation XPS measurements of the thin film coatings were carried out at the soft X-ray beam line (SXR) at the Australian Synchrotron in Melbourne. The storage ring was operated in the top-up mode with a beam current of 200 ± 1 mA at 3 GeV. A plane diffraction grating monochromator SX700 with a grating of 1200 lines/mm and 15 μm entrance/exit slits was used for collimating and monochromatizing the out coming X-ray beams. The samples were grounded and mounted on a stainless steel sample holder using double sided carbon tapes to avoid charging. A minimum base pressure of $1 \times 10^{-10}$ mbar was confirmed in the analysis chamber. The photon energy used was 1253.6 eV. Measurements were conducted at a glancing incidence of 55° (‘magic angle’) with the X-ray beam. The Co2p, Cu2p, C1s and O1s photoelectron lines were measured. The XPS spectra energy scale was calibrated using C1s (284.6 eV; saturated carbon: C-C/C–H). The data was processed using computer based SPECSLAB (V2.75-R25274) software.
5.7 Synchrotron Radiation Based Near-edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Synchrotron radiation is emitted by very high energy electrons circulating around a storage ring by a series of magnets separated by straight sections inside the synchrotron tunnels. Synchrotron radiation has many unique qualities such as polarization control, coherence, high brightness and photon-energy tuneability. Owing to their large skin depth in materials, synchrotron radiation can be directly used to probe the bulk and surface properties of the electronic structure of various material systems. X-ray absorption fine structure (EXAFS) spectroscopy, X-ray absorption near-edge structure (XANES) and near-edge X-ray absorption fine structure (NEXAFS) are powerful spectroscopic tools to enhance understanding of electronic structure and bonding states of the surface and interface of composite materials. XANES technique is mainly used for the structural investigations of solids and inorganic complexes while NEXAFS is employed for characterization of materials surfaces. Over the past few years, the synchrotron radiation based NEXAFS spectroscopy has been widely used as a powerful technique for investigation of physical and chemical properties such as atomic and molecular electronic structure of various compounds in pure and doped states. It is extensively used in the identification of the atoms, molecules and compounds in a wide variety of field in sciences and technology such as physics, chemistry, materials sciences and environmental science. Due to the correspondence between EXAFS oscillations and the local crystallographic structure about the central excited atom, for the last several years EXAFS spectroscopy has been more popular than NEXAFS spectroscopy. EXAFS spectroscopy is widely used as a powerful method in the understanding of the near edge structure of atoms, molecules, and many other systems. Since the 1990s, it has been reported that for the energy region of 30-50 eV above the absorption edge, the NEXAFS and EXAFS regions match nicely [394]. Since then, the development and applications of EXAFS have made remarkable progress in realizing the near-edge structure of compounds, molecules, crystalline and amorphous solids, inorganic complexes and biological systems [394]. However, in about last three decades the near-edge structure has been referred as the X-ray absorption near-edge structure (XANES) or the near-edge X-ray absorption fine structure (NEXAFS). In general, XANES spectroscopy is used for the study of inorganic complexes and solid materials whereas NEXAFS is involved more in surface analysis. NEXAFS spectroscopy is also used in characterizing the complex systems and identifying the co-existence of various crystalline or in amorphous phases.
5.7.1 Background of the NEXAFS Study

NEXAFS is a synchrotron radiation based powerful spectroscopic method which is used to probe the surface electronic structure and local co-ordination of materials. In a NEXAFS study, synchrotron radiation X-ray beams are allowed to fall upon the material and electrons are discharged from the inner shells. The empty spaces are filled with the electrons from the higher energy shells resulting in the emission of Auger electrons (Auger decay). These electrons are inelastically scattered, thereby generating a cascade of secondary electrons from the sample. By measuring the intensity of Auger electrons as a function of photon energy, sharp resonance features can occur which are associated with transitions from core occupied states into the lowest unoccupied molecular states. It is a well-established fact that an X-ray absorption spectrum encompasses excited electrons as a function of the incident photon energy. The absorption spectrum can be classified to the edge region where the electron has a low kinetic energy and is likely to undergo multiple scattering or can be excited into the empty states below the vacuum level (VL). This phenomenon is termed as NEXAFS extending from the ionization edge to ~50 eV towards higher energy regions [395]. Synchrotron radiation is produced by the acceleration of high-energy particles inside a central closed loop tube or storage ring. The path of the particles is bent by pulsed magnetic fields that follow a curved trajectory [396]. The electrons emit a continuous spectrum of white light which is directed away from the storage ring down to a tangential path known as the beamline. A series of mirrors, lenses, monochromators and filters are employed to produce a parallel beam of light with the wavelength of interest.

5.7.2 Modes of NEXAFS Measurements

NEXAFS spectroscopy probes the density of states (DOS) of partially occupied or completely unoccupied electronic states and therefore they are very sensitive to the local bonding structure e.g., coordination number of structural unit cell, number of valence shell electrons and their corresponding spin configurations, their symmetry and so on. Furthermore, because of their large skin depth in materials, synchrotron radiation can be directly used to probe the bulk properties of the electronic structure of various systems and their oxidation states. NEXAFS data can be recorded in either electron or fluorescence yield mode. In total electron yield (TEY) mode, electrons of all energies that are ejected from the sample are measured however, the signal is found to be dominated by the secondary electrons with energies less than 10 eV. The surface sensitivity of TEY
mode is controlled by the mean free path of the primarily released electrons. The surface sensitivity of TEY measurements can be improved by detecting the Auger electrons and primary valence electrons using a partial electron yield (PEY) \[397\]. Generally, the PEY mode includes higher signal to background ratios than TEY measurements and are suitable for measuring the adsorbates on surfaces. In addition to TEY and PEY modes, Auger electron yield (AEY) detection is also used to record the elastically scattered Auger electrons \[397\]. In total fluorescence yield (TFY) mode, the total number of photons emitted from the sample in a relaxed state can be detected without discrimination. TFY mode of measurements offers a high bulk sensitivity of the sampling depths up to 200 nm.

5.7.3 Experimental Technique of Synchrotron Radiation Based Near-edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Electrons strongly interact with matter, and as the incident X-rays pass into the sample, electrons will be generated throughout the depth of the material, however only those electrons generated close to the sample surface can escape and be detected. Accordingly, electron yield methods are always strongly surface sensitive. The fluorescence yield, similar to the electron emission, will be generated throughout the depth of the material. However, as these fluorescent X-rays pass relatively easily through matter, the sampling depth is always much deeper than that of electron yield methods. The fluorescent yield signal is therefore indicative that the bulk of the samples are free of artifacts produced by self-absorption, however this is not always the case for fluorescent yield. AEY investigated the surface oxide layer and probed the interaction of oxides with underlying materials while the TFY revealed the bulk structure of materials e.g., chemical bonding at the grain boundary. The surface electronic structures of 3d transition metal based nitride and oxide thin films can be successfully studied by means of X-ray absorption (XAS) and X-ray emission (XES) spectroscopies. Both of these techniques probe the empty and filled densities of states of a material on an element and orbital angular momentum based dipole selection rules \[60\]. NEXAFS spectroscopy essentially provides a unique opportunity to probe differences in the electronic structure as the composition of transition metal based nitride and oxide materials changes as seen in shifts in the Al K-, Ni L-, Cu L-, Co L-, Cr L-, N K- and Si K-edge absorption energies. This study focusses on establishing the bonding structural evolution in Cr\(_{1-x}\)M\(_x\)N upon progressive incorporation of Al, Si and Ni. The influence of Al, Si and Ni doping to the CrN matrix
from 14.3 to 28.5 at.% have been investigated by measuring the Al $K$-, Ni $L$-, Cr $L$-, N $K$- and Si $K$-edge NEXAFS spectra.

The NEXAFS measurements of our thin film coatings were performed using the synchrotron radiation soft X-ray spectroscopy (SXR) beam-line (shown in Fig. 20) at the Australian Synchrotron facility in Melbourne. The beamline was equipped with an Apple II undulator, adjusted to produce horizontally polarized soft X-ray. The storage ring was operated in the top-up mode with a beam current of 200 ± 1 mA at 3 GeV. A plane diffraction grating monochromator SX700 with a grating of 1200 lines/mm was used for collimating and monochromatizing the X-ray beam. The samples were grounded and mounted on a stainless steel sample holder using double sided carbon tapes to avoid charging. A standard pressure of $1 \times 10^{-10}$ mbar has been maintained in the analysis chamber. The photon energy used was 1253.6 eV. A gold mesh was used to monitor photon flux incident ($I_0$) on the sample. The photon flux on the beamline ranged from $1.3 \times 10^{11}$ photons/s/200 mA with an energy of 550 eV. The photon spot size on the sample was approximately $0.6 \times 0.6$ mm. Measurements were conducted at a glancing incidence of 55°, known as ‘magic angle’ with the X-ray beam [398].

![Figure 20. Soft X-ray beamline at Australian Synchrotron, Melbourne.](image)

The photoemission and the asymmetry parameter become zero for all electron energy orbital quantum numbers e.g., $2p3/2$, $4f7/2$ etc. In addition, the possible effects of the
preferred molecular orientations can be minimized for samples without azimuthal order. NEXAFS data was recorded in two different modes namely, the Auger electron yield (AEY) and the total fluorescence yield (TFY). For Cr$_{1-x}$A$_x$N thin film coatings, NEXAFS data were recorded at Si $K$-, Cr $L$-edge (570-610 eV), Ni $L$-edge (840-890 eV) and N $K$-edge (380-450 eV) in both modes with a channeltron facing the sample positioned 30° above the incoming beam and by monitoring drain current. NEXAFS experiments were performed at room temperature. The NEXAFS data collected in both modes were normalized with respect to the incident photon flux by dividing the samples signal, $I_s$ with the incident photon flux $I_o$ monitored using a gold grid with high transmissivity positioned in front of the sample. The linear background was subtracted from the spectra by fitting the pre-edge region. Prior to analysis, the NEXAFS spectra were normalized to the primary beam current. The obtained data was processed using SPECSLAB (V2.75-R25274) software.

5.8 Mechanical Properties of Thin Films Coatings: Nanoindentation Tests

Investigations of mechanical properties of various types of thin films and coatings are important in many electronic and mechanical systems including data storage technologies, integrated circuits and microprocessors. Mechanical properties such as Young’s modulus ($E$) and hardness ($H$) facilitate to estimate the reliability of the materials in parts and components. They also help to interpret the deformation mechanisms and strengthening in small scales [399, 400]. Furthermore, the Young’s modulus, $E$ and hardness, $H$ are very important to understand the wear resistance of optical thin film based SSA surfaces. The performance and function of the optical coatings during the period of operation can be maintained by monitoring the wear resistance behaviors of selective solar material. The wear resistance of the coating can be estimated from the known values of $E$ and $H$ obtained from nanoindentation tests [401].

Indentation is a well-established method which is widely applied in the mechanical characterization of materials while nanoindentation measurements are performed on the range of nanometre scale. The mechanical properties of thin film coatings can be successfully investigated by the nanoindentation test. In nanoindentation, a controlled load, $P$ is applied through a diamond tip which is in contact with the material's surface. The load and penetration depth, $h$ are monitored during the loading unloading contact cycle. The penetration depth of the tip into the material or displacement is recorded as a function of the applied load. Using the load vs penetration depth curve $i.e.$, $P$–$h$ curve,
various parameters such as Young's modulus, hardness, fracture toughness and residual stress can be computed [402].

Due to the loads and the diamond tip used in the nanoindentation, complexity arises in determining the contact area which might require using surface morphology techniques such as AFM and SEM. However, this challenge can be avoided by using an indenter with known geometry and good precision. Almost all indentation systems use a diamond indenter whether it be sharp, spherical or flat–ended cylindrical. Of these, the sharp indenters induce plastic deformation at the earliest stage during loading. For this reason, sharp indenters are preferred for the micro and nano-scale measurements with the thin films and specimens of volume.

According to the model proposed in Ref. [403], the physical hardness and Young's modulus can be estimated from a set of $P–h$ data recorded in a loading and unloading process without the need to image the hardness impression [403]. Using the $P–h$ diagram, maximum load, $P_{\text{max}}$ maximum displacement, $h_{\text{max}}$ and stiffness, $S$ can be estimated (see Fig. 21) [403]. The hardness, $H$, is a measure of how resistant a solid matter is to various permanent shape changes when force is applied. Hardness can be computed from the following equation:

$$H = \frac{P_{\text{max}}}{A} \quad (5.9)$$

where $P_{\text{max}}$ is the maximum load and $A$ is the area of the contact made by the indenter.

![Figure 21](image-url)  
**Figure 21.** A typical loading-unloading curve for the nanoindentation measurements [403].
Young's modulus, $E$ is a measure of a material's within the Hooke's limit. Physically, it is defined as the ratio of stress to strain within the elastic limit. Using the $P–h$ diagram presented in Fig. 21, Young's modulus can be calculated from the relationship between stiffness $S$ and contact area $A$ in the following equation.

$$S = \beta \frac{2}{\sqrt{\pi}} E_{\text{eff}} \sqrt{A}$$  \hspace{1cm} (5.10)

where $\beta$ is a dimensionless constant taken as unity and $E_{\text{eff}}$ can be defined as

$$\frac{1}{E_{\text{eff}}} = \left(\frac{1 - \sigma^2}{E} + \frac{1 - \sigma_i^2}{E_i}\right)$$  \hspace{1cm} (5.11)

where $E$ and $\sigma$ represent the Young's modulus and Poisson's ratio of the indenter and $E_i$ and $\sigma_i$ refer to the Young's modulus and Poisson's ratio of the thin film, respectively [404].

5.8.1 Experimental Technique of Nanoindentation Tests

In the nanoindentation method, the mechanical properties of thin film coatings can be measured either in lateral or depth geometry without removing the coatings from the substrate. The indenter is a main component of the nanoindentation system. The indentation system measures the depth of penetration using either an inductance or capacitance displacement sensor. Ideally, it should have a high precision in geometry to facilitate identification of the contact area. The mechanical characteristics of metal oxides and metal nitrides based coatings were investigated using a nanoindenter (Model No. Ultra–Micro Indentation System 2000, CSIRO, Sydney, Australia) equipped with a sharp indenter (Berkovich indenter) of 5 μm radius according to Oliver and Pharr model [403, 404]. Whilst undertaking the nanoindentation measurements, the area of the indenter tips was calibrated using a standard fused silica sample. A maximum load of 0.5 mN was maintained during the nanoindentation measurements. The indenter was pressed into the sample surface under load control, and the load and displacement were monitored during the loading and unloading process. For each sample, 20 indentation measurements were made, of which 10 incremental and 10 decremental steps were confirmed. The maximum penetration depth during the tests was found to be <10% of the film thickness, which ensured that only the film properties were measured.
5.9 Optical Properties of Thin Film Coatings

The optical characteristics of any spectral solar absorber coating on the opaque substrates such as aluminum substrate, is defined by two parameters: the solar absorptance, \( \alpha \) in the solar spectrum region (0.3 to 2.5 \( \mu \text{m} \)) and the thermal emittance, \( \varepsilon \), i.e., reflection in the infra-red (IR) region (\( \geq 2.5 \mu \text{m} \)) [14, 26] at the operating temperature. These parameters can be calculated from the measurements of the monochromatic reflectance in wavelengths ranges of 0.3–2.5 \( \mu \text{m} \) and \( \geq 2.5 \mu \text{m} \) using an UV-Vis-NIR and FTIR instruments respectively [168].

The response of reflectance from an opaque material can be classified into two parts: (a) specular reflectance (also known as mirror-like reflection) where the incident polar angle is equal to the reflected polar angle and (b) diffuse reflectance which removes all directional characteristics of the incoming light by uniform distribution of the radiation in all possible directions. For practical purposes, generally a highly polished and smooth surface shows a specular reflectance whereas a cracked and rough surface reflects diffusely. Since, in actual practice, almost all of the materials give rise to a combination of specular and diffuse reflectance, specular reflectance and diffuse reflectance can be separately measured. The total reflectance can be measured using an integrating sphere, the wall of which is coated with diffusing and highly reflecting materials. A typical diagram of an integrating sphere is shown in Fig. 22. In the solar spectrum range, barium-sulphate (BaSO\(_4\)) is used for the coating of integrated wall while in the IR region, a gold coated wall is most often used [405, 406].
Figure 22. The reflection mode of an integrated sphere showing specular reflectance ($R_s$) and diffuse reflectance ($R_d$). This picture is reprinted from Refs. [185, 406, 407].

Infrared (IR) spectroscopy is concerned with the infrared region of the electromagnetic spectrum and is based on absorption spectroscopy. IR spectroscopy exploits the fact that molecules absorb frequencies specific to the structure of the functional groups. For this reason, IR spectroscopy is widely applied to identify and study the functional group of chemicals. As a result of vibrational or rotational motion, the dipolar character of a molecule changes onto the exposure of IR radiation. The corresponding energy of vibrations of the atoms and bonds in the molecules is quantized and results in the transition of two vibrational levels of the molecule in a ground state corresponding to the mid–infrared region. As a result of the differences in energy between the quantum states, a number of bands are observed in the absorption spectra.

A Fourier transform infra-red (FTIR) device consists of an infrared source, an interferometer, a sample holder and a detector. The infra-red light is generated from a glowing black-body source. The amount of energy in the infra-red light is controlled by an aperture. The aperture controlled beam passes through the interferometer where the spectral encoding takes place. The resultant interfering signal enters to the sample holder where the beam is reflected off or transmitted through the sample surface based on the type of FTIR application. Finally, the signal is captured by the detector and a digital
signal is sent to the computer program for the Fourier transformation analysis of the detected spectrum.

5.9.1 Measurements of Optical Properties via UV-Vis-NIR Spectroscopy

A UV-Vis-NIR spectrophotometer comprises of a light source, a sample holder, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. A tungsten filament (300-2500 nm) is often used as the radiation source. A scanning monochromator is used with the photodiode detector and photomultiplier tubes. The monochromator filters the light so that only light of a single wavelength such (monochromatic light) reaches the detector at once. To measure the intensity as a function of wavelength, the scanning monochromator moves the diffraction grating to step-through each wavelength. The solar absorptance and emittance of the thin film coatings were computed from the reflectance data as delineated by Duffie and Beckman [168]. A UV–Vis-NIR Jasco V-670 double beam spectrophotometer with 60 mm integrating sphere (See Fig. 23) was used to record the near normal hemispherical solar reflectance spectrum in the range of 300 to 2700 nm. Deuterium (300 to 350 nm) and Halogen (330 to 2700 nm) lamps were employed as the two light sources.

Figure 23. UV–Vis-NIR Jasco V-670 double beam spectrophotometer.
5.9.2 Measurements of Optical Properties via FTIR Spectroscopy

The FTIR measurements allow for the simultaneous collection of data in a wide range of spectrum. FTIR measurements offer high speed data collection and enhanced resolution \textit{i.e.}, high signal–to–noise ratio. Light elements such as carbon, oxygen and nitrogen are suitable for FTIR analysis. The attenuated total reflectance (ATR) method has revolutionized the analysis of solid and liquid samples because it resolves the difficulties associated with specimen preparation for FTIR measurements and spectral irreproducibility [408]. ATR also confirms that the solid and liquid samples are suitable for investigation without any further special processing technique. The infrared reflectance spectra of the deposited coatings were obtained using a “reflected off” type of Perkin Elmer Spectrum 100 FTIR spectrometer (See Fig. 24) in a wavelength range of 2.5 to 15.4 μm. The coating surface was placed on the crystal surface area and a pressure arm was positioned and locked at force of 80 N in order to maintain the coating surface touching evenly onto the diamond surface. A total of 4 timed scans were performed for the reflectance spectrum with the resolution of 2 cm\(^{-1}\). Background correction was done before the collection of each spectrum. The collected spectra were then ATR corrected using a computer software.

\textbf{Figure 24.} Perkin Elmer Spectrum 100 FTIR spectrometer.
CHAPTER SIX: STRUCTURAL THERMAL STABILITY OF GRAPHENE OXIDE DOPED COPPER-COBALT OXIDE COATINGS AS A SOLAR SELECTIVE SURFACE

6.1 Introduction

Over the years, cobalt based mixed metal oxide thin films have been extensively studied by different groups around the world owing to their wide-spread applications [98-101]. Pure copper oxide [6], cobalt-copper oxide, manganese-cobalt oxide, nickel-cobalt oxide [21, 225], and copper-aluminium oxide [102] have been used as high performance optical selector or absorbers. The physicochemical and electrochemical properties of Cu$_{x}$Co$_{3-x}$O$_{4}$ powder has been investigated for their practical applications as catalysts in oxygen evolutions reactions (EOR) [409]. There have been numerous investigations of mixed metal oxide thin films pursuing improved physicochemical, optical, thermal, electrochemical, photo-chemical, magnetic, dielectric and electro-magnetic properties focusing on their potential practical applications in the areas such as clean energy devices, solar cells, photovoltaics, thermal collectors, solar selective absorbers, and smart windows. Sol-gel derived Cu$_{2}$O and CuO coatings are developed as photocatalytic materials for water splitting applications [410]. Optical characterizations, thermal durability studies, physicochemical and mechanical properties of sol-gel derived Cu-Co oxide coatings have been investigated by other groups [110, 228]. Synthesis mechanisms, cyclic stability and electrochemical performance of graphene-carbon nanotube hybrid films, graphene based metal/metal oxides nanocomposite and nano-sized Co$_{3}$O$_{4}$ materials have been extensively discussed in earlier studies [411-413].

Optical applications of graphene oxide are also well-known [123]. The high optical absorption and tuneable optical band-gap are the most appealing characteristics of graphene that make it an ideal material for the effective light harnessing [124]. Light absorbing photovoltaic applications of graphene based materials have been reported in an earlier study [125]. Optical absorption and power conversion efficiency of layer-transferred graphene in organic hybrid solar cells have been reported [126]. The application of graphene in organic photovoltaic devices has been fabricated by Arco et al and Liu et al. [127, 128]. Graphene has been reported to be a promising candidate for offering improved efficiency of light harvesting devices e.g., inorganic [129], organic [130, 131], hybrid [132], and dye sensitized solar cells [133]. A series of comprehensive
reviews focused on investigating manufacturing aspects, properties, and applications of graphene and graphene-based materials in energy related areas [114, 134, 135]. Optimization of optical properties of inorganic compounds mixing with graphene oxide forming a hybrid system is also feasible in the development of graphene oxide-based selective surface. As graphene oxide offers good solubility in aqueous and polar solvents, the sol-gel method is a feasible technique to prepare graphene oxide based thin films. These coatings exhibit high transmittance and the strong ability of resist abrasion which make them suitable for applications in some harsh conditions.

In the past few years, numerous strategies have been adopted in the design of metal oxide based light harvesting assemblies. For instance, sol-gel derived mixed metal oxides based thin film selective solar surfaces attracted attention due to their flexibility and advantages e.g., cost-effective, good thermal and physico-chemical stability, easy preparation process, shorter processing time, low-toxicity, less equipment needed, tuneable electronic band gap, and high electron mobility. Despite the availability of numerous literatures on metal oxide thin films and graphene oxide thin films for their optical and light harvesting purposes, however, to the best of our knowledge, utilization of mixed metal oxide with graphene oxide thin films as solar selective surface is yet to be explored. Nowadays, synchrotron radiation has emerged as a powerful and versatile analytical tool for materials production (e.g., fabrication of microelectronic devices), quality control, and materials evaluation in industrial research and development. Synchrotron radiation possesses some salient features; very high intensity, high brightness, good stability, higher degree of polarization, wide energy range extending from infrared to X-ray wavelengths and so on. In synchrotron radiation, many different beamlines are involved and each beamline is designed for a specific type of research. For different beamlines, various techniques such as X-ray absorption, scattering, diffraction, and fluorescence analysis are available for synchrotron research. Synchrotron radiation facilities demonstrate superior capabilities to characterise various properties of materials. A wide range of experiments such as DFT structure resolutions, variable temperature studies, structural studies of microporous materials, structure and property investigations of solid metal oxides, phase identification and quantification of pharmaceuticals etc can be successfully conducted at the synchrotron radiation-based powder diffraction (PD) beamline’s primary end station. Synchrotron radiation-based spectroscopy is also used to investigate semiconductor and thin film surfaces to realize the interface formation between among the constituents. Further, synchrotron radiation core level emission
spectra, the chemical composition of the surface of the films, detection of the surface core level components can be used to explain the bonding configurations of the thin film coatings. The synchrotron radiation based spectroscopy thus assists revealing the interface formation and new development and applications can be evolved. For example, synchrotron radiation based near-edge X-ray absorption fine structure (NEXAFS) initiated by the electron transfer from a core orbital to discrete or quasi-discrete unoccupied levels provides us with valuable information pertinent to the electronic structures and local atomic structures. The local bonding structures around a specific atom such as the coordination number, the bonding length, and the distribution of defects can be estimated by analysing the peak positions of synchrotron radiation based experiments. In a recent work [226], we conducted NEXAFS experiments to sol-gel derived copper-cobalt oxide coatings by measuring the Cu$L_{2,3}$-edges, Co$L_{2,3}$-edges and O $K$-edges. Our study demonstrated that the local environments of Cu, Co and O remained invariant with the change in the copper to cobalt concentration ratios except for the $[\text{Cu}]/[\text{Co}] = 2$ sample whereas the local coordination appeared to slightly change due to the loss of octahedral Cu$^+$. The Cu-$L_3$ and Cu-$L_2$ absorption edges arisen from the dipole transitions of the Cu$2p_{1/2}$ for $L_2$ and Cu$2p_{3/2}$ for $L_3$ into the empty $d$ states while the Co-$L_3$ and Co-$L_2$ absorption edges were appeared from Coulomb interactions and exchange interactions of $2p$ core holes with the $3d$ electrons. The hybridization of the Co$3d$ states with O$2p$ states; and O$2p$ states with Co$4sp$ states and O$2p$ states was extended to a Co higher orbital that was seen in the O $K$-edge NEXAFS peaks of copper-cobalt oxide coatings. In this study, we attempt to develop the graphene oxide as a mixture into the Cu$_x$Co$_y$O$_z$ systems for the development of the thin film based light harvesting devices with improved selectivity. We focus on the structural thermal stability and optical effects of graphene oxide modified Cu$_x$Co$_y$O$_z$ composites in order to achieve better solar selective performance of coatings fabricated via dip-coating sol-gel technology.

6.2 Materials and Methods

6.2.1 Sample Preparation Technology

Cobalt (II) chloride (CoCl$_2$.6H$_2$O, APS Chemical, >99%), copper (II) acetate monohydrate (Cu(OOCCH$_3$)$_2$.H$_2$O, Alfa Aesar, >98%), propionic acid (C$_2$H$_5$COOH, Chem Supply, >99%), graphene oxide (concentration 1 mg/cc), and absolute ethanol (E. Mark of Germany, >99%).) were used to make the sols for synthesizing thin films. The
highly-reflective commercial aluminum material (Anofol, size 2x4 cm²) was used as substrate for the deposition of the coatings. The substrates were cleaned using a hot etching solution (85 °C) prepared by mixing chromium (VI) oxide, phosphoric acid and deionized for 10 minutes in order to remove the alumina layer. Substrates then were rinsed in hot deionized water followed by a flush of cooled distilled water and dried in a flow of high purity nitrogen gas.

In preparing the sols, cobalt (II) chloride (CoCl₂·6H₂O, 0.25 M), graphene oxide, and copper (II) acetate monohydrate (Cu(OOCCH₃)₂·H₂O were mixed with absolute ethanol. Propionic acid (C₃H₅COOH) was used as the complexing agent to the solution. After stirring the mixed solution for 2 hrs, the resultant solution was used for thin film deposition on aluminum substrates using a dip-coating technique. The dip and withdrawal rate were 180 mm/min and 60 mm/min, respectively. The sample coating was heated at 150 °C for 60 seconds. A relative humidity of 50% was maintained during the entire period of the coatings preparation process. The same dip coating process, using same sol solution, was repeated four times to increase the thickness of film with better uniformity. Finally, the samples were annealed at 500 °C in air for 1 hour. The heating rate of the furnace for annealing was kept at 50 °C/min and the samples were remained in the furnace for 10 minutes after power off.

6.2.2 Characterization of the Thin Film Coatings

High resolution synchrotron radiation X-ray diffraction (SR-XRD) measurements of the CuₓCoᵧOₓ coatings with and without graphene oxide were conducted with the powder diffraction (PD) beamline 10-BM-1 at the Australian Synchrotron, Melbourne. The PD beamline at Australian Synchrotron utilizes a bending magnet source. The beamline was operated at 2.5 GeV which produces a continuous spectrum of photons in the range 5–30 keV with a maximum flux of about 10¹³ photons/sec at an angular acceptance of 0.23 mrad vertical by 2.5 mrad horizontal. The samples were loaded in 0.3 mm diameter quartz capillaries with diamond powders that are rotated during the measurements. A MYTHEN II microstrip detector system was used in a 2θ = 18° to 44° geometry in steps of 0.002° for 5 minutes at each detector settings for SR-XRD data acquisition. The MYTHEN detector consists of 16 position sensitive detectors keeping a 0.2° gap between detector modules. X-rays of wavelength λ = 0.11267 nm as estimated with a LaB₆ standard NIST 660a standard was used for SR-SRD measurements at a beam size 7 mm width and 1 mm height with an exposure time of 145 mins. High temperature
measurements were achieved using an Anton Parr HTK20 furnace. The real time temperature was monitored by a thermocouple in direct contact with the bottom substrate of the coatings close to the irradiated area. The temperature difference between the top of the coating and the bottom of the substrate was calibrated before XRD measurement. The heating and cooling were remotely controlled via a computer interface. The acquired data were processed with the PDViPeR software in order to obtain the XRD patterns as presented in Fig. 25.

Chemical analysis of the outermost 5-10 nm atomic layers of the thin film coatings was performed via the XPS technique. The Kratos Axis-Ultra photoelectron spectrometer uses Al Kα monochromatic X-ray source with beam energy of 1486.6 eV at a power of ~10 mA and ~15 kV. Square size samples (2mm×2mm) were mounted on steel sample holder. The pressure of the XPS analyzer chamber was maintained at 3.87×10−7 Pa. The Cu2p, Co2p, O1s, C1s photoelectron lines were recorded with a 2D delay line detector. The photoelectron energy scale was calibrated using C1s (hydrocarbon; C-H) line at 284.6 eV. CASA XPS (version 2.3.15) software was employed for data processing and curve fitting in order to define the component of photoelectron lines.

The photon energy dependence of absorption coefficient helps to study the band structure and the type of electron transition involved in absorption process. In crystalline and amorphous materials the photon absorption obeys the Tauc relation [414, 415],

\[ a h \nu = A (h \nu - E_g)^n \]  

(6.1)

where, \( \alpha \) is the absorption coefficient, \( h \nu \) is the incident photon energy, \( A \) is an energy independent constant, \( E_g \) is the band-gap energy and \( n \) is an index depending on the type of optical transition involved in photon absorption. The index \( n = 1/2 \) and 2 for direct and indirect allowed transitions and \( n = 3/2 \) and 3 for direct and indirect forbidden transitions, respectively [415]. Thus, the direct transition energy gap (direct band-gap energy) can be obtained by plotting \( h \nu \) vs \( (a h \nu)^2 \) and extrapolating the linear portion of the curve to \( (a h \nu)^2 = 0 \) in the energy axis. Similarly the indirect energy band-gap can be found by plotting \( h \nu \) vs \( (a h \nu)^{1/2} \) and extrapolating the linear portion of the curve to \( (a h \nu)^{1/2} = 0 \) in the X-axis.

Solar absorptance of the coatings was determined using a double-beam UV–Vis spectrophotometer (Model: UV-670 UV-Vis spectrophotometer, JASCO, USA) with a
unique, single monochromator design covering a wavelength range from 190 to 2200 nm. The monochromator consists of a 1200 grooves/mm grating and a photo multiplier tube (PMT) detector for the UV-Vis measurements. The solar reflectance of the thin film coatings were measured using a FTIR spectrometer (Perkin Elmer Spectrum 100 FTIR Spectrometer, USA) in the wavelength of 2.5 to 15.5 µm. The solar absorptance and the thermal emittance of a material can be conveniently computed by measuring its reflectance data recorded in the visible and infrared range of the solar spectrum respectively [349]. For a range of solar wavelengths, the total solar absorptance, \( \alpha \) is defined as a weighted fraction between absorbed radiation and incoming solar radiation \( (I_{sol}) \), while thermal emittance, \( \varepsilon \) is defined as a weighted fraction between emitted radiation and the Planck black-body distribution \( (I_p) \) and can be computed using Eqs. (6.2) and (6.3) [349]:

\[
\alpha = \frac{\int_{2.0}^{2.2} I_{sol}(\lambda)(1-R(\lambda))d\lambda}{\int_{0.19}^{2.0} I_{sol}(\lambda)d\lambda} \tag{6.2}
\]

\[
\varepsilon = \frac{\int_{15.4}^{15.4} I_p(\lambda)(1-R(\lambda))d\lambda}{\int_{2.5}^{15.4} I_p(\lambda)d\lambda} \tag{6.3}
\]

The solar spectrum, \( I_{sol} \) has an air mass (AM) of 1.5 in accordance with the ISO standard 9845-1 (1992). A key parameter of a selective surface is its selectivity, \( s \), which is defined as a ratio of the solar absorptance \( (\alpha) \) and the emittance \( (\varepsilon) \) [416] as given in Eq. (6.4):

\[
s = \frac{\alpha}{\varepsilon} \tag{6.4}
\]

where \( \alpha \) signifies solar absorptance of the coatings estimated between the wavelength range of 190 nm and 2200 nm while \( \varepsilon \), the emittance lies between 2.5 µm and 15.5 µm.

6.3 Results and Discussion

6.3.1 Synchrotron Radiation based High Resolution XRD Studies of the \( \text{Cu}_x\text{Co}_y\text{O}_z \) Thin Film Coatings

High temperature synchrotron radiation X-ray diffraction (SR-XRD) measurements of \( \text{Cu}_x\text{Co}_y\text{O}_z \) with and without graphene oxide were carried out at room temperature, 100, 200 and 300 °C in a 2θ geometry from 18° to 44° and 0.002° increment. SR-XRD data presented in Fig. 25 provide information with the crystalline structures, phase transitions and thermal stability of these coatings.
In CuCoO films, multiple and stable phases e.g., CuO, CoO, CuCoO exist until to 300 °C. However Cu$_3$Co$_2$O$_5$ films with 1.5 wt% of graphene oxide, in addition to the above phases, a new phase orthorhombic/CoCu$_2$O$_3$ (space group $P_{nnm}$ (59)) was also observed. Monoclinic CuO and hexagonal CoO were the dominant phases in each case. All the coatings exhibited sharp diffraction lines at all temperatures indicating well defined crystalline phases. Absence of any impurity diffraction peaks reveals that the samples are...
formed with highly pure precursors. The detailed results of SR-XRD analysis of both sets of coatings for few major phases are delineated in Table 10 and Table 11. According to the data presented in Table 10 and Table 11, it is clearly seen that the $2\theta$ positions of all the existing phases are invariant at all measuring temperatures. This reflects the fact that these coatings possess good physical and chemical stability within the operating temperature up to 300 °C. Further observation shows with the addition of 1.5 wt% of graphene oxide to the copper-cobalt oxide coatings, $2\theta$ positions of the Bragg reflections is slightly shifting towards the lower angle sides. Due to the lowering of $2\theta$ values the residual stress of the coatings is reduced. The reduction in internal residual stresses result in lattice distortion. As a consequence of all these factors, it is believed that the coatings achieve greater mechanical and thermal stability in the operating temperature range. The existence of CuO and Co$_3$O$_4$ phases in Cu-Co spinel was detected by SR-X-ray diffraction analysis. The phase crystallinity of deposited films is also in good agreement with the reported data for CoO [417]. However, the CuO lines show the relatively low intensity in the X-ray pattern on these coatings. Incorporation of the carbon materials into the mixed metal oxide networks leads to reduce the scattering intensities of the Bragg reflections. As a result, a subtle shift to smaller $d$-spacings is taken place [418, 419] and spinel structures with enhanced solar selectivity and better physical stability are attained. In these films, copper ions occupy both the tetrahedral and the octahedral sites of the spinels. The difference of ionic radius in the tetrahedral and octahedral sites of copper ions (16 pm) and cobalt ions (5.5 pm) also forms a basis for stable structural configurations of these coatings. The films are also stable towards air and moisture having well defined grain boundaries. Cu-Co oxide based thin films form a single phase together with a partially inverted spinel structure [420-424] and the segregation of Cu and/or Co oxide phases depend on the Cu/Co ratio and annealing temperatures. Comparing to other methods the sol–gel dip-coating method allows the preparation of the Co$_3$O$_4$ stable phase at relatively low temperature [425]. Annealing of the coatings promotes the migration of the cobalt towards the surface of the coating, where it is oxidized by the atmospheric oxygen and forms the cobalt oxide layer. In a previous publication[426], annealing in air at 500 °C showed that the bulk cobalt films migrate towards the coating surface and forms a layer of Co$_3$O$_4$ having a thickness of 40–50 nm. Since the mixed CuCo oxide thin films can exist in a variety of compositions and crystal structures, their properties also vary widely. As a result, these coatings show a broad variety of potential applications [427] such as solar selective surfaces.
Table 10. $\theta$ positions, crystal phases, Miller indices and space groups of sol-gel derived Cu$_x$Co$_y$O$_z$ thin film coatings as observed from synchrotron radiation XRD studies.

<table>
<thead>
<tr>
<th>2\theta position at room temperature (°C)</th>
<th>2\theta position (±0.02) at 100°C</th>
<th>2\theta position (±0.02) at 200°C</th>
<th>2\theta position (±0.02) at 300°C</th>
<th>Crystal structure</th>
<th>Miller index</th>
<th>Space group</th>
<th>JCPDS reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.11 (A)</td>
<td>20.09</td>
<td>20.08</td>
<td>20.08</td>
<td>Monoclinic/CuO</td>
<td>(200)</td>
<td>Cc(9)</td>
<td>89-5899</td>
</tr>
<tr>
<td>20.48 (B)</td>
<td>20.44</td>
<td>20.46</td>
<td>20.47</td>
<td></td>
<td>(111)</td>
<td>(022)</td>
<td></td>
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<tr>
<td>36.76 (F)</td>
<td>33.75</td>
<td>33.77</td>
<td>33.76</td>
<td></td>
<td>(111)</td>
<td>(022)</td>
<td></td>
</tr>
<tr>
<td>41.59 (J)</td>
<td>41.56</td>
<td>41.56</td>
<td>41.58</td>
<td></td>
<td>(222)</td>
<td>(222)</td>
<td></td>
</tr>
<tr>
<td>20.11 (A)</td>
<td>20.11</td>
<td>20.10</td>
<td>20.09</td>
<td>Cubic/CoCo$_2$O$_4$</td>
<td>(400)</td>
<td>Fd-3m(227)</td>
<td>78-1980</td>
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<tr>
<td>23.28 (C)</td>
<td>23.28</td>
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<td>23.26</td>
<td></td>
<td>(440)</td>
<td>(222)</td>
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<td>33.75</td>
<td>33.77</td>
<td>33.76</td>
<td></td>
<td>(440)</td>
<td>(222)</td>
<td></td>
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<tr>
<td>39.15 (G)</td>
<td>39.16</td>
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<td>39.13</td>
<td></td>
<td>(622)</td>
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<td>20.11 (A)</td>
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<td>20.10</td>
<td>Hexagonal/CoO</td>
<td>(101)</td>
<td>P6$_3$mc(186)</td>
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<td>33.16 (E)</td>
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<td>33.14</td>
<td></td>
<td>(103)</td>
<td>(202)</td>
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<tr>
<td>39.91 (H)</td>
<td>39.90</td>
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<td>39.89</td>
<td></td>
<td>(104)</td>
<td>(104)</td>
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<td>40.98 (I)</td>
<td>40.96</td>
<td>40.97</td>
<td>40.97</td>
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<td>(221)</td>
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<tr>
<td>23.84 (D)</td>
<td>23.84</td>
<td>23.85</td>
<td>23.83</td>
<td></td>
<td>(444)</td>
<td>(444)</td>
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<tr>
<td>33.76 (F)</td>
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<td>33.75</td>
<td>33.75</td>
<td></td>
<td>(444)</td>
<td>(444)</td>
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<tr>
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<td>39.88</td>
<td>39.89</td>
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<td>R-3m(166)</td>
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<tr>
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<td>41.58</td>
<td>41.57</td>
<td>41.59</td>
<td></td>
<td>(020)</td>
<td>(131)</td>
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</table>
**Table 11.** $2\theta$ positions, crystal phases, Miller indices and space groups of sol-gel derived (Cu$_x$Co$_y$O$_z$ + 1.5 wt.% GO) coatings as observed from synchrotron radiation XRD studies.

<table>
<thead>
<tr>
<th>$2\theta$ position at room temperature</th>
<th>$2\theta$ position (±0.02) at 100°C</th>
<th>$2\theta$ position (±0.02) at 200°C</th>
<th>$2\theta$ position (±0.02) at 300°C</th>
<th>Crystal structure</th>
<th>Miller index</th>
<th>Space group</th>
<th>JCPDS reference</th>
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<tbody>
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<td>20.09</td>
<td>20.08</td>
<td>20.08</td>
<td>Monoclinic/CuO</td>
<td>(200)</td>
<td>Cc(9)</td>
<td>89-5899</td>
</tr>
<tr>
<td>20.48 (B)</td>
<td>20.45</td>
<td>20.46</td>
<td>20.47</td>
<td></td>
<td>(111)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.74 (F)</td>
<td>33.73</td>
<td>33.74</td>
<td>33.74</td>
<td></td>
<td>(022)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.57 (J)</td>
<td>41.56</td>
<td>41.56</td>
<td>41.57</td>
<td></td>
<td>(222)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.11 (A)</td>
<td>20.11</td>
<td>20.10</td>
<td>20.09</td>
<td>Cubic/CoCo$_2$O$_3$</td>
<td>(222)</td>
<td>Fd-3m(227)</td>
<td>78-1980</td>
</tr>
<tr>
<td>23.28 (C)</td>
<td>23.28</td>
<td>23.26</td>
<td>23.26</td>
<td></td>
<td>(400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.76 (F)</td>
<td>33.75</td>
<td>33.77</td>
<td>33.76</td>
<td></td>
<td>(440)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.15 (G)</td>
<td>39.16</td>
<td>39.14</td>
<td>39.13</td>
<td></td>
<td>(622)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.11 (A)</td>
<td>20.10</td>
<td>20.09</td>
<td>20.10</td>
<td>Hexagonal/CoO</td>
<td>(101)</td>
<td>P6$_3$mc(186)</td>
<td>89-2803</td>
</tr>
<tr>
<td>33.16 (E)</td>
<td>33.13</td>
<td>33.15</td>
<td>33.14</td>
<td></td>
<td>(103)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.91 (H)</td>
<td>39.90</td>
<td>39.89</td>
<td>39.89</td>
<td></td>
<td>(202)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.98 (I)</td>
<td>40.96</td>
<td>40.97</td>
<td>40.97</td>
<td></td>
<td>(104)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.84 (D)</td>
<td>23.82</td>
<td>23.83</td>
<td>23.83</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>33.74 (F)</td>
<td>33.73</td>
<td>33.73</td>
<td>33.74</td>
<td>Rhombohedral/CoCuO$_2$</td>
<td>(444)</td>
<td>R-3m(166)</td>
<td>74-1855</td>
</tr>
<tr>
<td>39.90 (H)</td>
<td>39.90</td>
<td>39.89</td>
<td>39.89</td>
<td></td>
<td>(020)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.57 (J)</td>
<td>41.57</td>
<td>41.57</td>
<td>41.56</td>
<td></td>
<td>(131)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.48 (B)</td>
<td>20.84</td>
<td>20.47</td>
<td>20.47</td>
<td>Orthorhombic/CoCu$_2$O$_3$</td>
<td>(020)</td>
<td>Pmmn(59)</td>
<td>76-0442</td>
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<tr>
<td>23.84 (D)</td>
<td>23.83</td>
<td>23.84</td>
<td>23.83</td>
<td></td>
<td>(301)</td>
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<td></td>
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<tr>
<td>33.74 (F)</td>
<td>33.74</td>
<td>33.73</td>
<td>33.74</td>
<td></td>
<td>(020)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.10 (G)</td>
<td>39.10</td>
<td>39.10</td>
<td>39.09</td>
<td></td>
<td>(302)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**6.3.2 XPS Analysis of the (Cu$_x$Co$_y$O$_z$ + graphene oxide) Coatings**

The XPS survey scans (not shown here) of these coatings were conducted before etching and after 2 minutes etching of each sample. An Ar gas etching of 2 minutes was chosen to remove the surface contamination around the coatings. The elemental analyses of the copper cobalt oxide thin film coatings with the addition of various wt% of graphene oxide are presented in Table 12. From Table 12, it is noticed that the at.% of carbon is monotonically increased with the subsequent addition of graphene oxide to the copper cobalt oxide coatings which in turn indicates that the progressive amount of graphene oxide been introduced to the copper cobalt oxide coatings.
Table 12. Atomic compositions of Cu$_{x}$Co$_{y}$O$_{z}$ thin film coatings with and without graphene oxide addition before and after etching as estimated via XPS measurements.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elements</th>
<th>Atomic percentages (at%) of elements</th>
<th>Before etching</th>
<th>After etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{x}$Co$</em>{y}$O$_{z}$</td>
<td>Cu</td>
<td>12.54</td>
<td>28.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>11.67</td>
<td>33.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>43.11</td>
<td>33.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>32.67</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{x}$Co$</em>{y}$O$_{z}$</td>
<td>Cu</td>
<td>14.46</td>
<td>30.57</td>
<td></td>
</tr>
<tr>
<td>+0.1wt%GO</td>
<td>Co</td>
<td>20.58</td>
<td>35.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>40.92</td>
<td>28.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>24.04</td>
<td>5.32</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{x}$Co$</em>{y}$O$_{z}$</td>
<td>Cu</td>
<td>19.13</td>
<td>29.87</td>
<td></td>
</tr>
<tr>
<td>+0.5wt%GO</td>
<td>Co</td>
<td>20.27</td>
<td>34.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>36.08</td>
<td>30.09</td>
<td></td>
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<tr>
<td></td>
<td>C</td>
<td>24.52</td>
<td>5.38</td>
<td></td>
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<tr>
<td>Cu$<em>{x}$Co$</em>{y}$O$_{z}$</td>
<td>Cu</td>
<td>12.96</td>
<td>30.35</td>
<td></td>
</tr>
<tr>
<td>+1.0wt%GO</td>
<td>Co</td>
<td>15.75</td>
<td>36.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>40.55</td>
<td>27.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>30.74</td>
<td>5.54</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>{x}$Co$</em>{y}$O$_{z}$</td>
<td>Cu</td>
<td>14.41</td>
<td>28.47</td>
<td></td>
</tr>
<tr>
<td>+1.5wt%GO</td>
<td>Co</td>
<td>17.83</td>
<td>30.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>39.03</td>
<td>35.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>28.73</td>
<td>6.32</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 26 (a-e) exhibits the deconvolution of the XPS spectra of the Cu2$p_{3/2}$ peak of Cu$_{x}$Co$_{y}$O$_{z}$ coatings deposited with various wt.% of GO. The two main peaks of Cu2$p_{3/2}$ and Cu2$p_{1/2}$ (Cu2$p_{1/2}$ are not shown here) have a binding energy difference of 19.9 eV. The difference in binding energy between Cu2$p_{1/2}$ and Cu2$p_{3/2}$ peaks suggests the occurrence of low oxidation states of copper. Our findings herein are in accord with earlier reports [226, 428]. Compared to the CuO, the covalent nature of the Cu-O bond in copper cobaltite was reduced due to the higher intensity of the satellite peak [407]. The deconvolution of Cu2$p_{3/2}$ photoelectron lines illustrates two curve-fitting components in the vicinity of 932–934.5 eV. The main Cu2$p_{3/2}$ peaks around 932-933 eV are due to the metal (octahedral) Cu$^{+}$ ions whereas peaks due to the Cu$^{2+}$ ions were found at 934-935 eV. It is believed that the Cu2$p_{3/2}$ photoelectron peaks reveal the tetrahedral Cu$^{+}$ with its counterpart peak from the octahedral Cu$^{+}$ [429]. The Cu2$p_{3/2}$ photoelectron peak with shake-up satellite is ascribed to the copper oxides. In copper cobalt oxides system, the reduction of Cu$^{2+}$ to Cu$^{+}$ has been previously detected [407, 430]. The oxidation state of copper with different coordinations is possibly due to the evolution of Cu$^{2+}$ A-sites originating from the disintegration during the high-temperature annealing at 500 °C.
Other reports mentioned that portion of octahedral Cu$^{2+}$ (satellites of cupric oxide) further reduced to octahedral Cu$^+$ [431, 432]. The Cu$^{2+}$ ions are merged into the surface octahedral vacancy, accommodate oxygen with neighboring Co$^{2+}$ ions and thereby forming Cu–O–Co like species [407, 433]. The Cu$^+$ and Cu$^{2+}$ ions indicate the presence of Cu$_2$O and CuO in the copper-cobalt system. The presence of CuO was also confirmed by our synchrotron radiation XRD studies.
Figure 26. Decoupling of XPS spectra of Cu$2p_{3/2}$ peak of CuCoO thin film coatings deposited with different wt.% of GO: (a) Cu$_x$Co$_y$O$_z$ (b) Cu$_x$Co$_y$O$_z$ + 0.1wt.% GO, (c) Cu$_x$Co$_y$O$_z$ + 0.5wt.% GO, (d) Cu$_x$Co$_y$O$_z$ + 1wt.% GO, (e) Cu$_x$Co$_y$O$_z$ + 1.5wt.% GO. Red color stands for raw data black color stands for fitting envelope.
The XPS spectra of the Co2p peaks and the decomposition of the Co2p3/2 peak of copper-cobalt oxide thin film coatings synthesized with various wt% of graphene oxide are presented in Fig. 27 (a-e). In each of the Co2p spectrum, the two main peaks are assigned as Co2p3/2 and Co2p3/2, along with a satellite in the neighbourhood of the higher binding energy region of each peaks. In each coating, the peak-fitting of Co2p3/2 and its satellite give rises to three components (See Fig. 27 (a-e)). Peaks Co2p3/2 and Co2p3/2 are separated (not shown here) with binding energy of ~16eV due to the spin-orbit coupling of mixed Co2+ and Co3+ ions. The existence of the satellite in the neighbourhood of Co2p3/2 peak implies the feature of Co ions is occupied in a partial spinel crystal structure. The low intensity of the satellites also confirms the presence of Co2+ ions mixing with Co2+ ions [421]. The peaks I and II are due to the formation of Co3O4, and Co2O3 which are mostly due to octahedral Co2+ or mixed Co2+ and Co3+ bonding states. Formation of Co3O4 was also revealed in the high resolution X-ray diffraction studies employed by synchrotron radiation. Since the binding energy of Co2+ is higher than that of Co3+, the shake-up satellite was mostly recorded above 785 eV. The Co2p3/2 peaks above 785 eV with a shake-up satellite is characteristic of copper (Cu2+) oxides in tetrahedral coordination. From the Cu2p3/2 features, we saw that the Cu2+ ions partially substitute the Co2+ ions thus forming a lower degree of crystallization of Cu2+Co2+3+O4 spinel systems [226, 409]. The satellite peak noticed above 785.00 eV was identified to be the contribution from cobalt oxide bonds.
Figure 27. Decoupling of XPS spectra of Co$_2$p$_{3/2}$ peak of CuCoO thin film coatings deposited with different wt.% of GO: (a) Cu$_x$Co$_y$O$_z$ (b) Cu$_x$Co$_y$O$_z$ + 0.1wt.% GO (c) Cu$_x$Co$_y$O$_z$ + 0.5wt.% GO (d) Cu$_x$Co$_y$O$_z$ + 1wt.% GO (e) Cu$_x$Co$_y$O$_z$ + 1.5wt.% GO. Red color stands for raw data black color stands for fitting envelope.
Fig. 28 (a-e) demonstrates the O1s XPS spectra and the corresponding curve-fitting arisen from the decomposition O1s peak of CuₓCoᵧO₂ coatings without and with various wt.% of graphene oxide. The decomposition of O1s peak and the satellite give out three curve fitting components (See Fig. 28 (a-e)). All the O1s spectrum shows a strong peak with a shoulder at the high energy side which is a typical feature of CuₓCoᵧO₂ coatings [409]. Comparatively, flat shoulder peak in the high energy side of O1s peak arises from the high volume fraction of surface oxygen and the low amount of subsurface oxygen in the coated films. Further, the shoulders at the high energy side of the O1s peaks are the characteristic feature of the copper-cobalt oxide systems that differentiates them from O1s on Co₃O₄ [409]. The decoupling curve-fitting peaks (on the lower energy side) are mostly due to the lattice O²⁻ in a Co₃O₄ spinel structure while the other peaks (on the higher energy side) are due to the OH-originated groups e.g., carbonate, hydroxyl etc [407, 409, 421, 434, 435]. It is also assumed that these peaks are arisen from (Cu-O, Co-O) covalent bonds [226, 421].
Figure 28. Decoupling of XPS spectra of O1s peak of CuCoO thin film coatings deposited with different wt.% of GO: (a) Cu$_x$Co$_y$O$_z$ (b) Cu$_x$Co$_y$O$_z$ + 0.1 wt.% GO (c) Cu$_x$Co$_y$O$_z$ + 0.5 wt.% GO (d) Cu$_x$Co$_y$O$_z$ + 1 wt.% GO (e) Cu$_x$Co$_y$O$_z$ + 1.5 wt.% GO. Red color stands for raw data black color stands for fitting envelope.

The deconvolution of high resolution C1s XPS data and their corresponding peak-fitting of copper fitting components above 286 eV and 288 eV are the surface contamination of the oxygen, surface oxygen such as chemisorbed water or chemisorbed oxygen O" etc.
introduced during the synthesis and annealing processes of the thin film coatings. In a bulk structure, the oxygen ions near the surface, generally, have lower electron density than the lattice O\(^{2-}\) ions [436]. It is also seen that the coordination number of oxygen ions is much smaller than in cobalt oxide thin film coatings with and without the addition of various wt.% of graphene oxide (See Fig. 29). The C\(1s\) XPS spectra display a single peak at 284.6 eV together with an asymmetrical tail at high energy side. The principal component of decoupled peak represents the graphitic carbon or hydrocarbon bonds (C–C/C-H bonds) at 284.60 eV and the remainder a regular site together with stronger metal-oxygen assigned as C-OH/C-O-C and C=O/O=C-O structures originated from graphite stacking material [437]. In Ref. [438], \(\pi-\pi^*\) shake-up at higher energy side corresponding to sp\(^2\) hybridized carbon was noticed. However, in the present investigation no \(\pi-\pi^*\) shake-up was identified. A reduction in the peak intensities of C=O/O=O-C-O bonds was seen on the deconvoluted C\(1s\) peak and indicates the incomplete removal of the carbonyl, hydroxyl, and epoxy groups (originated from the oxidation and destruction of the sp\(^2\) bonded pristine graphene) after the heat treatment [439]. The C=O bonds were detected at 288.01-288.40 eV which eventually confirmed the presence of C=O bonds observed in O\(1s\) spectra at 531.33-531.44 eV. A detailed tabulated information on the bonding states of various elements and compounds and their corresponding binding energy positions and percentages of the different components of Cu\(_x\)Co\(_y\)O\(_z\) coatings and Cu\(_x\)Co\(_y\)O\(_z\) coatings with the addition of graphene oxide as achieved from XPS fitting curves of Cu\(2p_{3/2}\), Co\(2p_{3/2}\), O\(1s\) and C\(1s\) spectra via CASA XPS (version 2.3.1.5) software are presented in Table 13. A slight change in peaks broadening and peaks shifting towards the lower binding energy was noticed while controlled amount of graphene oxide were incorporated to the sol-gel derived copper-cobalt oxide coatings. This peak shifting and peak broadening indicates the appearance of the reduced states of Cu and Co species on the surface. This also reveals the occurrence of a larger number of oxygen vacancies around the surface of the films. However, a subtle peak shift observed in C\(1s\) peak towards the higher binding energies revealing that the presence of graphene oxide modifies the bonding environments of the carbon atoms. It is probably due to the variation in the relative proportions of carbon-carbon and carbon-oxygen contributions. The XPS-peak intensity of all the five samples is identical although measured peak intensities varied significantly with the addition of graphene oxide to the copper-cobalt oxide films. However, to realize the substantial information of measured XPS peak intensities depth profile analysis of the atoms is essential.
Figure 29. Decoupling of XPS spectra of C1s peak of CuCoO thin film coatings deposited with different wt.% of GO: (a) Cu$_x$Co$_y$O$_z$ (b) Cu$_x$Co$_y$O$_z$ + 0.1wt.% GO (c) Cu$_x$Co$_y$O$_z$ + 0.5wt.% GO (d) Cu$_x$Co$_y$O$_z$ + 1wt.% GO (e) Cu$_x$Co$_y$O$_z$ + 1.5wt.% GO. Red color stands for raw data black color stands for fitting envelope.
Table 13. Fitting results of the XPS data of sol-gel derived Cu\textsubscript{x}Co\textsubscript{y}O\textsubscript{z} coatings with and without graphene oxide addition for the core level binding energies.

<table>
<thead>
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<th>Samples</th>
<th>Photoelectron lines</th>
<th>Bonding states</th>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Percentages of the component (%)</th>
</tr>
</thead>
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<td></td>
<td>Metal Cu\textsuperscript{+} ions (Cu\textsubscript{2}O\textsubscript{2} bonds)</td>
<td>932.53</td>
<td>1.80</td>
<td>74.03</td>
</tr>
<tr>
<td>Cu\textsubscript{2}p/2</td>
<td></td>
<td>Metal Cu\textsuperscript{2+} ions (CuO bonds)</td>
<td>934.55</td>
<td>2.00</td>
<td>25.97</td>
</tr>
<tr>
<td>Co\textsubscript{2}p/2</td>
<td></td>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>779.40</td>
<td>2.00</td>
<td>24.54</td>
</tr>
<tr>
<td>Co\textsubscript{2}p/2</td>
<td></td>
<td>Co\textsubscript{2}O\textsubscript{3}</td>
<td>781.15</td>
<td>3.26</td>
<td>37.34</td>
</tr>
<tr>
<td>Co\textsubscript{2}p/2 sat.</td>
<td></td>
<td>Co\textsubscript{2}O\textsubscript{2}/Co\textsubscript{2}O\textsubscript{3}</td>
<td>785.96</td>
<td>5.96</td>
<td>38.12</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{1}s</td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.26</td>
<td>1.00</td>
<td>54.33</td>
</tr>
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<td></td>
<td></td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.81</td>
<td>1.30</td>
<td>28.07</td>
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<td>Surface oxygen/C=O/O=C-O bonds</td>
<td>531.37</td>
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<td>17.60</td>
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<td>C=O/C-H bonds</td>
<td>284.40</td>
<td>1.30</td>
<td>60.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{1}s</td>
<td>C-OH/C-O-C bonds</td>
<td>286.28</td>
<td>1.25</td>
<td>23.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C=O/O=C-O bonds</td>
<td>288.14</td>
<td>1.30</td>
<td>16.74</td>
</tr>
<tr>
<td>Cu\textsubscript{x}Co\textsubscript{y}O\textsubscript{z} + 0.1wt%GO</td>
<td>Cu\textsubscript{2}p/2</td>
<td>Metal Cu\textsuperscript{+} ions (Cu\textsubscript{2}O\textsubscript{2} bonds)</td>
<td>932.53</td>
<td>1.80</td>
<td>74.03</td>
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<tr>
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<td></td>
<td>Metal Cu\textsuperscript{2+} ions (CuO bonds)</td>
<td>934.45</td>
<td>2.20</td>
<td>25.97</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2</td>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>779.15</td>
<td>2.00</td>
<td>30.75</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2 sat.</td>
<td>Co\textsubscript{2}O\textsubscript{2}/Co\textsubscript{2}O\textsubscript{3}</td>
<td>785.78</td>
<td>6.00</td>
<td>33.96</td>
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<td></td>
<td>O\textsubscript{1}s</td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.24</td>
<td>1.07</td>
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<td>Metal oxides (Cu/Co oxides)</td>
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<td>18.58</td>
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<td>Surface oxygen/C=O/O=C-O bonds</td>
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<td>1.50</td>
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<td>1.32</td>
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<td>C-OH/C-O-C bonds</td>
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<td>C=O/O=C-O bonds</td>
<td>288.01</td>
<td>1.32</td>
<td>12.59</td>
</tr>
<tr>
<td>Cu\textsubscript{x}Co\textsubscript{y}O\textsubscript{z} + 0.5wt%GO</td>
<td>Cu\textsubscript{2}p/2</td>
<td>Metal Cu\textsuperscript{+} ions (Cu\textsubscript{2}O\textsubscript{2} bonds)</td>
<td>934.40</td>
<td>1.70</td>
<td>73.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal Cu\textsuperscript{2+} ions (CuO bonds)</td>
<td>934.30</td>
<td>1.74</td>
<td>26.03</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2</td>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>779.12</td>
<td>2.00</td>
<td>28.66</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2 sat.</td>
<td>Co\textsubscript{2}O\textsubscript{2}/Co\textsubscript{2}O\textsubscript{3}</td>
<td>785.71</td>
<td>5.97</td>
<td>37.25</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{1}s</td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.15</td>
<td>1.08</td>
<td>63.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.71</td>
<td>1.32</td>
<td>13.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface oxygen/C=O/O=C-O bonds</td>
<td>531.10</td>
<td>1.68</td>
<td>22.65</td>
</tr>
<tr>
<td></td>
<td>C=O/C-H bonds</td>
<td>284.34</td>
<td>1.34</td>
<td>78.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{1}s</td>
<td>C-OH/C-O-C bonds</td>
<td>286.79</td>
<td>1.32</td>
<td>11.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C=O/O=C-O bonds</td>
<td>288.58</td>
<td>1.33</td>
<td>10.68</td>
</tr>
<tr>
<td>Cu\textsubscript{x}Co\textsubscript{y}O\textsubscript{z} + 1.0wt%GO</td>
<td>Cu\textsubscript{2}p/2</td>
<td>Metal Cu\textsuperscript{+} ions (Cu\textsubscript{2}O\textsubscript{2} bonds)</td>
<td>934.28</td>
<td>1.77</td>
<td>67.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal Cu\textsuperscript{2+} ions (CuO bonds)</td>
<td>934.28</td>
<td>2.20</td>
<td>32.04</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2</td>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>779.08</td>
<td>2.00</td>
<td>25.47</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2 sat.</td>
<td>Co\textsubscript{2}O\textsubscript{2}/Co\textsubscript{2}O\textsubscript{3}</td>
<td>785.67</td>
<td>5.99</td>
<td>37.27</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{1}s</td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.06</td>
<td>1.10</td>
<td>61.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.49</td>
<td>1.35</td>
<td>28.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Surface oxygen/C=O/O=C-O bonds</td>
<td>530.98</td>
<td>1.39</td>
<td>9.93</td>
</tr>
<tr>
<td></td>
<td>C=O/C-H bonds</td>
<td>284.37</td>
<td>1.40</td>
<td>62.84</td>
<td></td>
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<tr>
<td></td>
<td>C\textsubscript{1}s</td>
<td>C-OH/C-O-C bonds</td>
<td>286.32</td>
<td>1.36</td>
<td>10.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C=O/O=C-O bonds</td>
<td>288.15</td>
<td>1.35</td>
<td>27.00</td>
</tr>
<tr>
<td>Cu\textsubscript{x}Co\textsubscript{y}O\textsubscript{z} + 1.5wt%GO</td>
<td>Cu\textsubscript{2}p/2</td>
<td>Metal Cu\textsuperscript{+} ions (Cu\textsubscript{2}O\textsubscript{2} bonds)</td>
<td>932.30</td>
<td>1.70</td>
<td>68.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal Cu\textsuperscript{2+} ions (CuO bonds)</td>
<td>934.25</td>
<td>2.20</td>
<td>31.92</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2</td>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>779.07</td>
<td>2.08</td>
<td>30.65</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{2}p/2 sat.</td>
<td>Co\textsubscript{2}O\textsubscript{2}/Co\textsubscript{2}O\textsubscript{3}</td>
<td>785.64</td>
<td>5.99</td>
<td>36.02</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{1}s</td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.03</td>
<td>1.08</td>
<td>80.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal oxides (Cu/Co oxides)</td>
<td>529.45</td>
<td>1.37</td>
<td>9.65</td>
</tr>
</tbody>
</table>

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### 6.3.3 Energy Band-gaps of \((\text{Cu}_x\text{Co}_y\text{O}_z + \text{graphene oxide})\) Coatings

The UV-Vis absorptance spectra presented in Fig. 30 were used to inspect the optically induced transition and to acquire information about the band structure of the films. Fig. 30 shows that in the visible range of the spectra, the solar absorptance of these coatings increases with the increase in wavelengths. At a wavelength of 350-460 nm, the absorbance values attain its maximum and then decreases. Another maxima was detected at a wavelength of 1360-1500 nm.

![UV-Vis absorptance spectra of sol-gel Cu$_x$Co$_y$O$_z$ thin film coatings without and with the addition of graphene oxide.](image)

**Figure 30.** UV-Vis absorptance spectra of sol-gel Cu$_x$Co$_y$O$_z$ thin film coatings without and with the addition of graphene oxide.

The spectral dependence of \(\alpha\) on the photon energy \((h\nu)\) helps to estimate the energy band-gaps of a material. Photon absorptions in crystalline and amorphous materials are known to follow the Tauc relation as given in Eq. (6.1). The energy band-gap, \(E_g\) involved in CuCoO coatings with and without the addition of graphene oxide was estimated by Tauc plot, by plotting the function \((ah\nu)^2\) vs \(h\nu\) (the photon energy), by extrapolating the linear portion of the curve to zero absorption. Tauc plots of \(h\nu\) vs \((ah\nu)^2\) for CuCoO coatings with and without the addition of graphene oxide films are shown in
Fig. 31 and energy band-gaps were estimated from the intercepts of the linear part of the curves extrapolated to zero in the photon energy axis. The energy band-gap values computed for CuCoO coatings with and without the addition of graphene oxide films are presented in Table 14. The values of direct and indirect transition energy gaps lie between 1.6 and 2.4 eV. From Table 14 it is found that the energy band-gaps of CuCoO coatings slightly decrease with the subsequent incorporation of graphene oxide to the CuCoO system. This decrease in energy band-gaps play significant role in enhancing the photon absorption capability of these coatings with the subsequent addition of graphene oxide to the CuCoO matrix.

![Graph showing energy band gaps](image)

**Figure 31.** Estimation of energy band-gaps of sol-gel derived Cu$_x$Co$_y$O$_z$ thin film coatings with and without the addition of graphene oxide.

**Table 14.** Energy band-gaps of Cu$_x$Co$_y$O$_z$ thin film coatings with and without the addition of graphene oxide.

<table>
<thead>
<tr>
<th>Coatings name</th>
<th>Band-gap ($E_g$), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_x$Co$_y$O$_z$</td>
<td>2.4</td>
</tr>
<tr>
<td>Cu$_x$Co$_y$O$_z$ + 0.1wt.% GO</td>
<td>2.2</td>
</tr>
<tr>
<td>Cu$_x$Co$_y$O$_z$ + 0.5wt.% GO</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu$_x$Co$_y$O$_z$ + 1wt.% GO</td>
<td>1.7</td>
</tr>
<tr>
<td>Cu$_x$Co$_y$O$_z$ + 1.5wt.% GO</td>
<td>1.6</td>
</tr>
</tbody>
</table>
6.3.4 Optical Properties of \((\text{Cu}_x\text{Co}_y\text{O}_z + \text{graphene oxide})\) Coatings

Fig. 32 shows the UV-Vis spectra of \(\text{Cu}_x\text{Co}_y\text{O}_z\) thin film coatings on aluminum substrates with and without the progressive addition of graphene oxide. The solar absorptance of the coatings, synthesized using concentrations of 0.25 M copper acetate and 0.25 M cobalt chloride (Cu/Co ratio = 1) at a dip-speed 120 mm/min and with four times of dip-coating, was calculated based on the AM1.5 solar spectrum standard using the hemispherical reflectance data recorded via UV–Vis-NIR Jasco V-670 double beam spectrophotometer with 60 mm integrating sphere in the wavelength range of 190 to 2200 nm. The solar absorptance values estimated in terms of reflectance as described by Duffie and Beckman [349] are displayed in Table 15. The UV-Vis reflectance data presented in Fig. 32, indicate that the coatings offer low reflectance (<50 %) to UV light, moderate reflectance (<80 %) in the visible spectrum and high reflectance (up to 100 %) in infrared ~ far-infrared region of the solar spectrum. In the shorter wavelength region, all the UV-Vis spectra are similar showing an interference peaks and absorption edges. Consistency between present investigation along with the more elaborate interpretation of such phenomena is discussed elsewhere [225].

![Figure 32. UV-visible reflectance spectra of \(\text{Cu}_x\text{Co}_y\text{O}_z\) thin film coatings without and with the addition of graphene oxide.](image)
The solar absorptance of the coatings without graphene oxide was found to be 83.4%, however with the addition of 1.5 wt% of graphene oxide, the absorptance increased to 86.14%. Thus, the introduction of controlled amount of graphene oxide to the Cu_{x}Co_{y}O_{z} thin film coatings, the solar absorptance increased significantly. This superior absorptance would make them smart candidates for their practical application as a selective surface. This result is in good agreement with earlier reported sol-gel derived coatings [40, 95, 440]. Optical absorptance of the copper–cobalt oxide films is influenced by the film thickness, the composition of the substrate, the roughness of the film surface and surface pores among others. Aluminium substrate was used for the films because of its low cost and high reflectivity [21]. The highly reflective aluminium surface serves to reflect back the infra-red radiation that penetrates the film coating. The copper-cobalt films deposited on the aluminium substrate exhibit significantly higher degree of solar absorption compared to that deposited on a glass substrate [21]. A rough surface results in a decrease in reflection of the incident solar energy from the surface and the refractive index is reduced by the presence of pores in the Cu_{x}Co_{y}O_{z} graphene oxide surface. These factors promote the solar absorptance by means of multiple reflections and resonant scattering in the pores.

Fig. 33 shows the FTIR spectra of Cu_{x}Co_{y}O_{z} thin film coatings with and without the addition of graphene oxide in the wavelength range of 2.5 to 15.5 µm.

![Figure 33. FTIR reflectance spectra of sol-gel derived Cu_{x}Co_{y}O_{z} coatings without and with the addition of graphene oxide.](image)

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The thermal emittance of the coatings was calculated in terms of reflectance as described by Duffie and Beckman [349] and the corresponding solar selectivity was computed. Results of such calculations are displayed in Table 15.

Table 15. Optical properties of the Cu,Co,O thin film coatings with the addition of graphene oxide.

<table>
<thead>
<tr>
<th>Sample compositions</th>
<th>Absorptance, α (%)</th>
<th>Emittance, ε (%)</th>
<th>Selectivity, s = α/ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu,Co,O</td>
<td>83.40</td>
<td>5.70</td>
<td>14.63</td>
</tr>
<tr>
<td>Cu,Co,O + 0.1wt% GO</td>
<td>84.00</td>
<td>5.27</td>
<td>15.85</td>
</tr>
<tr>
<td>Cu,Co,O + 0.5wt% GO</td>
<td>84.30</td>
<td>4.80</td>
<td>17.56</td>
</tr>
<tr>
<td>Cu,Co,O + 1wt% GO</td>
<td>85.60</td>
<td>3.20</td>
<td>26.75</td>
</tr>
<tr>
<td>Cu,Co,O + 1.5wt% GO</td>
<td>86.14</td>
<td>2.97</td>
<td>29.01</td>
</tr>
</tbody>
</table>

From our measurements, it is observed that in the infra-red and far infra-red region, the solar emittance of the coatings decreased significantly with the progressive addition of the graphene oxide to the Cu,Co,O thin film coatings. This reveals that graphene oxide plays a remarkable role in improving the selectivity of the Cu,Co,O coatings which reduces the energy loss of the selective surface substantially in the infrared region of the spectrum. In all coatings, interference peak and absorption edge were detected at the shorter wavelength sides. It is well known that the interference peaks and the absorption edges are shifted towards the longer wavelengths regions subsequently when graphene oxide was added to the copper-cobalt films. With the incorporation of 1.5wt% of graphene oxide in the copper-cobalt oxide films, a highest absorptance of 95.19% was achieved while the average absorptance calculated via D-B method [349] was 86.14%. Relatively weaker phonon absorption in the vicinity of the wavelength range of 15 μm is also typically exhibited by the copper-cobalt oxide system. Following the same method as described in Ref. [349], an average thermal emittance of 2.97% was recorded by the copper-cobalt coatings doped with 1.5wt% of graphene oxide and thereby a high solar selectivity of 29.01 was attained for this coating. The increase of absorptance after the addition of graphene oxide is referred to the reduction of reflective properties of coating surface. This variation of reflective properties is attributed to the interference phenomena governed by film thickness and refractive index ratios. A non-uniform and inhomogeneous surface reduces the reflection of the incoming solar radiation at the film surface together with the lower refractive index. At the same time, multiple reflections and resonant scattering of the incident solar radiation also take place around the film surface [441]. As a result, the solar absorptance is raised up due to the interaction and
relaxation mechanisms in the coatings. The higher value of solar absorptance appears to be very promising for application of solar selective surface in photothermal collectors. Compared with other reports for sol-gel derived coatings whereby their \( \alpha = 83\% \) [40], 80–85\% [95] and 80\% [440], our findings are quite encouraging. We further assume that the highly reflective aluminium substrates benefits to reflect back the infrared light that pass through the coatings without being absorbed. The transmitted light is reflected back by the substrate which increases the reflectance and reduces the absorptance in the NIR range. As a result, a dark mirror absorber-reflector tandem concept is virtually produced.

The solar absorptance and emittance data manifest the fact that addition of a controlled amount of graphene oxide to the copper cobalt oxide coating increases solar selectivity due to the high absorptance in the visible region and increased reflectance in infrared–far-infrared region of the solar spectrum. Thus, copper-cobalt oxide thin film coatings with the addition of graphene oxide have a great potential to form the basis of an absorber material for solar selective surface applications in photothermal devices.

### 6.4 Conclusions

The structural characterization, solar selectivity and X-ray photoelectron spectroscopic investigations of the sol-gel derived copper-cobalt oxide thin film coatings with addition of graphene oxide has been investigated. Synchrotron radiation-based high resolution XRD tests show existence of physically, thermally and chemically stable multiple phases. The energy band-gaps of these coatings were found to be decreased systematically with the progressive addition of graphene oxide to the CuCoO films. The solar absorptance was found to increase with the progressive addition of graphene oxide to the Cu\(_x\)Co\(_y\)O\(_z\) system while the optical emittance was reduced and thereby the solar selectivity was significant increased. Hence, copper cobalt oxide thin films with the addition of graphene oxide display a good promise as a smart solar selective surface for photothermal applications. Such features are interesting aspects which may be prevalent in future research concerning designs of superior selective surface. In the present study, we have adopted the sol-gel dip coating method to fabricate mixed metal oxides-based thin film coatings. Sol-gel dip-coating is a popular and versatile technique that can produce mixed metal oxides based thin film coatings with very high solar selectivity up to 29.01. Surface analysis of these coatings via XPS route confirmed the presence of various metal oxide phases (e.g., Cu\(_2\)O, CuO, Co\(_3\)O\(_4\)) which protect them from further oxidization and corrosion. As a solar selective surface, these types of coatings possess some unique
advantages *e.g.*, easy operation, convenient and environment friendly, higher efficiency coupled with lower processing costs over other conventional techniques.
CHAPTER SEVEN: SURFACE BONDING STRUCTURES AND SOLAR SELECTIVITY OF SPUTTERED Ti$_x$M$_{1-x}$N$_y$ FILMS

7.1 Introduction

A spectrally selective surface is, generally, used to improve the photothermal conversion performance and possesses two characteristics: high absorptance, $\alpha$ in the visible region of solar spectrum (0.3 to 2.5 µm) and low emittance, $\varepsilon$ (i.e., high reflection) in the infrared (IR) region ($\geq$ 2.5 µm) at operating temperatures. An excellent selective surface maximises the absorption of incoming photons in the visible region and minimises photon emission through thermal radiation in the IR energy region. Such a surface can be designed by an absorber-reflector assembly. In such approach, the reflector is coated with a highly absorbing layer over the visible solar spectrum, while the infrared region is made transparent. Various types of metal nitrides based selective solar surfaces such as TiN, ZrN, HfN, TiAlN, TiAlON, NbAIN, NbAlON, MoAIN, and WAIN have been investigated by numerous groups [12-15, 51, 53, 57, 150-153]. Over the past few years, transition metal nitride based thin films have attracted significant research interest as selective solar surfaces in solar thermal conversion devices. Generally, the energy conversion performance of a selective solar surface depends on the coating materials, coating design and fabrication technique used. A multi-layer film stack with mixture of metal nitride, metal oxide and metal oxinitride coatings e.g., TiAIN/AION, and TiAl/TiAIN/TiAlON/TiAlO has been explored for the potential commercial development of selective solar surfaces [13, 154]. TiAIN/TiAlON/\text{Si}_3\text{N}_4 selective absorbers have been produced on various substrates such as copper, nickel, stainless steel, glass and nimonic alloys [55]. However, these materials are yet to be commercialized for solar energy conversion applications [13, 58, 153].

Various synthesis methods such as evaporation, electrodeposition, chemical conversion, chemical vapour deposition and magnetron sputtering have been employed in manufacturing selective solar surfaces. Owing to its advantages in large area deposition, dry, clean and environment friendliness, magnetron sputtered technique is widely used for synthesizing selective solar absorbers. Moreover, magnetron sputtered coatings have already shown promising optical behaviour that potentially allow them to be utilized in solar selective surfaces [18, 55]. The optical properties of transition metal based nitride coatings can be regulated by selecting and tuning the stoichiometry of the nitrides. Furthermore, the density of free electrons in the $d$-bands of transition metals is impacted...
Introduction of an appropriate dopant (e.g. Al or AlSi) in the transition metal nitride alters the bonding structure of the matrix which, in turn, modifies the optical properties and electrical behavior of such coatings. For this reason, a high solar absorptance and low thermal emittance can be achieved by TiAIN and TiAlSiN coatings. Similarly, nickel-doped chromium nitride sputtered coatings have been reported in a previous study [159].

The optical properties can be also regulated by integrating another metal component into the transition metal nitride systems which transforms the bonding nature from metallic to covalent [57]. Since the solar selective surfaces are the easiest and most direct way of harvesting solar energy, in recent years, transition metal nitrides have received significant attention for mid and high temperature applications [9, 11-19, 151, 153]. Spectrally selective behaviors of transition metal nitride coatings have been previously studied [150]. Studies of magnetron sputtered TiAlN/TiAlON coatings synthesized onto a metal substrate exhibited high absorptance and low emittance were reported by Barshilia et al. [151]. The absorbance of the coatings was substantially enhanced to 0.95 by adding a Si$_3$N$_4$ anti-reflective coating on the top of these films [151]. A higher thermal stability and high solar selectivity of 0.95/0.07 = 13.57 was achieved by this tandem selective surface. The electronic properties of titanium nitride-based materials have been extensively studied under different experimental and theoretical approaches, but research on optical properties of these materials have been relatively scarce [354, 359, 360] and this is especially true for (the lack of) studies on solar selectivity [71-75, 151]. Considering the above circumstances, the focus of the present study is emphasized on investigating the potential development of magnetron sputtered Ti$_{x}$M$_{1-x-y}$N$_y$ (where M = Al, AlSi, $x = 0.50$, 0.25 and $y = 0.50$) coatings as the selective solar surfaces. UV-Vis and Fourier transform infrared reflectometry (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), band-gap analysis, scanning electron microscopy (SEM) and nanoindentation measurements will be undertaken to investigate and characterize the crystal structure, surface bonding structure, surface morphology, optical and mechanical parameters of the as-deposited films.
7.2 Experimental Technique

The Ti$_{0.5}$N$_{0.5}$, Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$, and Ti$_{0.25}$Al$_{0.2}$Si$_{0.05}$N$_{0.5}$ thin film coatings were deposited onto AISI M2 tool steel substrates via closed field unbalanced magnetron sputtering system (UDP650, Teer Coating Limited, Droitwich, Worcestershire, UK). The magnetron sputtered system is equipped with a four-target configuration. The substrates were ultrasonically cleaned in acetone and methanol solution and then dried with nitrogen gas, before putting them into the vacuum chamber. A background pressure of 2.67×10$^{-4}$ Pa was attained in the chamber before the deposition process. The substrates were sputter cleaned with Ar plasma at a bias of -450 V for 30 minutes. In order to achieve a homogeneous film thickness, the substrates were rotated at a speed of 10 rpm throughout the synthesis process. Ti$_{0.5}$N$_{0.5}$ films were produced at a Ti target current of 8 A while Al target current was varied between 0 and 7 A for the synthesis of TiAlN, and TiAlSiN coatings. However, in the case of TiAlSiN coating deposition, a Si target current of 1.5 A was confirmed. The nitride coatings of different compositions were prepared in a mixed Ar+N$_2$ mixed gas atmosphere. Prior to any measurements, all the samples were mechanically cleaned in ultra-high vacuum via a diamond needle file and tungsten-wire brush. The details of the deposition parameters of these sputtered coatings are displayed in Table 9 (Chapter 4).

7.2.1 XRD Analysis

XRD measurements were performed to determine various phases of the coatings. A Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector was used for this purpose. The XRD machine was operated at 40 kV and 40 mA at room temperature. The XRD data of the coatings were acquired with Cu-Kα radiation ($\lambda = 0.154 \pm 10^{-5}$ nm) over a 2θ range of 30° to 50° with a step size of 0.01°.

7.2.2 Nanoindentation Studies

Mechanical properties, such as Young’s modulus and hardness, of the thin films were measured by a depth-sensing indentation system (Ultra-Micro Indentation System, UMIS-2000, CSIRO, Australia) equipped with a Berkovich indenter. The indenter tip was calibrated by conducting single-cycling indentation tests on fused silica (a standard material having a known modulus of 72 GPa) at different loads. Load–unload tests were
run in a closed-loop under load control to determine the mechanical properties of the samples. A maximum load of 20 mN was applied in 10 increments. The loading rate set to 2.5 mN/s represents the static response of the materials. Following each increment there were 10 decrements, from which the Young's modulus and hardness were calculated. Five indentation tests were performed on each specimen.

7.2.3 SEM Investigations

The surface morphology of the films were investigated with scanning electron microscopy (SEM) using a PHILIPS XL 20 (Eindhoven, The Netherlands) instrument. The SEM was operated at 25 kV. The elemental composition of the films was obtained by energy dispersive spectroscopy (EDS) from an OXFORD Link ISIS unit attached to the SEM.

7.2.4 XPS Analysis

XPS analysis provides comprehensive information on the chemical state, bonding structure and elemental composition of the outermost layers of surfaces. XPS data of all thin films was acquired using a Kratos Axis Ultra XPS spectrometer (Kratos, Manchester, UK) with Al-Kα monochromatic radiation ($hν = 1486.6$ eV) source and at an operating power of ~10 mA and ~15 kV. The XPS machine is also equipped with a cold stage, and an Ar ion gun for etching and depth profiling. The samples were mounted on steel sample holder. The chamber pressure was reduced to $3.87 \times 10^{-7}$ Pa and maintained at that level during the analysis. XPS survey spectra were acquired with both etched (6 minutes of ion sputtering) and unetched samples. High resolution XPS spectra were recorded immediately after 6 minutes of Ar⁺ sputtering. Etching was done to remove any surface oxide layers and to reduce the Ti⁴⁺ ions in order to lower oxidation states. A pass energy of 20 eV was used for high resolution Ti 2$p$, Al2$p$, Si2$p$, O1$s$, and N1$s$ photoelectron lines measurement. CASA XPS (version 2.3.15) software was used for processing and fitting the peaks of the XPS spectra.

7.2.5 Solar Selectivity Studies of the Sputtered Thin Films

Optical properties of the thin film coatings were analyzed by measuring the optical reflectance as function of wavelength from ultraviolet through visible to the infrared range via UV-Vis and FTIR spectrometers. A double-beam UV–Vis spectrophotometer
(Model: UV-670 UV-Vis spectrophotometer, JASCO, USA) equipped with a unique, single monochromator design covering a wavelength range from 250 to 2500 nm measured solar absorptance of the coatings. The monochromator is designed with 1200 grooves/mm grating and a photo multiplier tube (PMT) detector. A PERKIN Elmer Spectrum 100 FTIR Spectrometer (USA) was used for measuring the reflectance of the coatings over the wavelength range from 2.5 - 15 μm.

7.3 Results and Discussion

7.3.1 XRD Studies of Sputtered TiₓM₁₋ₓ₋ₙᵧ Coatings

X-ray diffraction (XRD) data for Ti₀.₅N₀.₅, Ti₀.₂₅Al₀.₂₅N₀.₅, and Ti₀.₂₅Al₀.₂Si₀.₀₅N₀.₅ magnetron sputtered thin film coatings are displayed in Fig. 34. XRD peaks at approximately 2θ = 44° are due to the steel substrate. Ti₀.₅N₀.₅ films have a single TiN phase, with a face centred cubic (FCC) structure, and a maximum intensity peak at 2θ = 36.63° consistent with a (111) Bragg reflection with a minor peak at approximately 42.4° (JCPDS 87-0633). In contrast, extra phases were identified for the Ti₀.₂₅Al₀.₂N₀.₅, and Ti₀.₂₅Al₀.₂Si₀.₀₅N₀.₅ films. The main phase for all samples is TiN with a (111) preferred orientation. However, with the addition of Al and the simultaneous addition of Al + Si to TiN, the principal (111) peak shifts towards higher Bragg angles by 0.68 and 0.52° respectively, due to Ti sites being occupied by smaller Bragg atoms to form a TiAl(Si)N solid solution. These peak shifts reveal lattice contraction, of the TiN phase, by replacement of Ti atoms with Al and Si atoms, and are listed in Table 16. Doping the cubic TiN sample with Al and simultaneous Si + Al show extra XRD peaks at approximately 2θ = 36.06 – 36.71° and 38.28° that are identified respectively as hexagonal AlN (JCPDS 89-3446) and hexagonal Si₃N₄ (JCPDS 83-0701) phases. The formation of h-AlN in Ti₀.₂₅Al₀.₂N₀.₅ and simultaneous formation of h-AlN and h-Si₃N₄ in Ti₀.₂₅Al₀.₂Si₀.₀₅N₀.₅ suggests characteristic evidence of spinodal decomposition in these films through the addition of these elements to TiN. This type of spinodal decomposition of TiAlN reported in previous studies [442, 443] is also associated with the grain refinement and modifications of microstresses within AlN and Si₃N₄ domains.

XRD data was used to estimate the average crystallite size for the TiN phase by the Debye-Scherrer equation,

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  
(7.1)
where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum (FWHM) and $\theta$ is the diffraction angle. Estimates of the crystallite size are listed in Table 16.

Analysis of Table 16 shows a decrease in lattice parameter and grain size of the TiN phase as Al and Si dopants are added to TiN. The contraction of lattice parameter is due to the extra $h$-AlN and $h$-Si$_3$N$_4$ phases, formed from Al and Si interaction with N, around the grain boundaries of the TiN phase and the atomic radii of Al (0.143 nm) and Si (0.134 nm) being smaller than Ti (0.147 nm). The difference in atomic radius between titanium and the dopants (Al and/or Si) results in the solution strength which causes shrinkage in the lattice parameters and thereby a change in the internal stress of these films [444]. A subtle peak broadening and reduction of the residual stress in the crystal lattices also results in a slight reduction in grain sizes of the films.

Table 16. Structural properties, for TiN phase, of Ti$_x$M$_{1-x-y}$N$_y$ films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Grain size ($\pm$10%)</th>
<th>Lattice parameter $a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{0.5}$N$</em>{0.5}$</td>
<td>24</td>
<td>0.4257</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.25}$N$_{0.5}$</td>
<td>22</td>
<td>0.4215</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.2}$Si$<em>{0.05}$N$</em>{0.5}$</td>
<td>19</td>
<td>0.4195</td>
</tr>
</tbody>
</table>

Figure 34. XRD data of as-deposited sputtered Ti$_x$M$_{1-x-y}$N$_y$ coatings (TiN, TiAlN and TiAlSiN respectively stand for Ti$_{0.5}$N$_{0.5}$, Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ and Ti$_{0.25}$Al$_{0.2}$Si$_{0.05}$N$_{0.5}$).
7.3.2 Mechanical Studies of Ti$_x$M$_{1-x-y}$N$_y$ Coatings

The mechanical properties e.g., hardness and Young’s modulus, of the as-deposited thin films, were determined from nanoindentation testing using a depth indentation system and are presented in Table 17.

**Table 17.** Mechanical properties of the Ti$_x$M$_{1-x-y}$N$_y$ coatings achieved via nanoindentation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hardness, $H$ (GPa)</th>
<th>Young’s modulus, $E$ (GPa)</th>
<th>Yield strength, $H/E$</th>
<th>Plastic deformation factor, $H^3/E^2$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{0.5}$N$</em>{0.5}$</td>
<td>17</td>
<td>281</td>
<td>0.062</td>
<td>0.067</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.25}$N$_{0.5}$</td>
<td>23</td>
<td>347</td>
<td>0.067</td>
<td>0.102</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.2}$Si$<em>{0.05}$N$</em>{0.5}$</td>
<td>27</td>
<td>378</td>
<td>0.072</td>
<td>0.141</td>
</tr>
</tbody>
</table>

Table 17 shows that with aluminum additions, increase the hardness ($H$) of TiN is increased by ~32%, (i.e., from 17.38 to 23.08 GPa), whilst the Young’s modulus ($E$) is enhanced by ~23%. Using the measured $H$ and $E$ values, the yield strength ($H/E$) and plastic deformation factor ($H^3/E^2$) of the coatings were calculated. Whilst the additions of Al and Si to TiN led to a ~8 and ~16% increase in yield strength; and a ~52 and ~110% increase in plastic deformation factor. These data suggest that these coatings also possess good wear resistance. With additions of Al and AlSi, formation of AlN and Si$_3$N$_4$ phases (XPS results) help inhibit the grain boundary sliding and thereby increasing toughness of these films. Furthermore, the addition of subsequent dopants (Al/AlSi), the compressive residual stress of the coatings is increased which also enhances hardness [445]. Thus, the higher hardness values developed in the TiAlN and TiAlSiN coatings are due to the combined influence of modification of the grain boundary structure and enhanced residual stresses.

7.3.3 Surface Morphology of the Sputtered Films

The surface morphology of the coatings was analyzed by SEM in order to explore the effect of surface structure on optical properties. The TiN coating exhibited a number of randomly dispersed pores around the surface of the film, together with a distribution of non-uniform grains. The average grain size of this coating was observed to be around ~70 nm (See Fig. 35 (a)). With both the addition of Al and the simultaneous addition of Al and Si to TiN, most of the pores were no longer present and grains were refined (See Figs. 35 (b), and (c)). Addition of Al only reduced the grain sizes down to ~30 nm
(±10%), while simultaneous addition of Al and Si resulted in further decrease in grain size to ~27 nm (±10%). Concurrently some fine grains are also developed around the surfaces of these coatings. The SEM studies are consistent with XRD results, where the average grain sizes of these coatings were found to be reduced systematically with the addition of Al and AlSi dopants. Moreover with the addition of dopants, the surface morphology and shape of the grains both was altered together with irregular mould-like structures seen around the surface of the films. Further inspection confirms that the higher surface roughness is attained by the TiAlN coatings. It suggests that Al and AlSi additions hinder the diffusion of titanium and nitrogen atoms during deposition processes and thereby stimulate grain growth eventually acting as nucleation sites for lattice distortions. Similarly, in TiAlSiN coating, Al and Si reduce the mobility of both titanium and nitrogen atoms and thereby slowing down their diffusion.

**Figure 35.** SEM micrographs of: (a) Ti$_{0.5}$N$_{0.5}$ coating (b) Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ coating, and (c) Ti$_{0.25}$Al$_{0.2}$Si$_{0.05}$N$_{0.5}$ coating.

The surface roughness produces a gradient in the optical constants, rather than a sharp discontinuity at the interface. Kang and Kim (1999) indicated that the gradient in the optical constants strengthen optical behavior [446]. It was further noticed that the surface of TiAlN and TiAlSiN became more compact and denser with the addition of Al to the Ti and AlSi to Ti, respectively. The dense and closely packed structures show more stability as a selective surface at high temperatures. These kind of sputtered coatings are mechanically more reliable than similar coatings with large columns and open pores [447]. EDX provided approximate elemental compositions of these coatings (see Table 18 below). In TiAlN films, the content of Al is larger than content of Ti in TiAlSiN films.
due to the fact that EDX measurements were involved within a particular area of the films and do not provide with bulk information with reasonable degree of precision. However, these show data that are broadly consistent with the expected compositions of these coatings.

**Table 18.** EDX analysis for the elemental compositions of the as-deposited \( \text{Ti}_x\text{M}_{1-x} \text{N}_y \) magnetron sputtered coatings.

<table>
<thead>
<tr>
<th>Sample compositions</th>
<th>Element % of Ti</th>
<th>Element % of N</th>
<th>Element % of Al</th>
<th>Element % of Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ti}<em>{0.5} \text{N}</em>{0.5} )</td>
<td>48.43</td>
<td>51.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{Ti}<em>{0.25} \text{Al}</em>{0.25} \text{N}_{0.5} )</td>
<td>23.47</td>
<td>47.50</td>
<td>29.03</td>
<td>-</td>
</tr>
<tr>
<td>( \text{Ti}<em>{0.25} \text{Al}</em>{0.2} \text{Si}<em>{0.05} \text{N}</em>{0.5} )</td>
<td>22.86</td>
<td>45.21</td>
<td>26.80</td>
<td>5.13</td>
</tr>
</tbody>
</table>

### 7.3.4 Band-gap Studies of TiN, TiAlN and TiAlSiN Coatings

The wavelength of light that a material absorbs is the characteristic of its chemical assembly. Specific regions of the electromagnetic spectrum are absorbed by exciting specific types of molecular and atomic motion to higher energy levels. Absorption of ultraviolet and visible light is related with excitation of electrons, in both atoms and molecules, to higher energy states. Most molecules require very high energy radiation. The dependence of optical absorption coefficient on the photon energy helps to study the band structure and the type of electron transition involved in absorption process. In crystalline and amorphous materials the photon absorption obeys the Tauc relation,

\[
a h \nu = A (h \nu - E_g)^n
\]  

where, \( a \) is the absorption coefficient, \( h \nu \) is the incident photon energy, \( h \) is Planck’s constant, \( \nu \) is the frequency of incident light, \( A \) is an energy independent constant, \( E_g \) is the band-gap energy and \( n \) is an index depending on the type of optical transition involved in photon absorption.

The index \( n = 1/2 \) and 2 for allowed direct and indirect transitions respectively. Thus, the direct transition energy gap (direct band-gap energy) can be obtained by plotting \( h \nu \) vs \((ah \nu)^2\) and extrapolating the linear portion of the curve to \((ah \nu)^2 = 0\) in the energy axis. Similarly the indirect energy band-gap can be found by plotting \( h \nu \) vs \((ah \nu)^{1/2}\) and extrapolating the linear portion of the curve to \((ah \nu)^{1/2} = 0\) in the \(x\)-axis.

In the present study UV-visible absorptance spectra presented in Fig. 36 were used to investigate the solar absorptance, optically induced transition and to acquire information
about the band structure of the films. Plots from Fig. 36 demonstrate that in the visible range of the spectra, the solar absorbance of these coatings increases with the increase in wavelengths and a broadening of the absorption peak. At a wavelength of 500-530 nm, the absorbance values attain their maximum and then decrease linearly until the near infra-red region. The spectral dependence of $a$ on the photon energy ($h\nu$) (See Fig. 36) helps to realize the band structure and the type of electron transition involved in the absorption process. Fig. 36 indicates two different slopes in the experimental photon energy ranges of these coatings. These are ascribed as the presence of direct and indirect optical transitions involved in these coatings. Photon absorptions in crystalline and amorphous materials are known to follow the Tauc relation as given in Eq. (7.2). The band-gap involved in direct transition is estimated by plotting graphs between the photon energy $h\nu$ vs $(ah\nu)^2$ and then extrapolating the linear portion of the curve to $(ah\nu)^2 = 0$. Plots of $h\nu$ vs $(ah\nu)^2$ for TiN, TiAlN and TiAlSiN films are shown in Fig. 37 (A) and energy gaps were estimated from the intercepts of the linear part of the curves extrapolated to zero in the photon energy axis. From Fig. 37 (B), $h\nu$ vs $(ah\nu)^{1/2}$, the intercept of the linear part of the curves extrapolated to zero in the $x$-axis gives the energy gap involved in indirect transition.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure36.png}
\caption{Energy dependence of the UV-Vis absorption spectra of sputtered TiN, TiAlN and TiAlSiN coatings (TiN, TiAlN and TiAlSiN respectively stand for Ti$_{0.5}$N$_{0.5}$, Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ and Ti$_{0.25}$Al$_{0.2}$Si$_{0.05}$N$_{0.5}$).}
\end{figure}
In a similar fashion, the intercept of the linear part of the curves extrapolated to zero in the $x$-axis is taken as indirect transition energy gap. The energy band-gap values computed for direct and indirect transitions in TiN, TiAlN and TiAlSiN films are presented in the following Table 19. The values of direct and indirect transition energy gaps lie between 2.65 and 2.35 and 0.90 and 0.25 eV respectively. The results indicate a slight decrease in the energy band-gaps as the Al and Al + Si are incorporated in the TiN system.

![Graph (A)](image1)

![Graph (B)](image2)

**Figure 37.** Estimation of band-gaps of the sputtered TiN, TiAlN and TiAlSiN coatings for: (A) direct and (B) indirect allowed transitions (TiN, TiAlN and TiAlSiN respectively stand for $\text{Ti}_{0.5}\text{N}_{0.5}$, $\text{Ti}_{0.25}\text{Al}_{0.25}\text{N}_{0.5}$ and $\text{Ti}_{0.25}\text{Al}_{0.2}\text{Si}_{0.05}\text{N}_{0.5}$).

<table>
<thead>
<tr>
<th>Coatings name</th>
<th>Band-gap (direct transition), eV</th>
<th>Band-gap (indirect transition), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$<em>{0.5}$N$</em>{0.5}$</td>
<td>2.65</td>
<td>0.90</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.25}$N$_{0.5}$</td>
<td>2.45</td>
<td>0.45</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.2}$Si$<em>{0.05}$N$</em>{0.5}$</td>
<td>2.35</td>
<td>0.25</td>
</tr>
</tbody>
</table>

7.3.5 Evolution of Chemical Bonding Structures of Ti$_x$M$_{1-x-y}$N$_y$ Coatings: XPS Analysis

Table 20 delineates the details of the atomic compositions of the coatings as achieved from the XPS studies both before and after etching. It is apparent that 6 minutes of Ar$^+$ etching removed the surface contamination (see the 3rd and 4th columns in Table 20). That is, the oxygen content of these coating decreased from $\sim$ 50 at% before etching to $\sim$ 10 at.% afterwards.

Table 20. Details of the elemental compositions of the Ti$_x$M$_{1-x-y}$N$_y$ unbalanced magnetron sputtered coatings acquired via XPS survey scans.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elements</th>
<th>Atomic percentages of the elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before etching</td>
</tr>
<tr>
<td>Ti$<em>{0.5}$N$</em>{0.5}$</td>
<td>Ti</td>
<td>21.68</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>27.50</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>50.82</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.25}$N$_{0.5}$</td>
<td>Ti</td>
<td>8.36</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>24.92</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>21.15</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>45.57</td>
</tr>
<tr>
<td>Ti$<em>{0.25}$Al$</em>{0.2}$Si$<em>{0.05}$N$</em>{0.5}$</td>
<td>Ti</td>
<td>13.20</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>25.30</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>14.80</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>43.46</td>
</tr>
</tbody>
</table>

High resolution XPS spectra of the characteristic Ti$2p$, Al$2p$, Si$2p$, N$1s$, and O$1s$ peaks at different binding energies positions are shown in Figs. 38-40. The photon energy scales of all the spectra were calibrated by using the C$1s$ peak of C-H (or C-C) at 285 eV. The appearance of oxygen peaks reveals the existence of residual oxygen in the vacuum chamber, or subsequently following heat treatment in air. The Shirley method [448] was used to remove the background of spectra. The curve-fitting of the high resolution peaks
was performed using a nonlinear least squares fitting of a mixed Gaussian-Lorentzian product function via CASA version 2.3.5.1 XPS software.

Curve fitting of the core-level photoelectron lines of Ti, Al, Si, N and O was used to estimate the relative contributions of Ti–N, Al–N, Si–N, Ti-related oxides, Al-related oxides, Si-related oxides to the coatings. Table 21 displays the bonding states, elements/compounds, binding energies, FWHMs, and percentages of the different components from XPS fitting curves. The high-resolution Ti2p spectra show the spin-orbit doublet which gives out Ti 2p3/2 and Ti 2p1/2 peaks separated by a binding energy of 5.6 eV. The doublet separation value 5.6 eV between the two lines of Ti 2p3/2 and Ti 2p1/2 reveals that the bonding state of Ti is in the form of TiO2 [449]. In the TiN coatings (See Fig. 38): the deconvolution of the Ti2p spectrum can be assigned as three different chemical bonding states. The binding energy of the features ranging from 455.1 to 458.6 eV is assumed as the presence of the Ti2p3/2 state. The peaks at 455.1 eV and at 460.7 eV correspond to Ti-N bonds in TiN [450]. The peak at 455.2 eV is assigned to TiN bonds, and the peak 456.8 eV is related to Ti2O3 bonds and another peak at 458.4 eV may be attributed to suboxides based on TiO2 compounds [442]. This reveals the fact that the surface of these coatings has been oxidized. In the case of the Ti2p peak from the XPS spectra of the TiAlN, and TiAlSiN coatings, a shift to lower binding energy and peak broadening indicates the appearance of reduced Ti ions. This is because of a larger number of oxygen vacancies around the surface of the films. It is also expected that the possible formation of bonding states of Ti-Al(N) and Ti-AiSi(N) phases may cause the shifting and broadening of Ti2p peaks. Furthermore, some Ti may also exist as Ti3+ ions in the form of TiN. After a fitting, the N1s core level photoelectron spectra exhibited three components located at 396.8, 397.6 and 399 eV: the first peak from the low binding energy side corresponds to nitrogen in TiN, AlN, and/or SiN bonds, the second peak (in the middle) originates from titanium oxynitrides and the relatively low intense peak centered at 399 eV is due to the presence of impurities/pores/defects in the coatings such as free N2 or nitrogen associated with carbons. However, incorporation of aluminum and simultaneous addition of aluminum and silicon to the TiN system results in TiN/TiAlN, AlN and Ti-oxinitrides or Ti-and/or metal oxinitride phases at similar binding energy positions. In the case of TiN coatings, curves of O1s core level electrons were assigned into three different fragments: the first one at 530.7 eV is ascribed to TiO2, the second peak at 531.6 eV is assigned as the elemental O (or physically adsorbed molecular H2O) and the third peak at 532.8 is identified to be contributed from Ti-oxynitride phases.
In the TiAlN and TiAlSiN films (See Fig. 39 and Fig. 40), the deconvolution of Al2p spectrum can be resolved into two components: the first one located at 74.2 eV and the second component is seen at a binding energy position of 75.0 eV. The first component can be assigned to AlN, while the component seen at 75.0 eV is mainly due to the Al-O bonding in Al2O3 [451]. Similar features were also observed in the Al2p spectrum of the TiAlSiN films (as seen in Fig. 40 and Table 21). The Si2p core level electrons of the TiAlSiN coating are fitted with two segments: the first one at 101.7 eV is attributed to Si3N4 and the second peak at ~103 eV is identified to be the characteristic for Si-O bonds in SiOx phase.

![Figure 38](image_url)

Figure 38. Core level high resolution XPS spectra of Ti0.5N0.5 coatings and the peak fittings of (a) Ti2p (b) N1s and (c) O1s. Red color stands for raw data green color stands for fitting envelope.
Figure 39. Core level high resolution XPS spectra of Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ coatings and the peak fittings of (a) Ti2p, (b) Al2p, (c) N1s and (d) O1s. Red color stands for raw data green color stands for fitting envelope.
Figure 40. Core level high resolution XPS spectra of Ti$_{0.25}$Al$_{0.20}$Si$_{0.05}$N$_{0.5}$ coatings and the peak fittings of (a) Ti$2p$, (b) Al$2p$, (c) Si$2p$, (d) N$1s$ and (e) O$1s$. Red color stands for raw data green color stands for fitting envelope.
Table 21. Fitting results of the XPS data of Ti0.5N0.5, Ti0.25Al0.25N0.5 and Ti0.25Al0.2Si0.05N0.5 sputtered coatings for the core level binding energies.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Line</th>
<th>Bonding states</th>
<th>Binding energy (eV)</th>
<th>FWHM (eV)</th>
<th>Percentages of the component (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti0.5N0.5</td>
<td>Ti2p3/2</td>
<td>TiN</td>
<td>455.2</td>
<td>1.4</td>
<td>40.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti2O1</td>
<td>456.8</td>
<td>1.6</td>
<td>27.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO2</td>
<td>458.4</td>
<td>1.6</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>Ti2p1/2</td>
<td>TiN</td>
<td>460.7</td>
<td>1.2</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti2O1</td>
<td>461.5</td>
<td>1.1</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO2</td>
<td>463.0</td>
<td>1.1</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>N1s</td>
<td>Free N2 or N2</td>
<td>399.0</td>
<td>1.3</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>surface adsorbates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O1s</td>
<td>O2/TiN or TiO2</td>
<td>530.5</td>
<td>1.1</td>
<td>29.3</td>
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<tr>
<td></td>
<td></td>
<td>O2/Ti</td>
<td>531.6</td>
<td>1.3</td>
<td>49.1</td>
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<td></td>
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<td>TiON</td>
<td>532.8</td>
<td>1.3</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>Ti2p3/2</td>
<td>TiN/TiAIN</td>
<td>455.1</td>
<td>1.6</td>
<td>18.0</td>
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<td></td>
<td></td>
<td>Ti2O1</td>
<td>456.7</td>
<td>1.7</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO2</td>
<td>458.5</td>
<td>1.6</td>
<td>16.6</td>
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<tr>
<td></td>
<td>Ti2p1/2</td>
<td>TiN/TiAIN</td>
<td>460.4</td>
<td>1.0</td>
<td>1.4</td>
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<td></td>
<td></td>
<td>Ti2O1</td>
<td>461.3</td>
<td>1.6</td>
<td>12.7</td>
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<tr>
<td></td>
<td></td>
<td>TiO2</td>
<td>463.2</td>
<td>1.6</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>Al2p</td>
<td>AIN</td>
<td>74.2</td>
<td>1.0</td>
<td>69.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al2O3</td>
<td>75.0</td>
<td>1.0</td>
<td>30.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiN/TiAIN</td>
<td>396.5</td>
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<td>45.7</td>
</tr>
<tr>
<td></td>
<td>N1s</td>
<td>AIN</td>
<td>396.9</td>
<td>1.3</td>
<td>50.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO2, N and/or TiAlO:N</td>
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<td>1.0</td>
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<tr>
<td></td>
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<td>33.0</td>
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<td></td>
<td>TiON</td>
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<td>Ti2p3/2</td>
<td>TiN/TiAIN</td>
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<td></td>
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<td>O2/Si or SiO2</td>
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<td>1.1</td>
<td>44.8</td>
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<td>TiO2, N and/or Ti(Al/Si)O:N</td>
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<td>0.8</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
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<td>O2/TiN or TiO2</td>
<td>530.3</td>
<td>1.3</td>
<td>51.2</td>
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<td></td>
<td></td>
<td>O2/Ti or O2/Al or O2/Si</td>
<td>531.5</td>
<td>1.3</td>
<td>33.9</td>
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<td></td>
<td></td>
<td>TiON or SiO2</td>
<td>532.6</td>
<td>1.2</td>
<td>14.9</td>
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</tbody>
</table>
7.3.6 Solar Selectivity of Sputtered Ti$_x$M$_{1-x}$N$_y$ Coatings

Using the reflectance, $R(\lambda)$ data acquired via UV-Vis and FTIR measurements, the solar absorptance and the solar emittance of a material can be conveniently estimated [452]. For a range of solar wavelengths, the total solar absorptance, $a(\lambda)$ is defined as a weighted fraction between absorbed radiation and incoming solar radiation ($I_{\text{sol}}$), while thermal emittance, $\varepsilon(\lambda)$ is defined as a weighted fraction between emitted radiation and the Planck black-body distribution ($I_p$) [40]:

$$a = \frac{\int_{0.19}^{2.5} I_{\text{sol}}(\lambda)(1-R(\lambda))d\lambda}{\int_{0.19}^{2.5} I_{\text{sol}}(\lambda)d\lambda} \quad (7.3)$$

$$\varepsilon = \frac{\int_{2.5}^{15.4} I_p(\lambda)(1-R(\lambda))d\lambda}{\int_{2.5}^{15.4} I_p(\lambda)d\lambda} \quad (7.4)$$

The solar spectrum, $I_{\text{sol}}$ has an air mass (AM) of 1.5 in accordance with the ISO standard 9845-1 (1992). The figure of merit of a selective surface is expressed in terms of a parameter known as the selectivity, $s$. The selectivity of a material is defined by the ratio of the solar absorptance ($a$) to the thermal emittance ($\varepsilon$) [416]:

$$s = \frac{a}{\varepsilon} \quad (7.5)$$

The UV-Vis reflectance spectra of the TiN, TiAlN and TiAlSiN coatings deposited on M2 steel substrates are demonstrated in Fig. 41. The UV-Vis reflectance spectra was used to estimate the optical absorptance ($a$) of these coatings using the Duffie and Beckman method [452]. The optical absorptance evaluated as an average value computed from 20 values corresponding to the solar spectrum range between 190 nm and 2500 nm are shown in Table 22. As seen in Fig. 41, the coatings exhibit moderate absorptance ($a$) of $>70\%$ to UV radiation, high absorptance of $>80\%$ in the visible spectrum and high reflectance (up to $94\%$) in the near-infrared region of the solar spectrum. In the shorter wavelength region, all the reflectance spectra show a wavy curve with interference peaks along with a sharp absorption edge. In the visible region, up to 650 nm, compared to the TiN and TiAlN coatings, the reflectivity of the TiAlSiN coating was found to be decreased significantly, whilst above the visible range, the reflectance of the TiAlSiN coating was quite steady over the near-infrared range up to 2500 nm. In all three coatings, the highest absorption of solar radiation was measured in the visible spectrum and the lowest absorptance ($>90\%$ reflectance) in the near-infrared region. The major difference between the reflectance spectra of the TiAlSiN film and the other two samples is that the reduction in infrared reflectance is more pronounced. For this reason, the overall
absorptance of the coating with AlSi-additions was enhanced significantly. Our observation is found to be consistent with previous investigations [55, 362]. High absorptance of the coating makes it an ideal candidate for use as a selective solar absorber. A valuable approach of developing multilayer or gradient layer structures of selective solar surfaces are thoroughly discussed in Ref. [363]. The increase in solar absorption is associated with the gradual increase in the refractive index of the films from the outer surface to the substrate. In the case of single layered films on a steel substrate, we achieved the highest average solar absorptance of 81% which may be substantially enhanced by designing multilayered transition metal nitride coatings. Furthermore, an addition of a dielectric antireflection layer on the top of the outer film surface would further increase the photo absorption capacity of such coatings.

![Figure 41](image.png)

**Figure 41.** UV-Vis reflectance spectra of TiN, TiAlN and TiAlSiN unbalanced magnetron sputtered coatings (TiN, TiAlN and TiAlSiN respectively stand for Ti0.5N0.5, Ti0.25Al0.25N0.5 and Ti0.25Al0.2Si0.05N0.5).
**Figure 42.** FTIR reflectance spectra of TiN, TiAlN and TiAlSiN unbalanced magnetron sputtered coatings (TiN, TiAlN and TiAlSiN respectively stand for Ti$_{0.5}$N$_{0.5}$, Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ and Ti$_{0.25}$Al$_{0.2}$Si$_{0.05}$N$_{0.5}$).

The infrared reflectance spectra of the TiN, TiAlN and TiAlSiN coatings measured via FTIR spectroscopy are presented in Fig. 42. The infrared thermal emittance ($\varepsilon$) of these coatings calculated via the Duffie and Beckman method [452] are displayed in Table 22. As can be seen from Table 22, the thermal emittance of the coatings decreased with the addition of Al and the simultaneous addition of Al and Si to TiN. When Al and Si are added to TiN, the emittance decreased because the formation of the surface oxide layers (Al$_2$O$_3$, SiO$_2$) that resulted in high infrared reflectivity [453]. This is consistent with Al$_2$O$_3$, SiO$_2$ observed the XPS analysis.

TiN possesses metallic character, while AlN and Si$_3$N$_4$ are both dielectric in nature. Thus, the addition of Al and AlSi to the TiN matrix also transforms the electronic properties of TiAlN and TiAlSiN from metallic to a more dielectric character. The solar absorptance and emittance of the coatings is strongly related to the band-gap of the films. TiN matrix possesses a band-gap of 2.65 eV. The addition of Al and AlSi to the TiN phase reduces the energy band-gap from 2.65 eV to 2.45 and 2.30 eV, respectively. This designates that addition of Al and AlSi, effectively modifies the overall band structures of TiN coatings, and thereby the overall solar selectivity of the TiAlN and TiAlSiN films is increased. Moreover, with addition of Al to TiN coatings change their color from gold to blue grey. This change in color also enhances the optical absorption of TiAlN coatings and thereby
solar selectivity is increased. Further, the occurrence of Al₂O₃ (as confirmed by XPS studies) on the coating surface, which displays ionic character, has high electrical resistivity, good chemical stability, and a refractive index between 1.5–1.9 in the visible range of the solar spectrum [454, 455], also play significant role in improving the optical properties of these coatings. In addition, Al and AlSi dopants result in a change in structure of grains and grain boundaries, surface chemical bonding states and surface oxide layers which contributes to the surface morphology of the films as observed from SEM studies. This may also affect the overall optical constants, such as refractive index, optical dielectric constant and optical conductivity of the materials.

<table>
<thead>
<tr>
<th>Name of the samples</th>
<th>Solar absorptance (α)</th>
<th>Emittance (ε)</th>
<th>Solar selectivity (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₀.₅N₀.₅</td>
<td>0.51</td>
<td>0.0606</td>
<td>8.42</td>
</tr>
<tr>
<td>Ti₀.₂₅Al₀.₂₅N₀.₅</td>
<td>0.66</td>
<td>0.0511</td>
<td>12.92</td>
</tr>
<tr>
<td>Ti₀.₂₅Al₀.₂Si₀.₀₅N₀.₅</td>
<td>0.81</td>
<td>0.0358</td>
<td>22.63</td>
</tr>
</tbody>
</table>

The ratio of solar absorptance to the thermal emittance (α/ε), so-called solar selectivity (s) represents the spectral features of selective solar surfaces. The solar selectivity values of our coatings are listed in Table 22. From Table 22, it is clearly seen that the solar selectivity of TiN is improved significantly by the addition of both Al and Al/Si. Barshilia et al. [55] documented sputtered TiAlN/TiAlON/Si₃N₄ coatings on a stainless steel substrate for solar selective absorbers and obtained a solar selectivity of 7.4. These works utilized both a solar spectrum reflectometer and emissometer to compute the solar absorptance in the visible spectrum and thermal emittance in the infrared range. In addition to coatings on stainless steel substrates, other researchers also deposited the TiAlN/TiAlON/Si₃N₄ selective absorbers onto glass, copper and nickel substrates and the solar selectivity values recorded were 13.3, 13.6 and 6.7 respectively [13]. In the same study [13], TiAlN sputtered coatings were synthesized onto a copper substrate and a solar spectrum reflectometer and emissometer were used, respectively, to measure the solar absorptance in the visible spectrum and thermal emittance in the infrared range. An overall solar selectivity of 12.92 and 22.63 was attained by TiAIN and TiAlSiN solar selective coatings, respectively. In comparison with similar solar selective absorbers developed onto stainless steel and other substrates, our coatings were found to exhibit superior solar selectivity. The solar selectivity of these coatings depends on the
thicknesses of the films, surface roughness, materials used, processing techniques, processing conditions, and the reflective nature of the substrate used. Thus, it has been clearly seen that incorporation of the dopants (Al and/or AlSi) lead to microstructural modification (from SEM observations), grain refinements (XRD data), lattice contraction (XRD data), reaction between the elements to generate additional phases (XPS data), alternation in electronic bonding states (XPS results) and band structure of the coatings (band-gaps data). These structural factors significantly influence the scattering and the reflection of light and therefore the overall optical properties of the materials are, in turn, expected to be modified. As a result, the overall spectral selectivity of these coatings is enhanced.

7.4 Conclusions

Magnetron sputtered Ti$_{0.5}$N$_{0.5}$, Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ and Ti$_{0.25}$Al$_{0.2}$Si$_{0.05}$N$_{0.5}$ films were studied for their surface chemical bonding states and solar selective characteristics. XPS measurements are in good agreement with the XRD analysis, in which, both Si$_3$N$_4$ and AlN phases were detected. No signature peaks for either SiO$_2$, Al$_2$O$_3$ were detected in XRD suggesting that they are in low concentrations or in amorphous form. In TiAlSiN films, $sp^3$ Si bonding with $sp^2$ N was noted suggesting that the formation of Si$_3$N$_4$ was consistent with the XRD studies. The appearance of a small amount of oxide indicated oxidation has occurred during the synthesis (as well as subsequent annealing process) of thin films. The films exhibited lower reflectivity in the visible range of solar spectrum while they had high reflectivity in the infrared regions. It is possible that the amorphous nature of SiO$_2$, and Al$_2$O$_3$ (XPS and XRD results) enhances the bonding of Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ and Ti$_{0.25}$Al$_{0.2}$Si$_{0.05}$N$_{0.5}$ grains by serving as grain boundaries with a consequent increase of solar selectivity for these films. TiN films band-gap show consistent reduction of energy band-gaps (from 2.65 eV to 2.35 eV) with Al and Al + Si dopants. This reveals the overall band structures of TiN films are modified with dopant integrations. Therefore, these films can be used as selective solar surfaces that significantly improve the solar selective efficiency of TiN films from 8.42 to 22.63.
CHAPTER EIGHT: THERMAL STABILITY OF SOLAR SELECTIVE MAGNETRON SPUTTERED TiAlSiN COATINGS

8.1 Introduction

Transition metal nitride based quaternary TiAlSiN coatings are attractive candidates as cutting tools, protective and decorative coatings due to their many outstanding properties [456]. In recent years they have seen significant interest as solar selective absorbers for harvesting solar energy in various applications such as thermal solar collectors, solar steam generators and steam turbines for producing the electricity at mid and mid-to high temperatures [9, 11-19, 153, 457]. A good selective surface must have high absorptance ($\alpha$) in the visible spectrum up to 2.5 µm and low emittance ($\varepsilon$) in the infra-red (IR) region $\geq 2.5$ µm at the operating temperatures. In recent years, transition metal nitride based tandem coatings (e.g., TiAlN/AlON, and TiAl/TiAlN/TiAlON/TiAlO) have been suggested for use in solar selective surfaces to be used in photothermal applications [13, 154]. Barshilia et al. [55] developed a high thermal stable TiAlN/TiAlON/Si$_3$N$_4$ tandem absorber on a copper substrate for high temperature solar selective applications that exhibited an absorptance of 0.958 and an emittance of 0.07. Until now these materials have not been commercially produced [13, 58, 153].

Most of the coatings only exhibit good stability in a vacuum and in air they have very limited thermal stability. However, in a high temperature or for long period application purposes, these solar selective absorbers should have stable structural configuration without having any significant degradations. The oxidation resistance behavior of these coatings is also very important because they are frequently exposed at high temperature atmospheres in air. The addition of Al and Si in the TiN coatings increases their oxidation resistance by forming oxide layers around the surface which eventually work as a barrier for further oxygen penetrations at high temperatures. The formation of amorphous phases also provides better stability against degradation, corrosion and oxidation than that of crystalline metallic nitride phases. TiAlSiN coatings provide good thermal stability at temperatures above 800 °C [458, 459]. These coatings have been explored mostly for their extraordinary mechanical properties, but as applications in solar selective surfaces in thermal collector devices are relatively unexplored [460-463].

The synchrotron radiation X-ray diffraction (SR-XRD technique is successfully used to probe the crystalline and electronic structure of various systems in a wide range of fields
such as physics, chemistry, environmental sciences, materials sciences, biology, medicine, and geophysics. The SR-XRD offers many advantages over the conventional laboratory based XRD techniques such as: highly collimated and intense photon beams, photon-energy tune ability, exceptional photon wavelength resolution ($\Delta \lambda / \lambda \approx 2 \times 10^{-4}$), polarization control, coherence, very high signal-to-noise and signal-to-background ratio. The synchrotron techniques are extensively used in the identification of phases in compounds and unknown structural forms developed during the synthesis processes of the films. In recent years these techniques successfully investigated the local electronic structure of metal nitride thin films in pure and doped states [157, 464, 465].

To the best of our knowledge, investigations on structural thermal stability and oxidation resistance behaviors of these coatings via SR-XRD technique are yet to be established. This study addresses the temperature dependent surface morphology, mechanical properties, surface chemical bonding states, high temperature solar selective behaviors, and high temperature structural stability of magnetron sputtered TiAlSiN coatings via mechanical, SEM, XPS, UV-Vis and FTIR, and SR-XRD techniques.

8.2 Experimental Section

8.2.1 Thin Film Deposition Technique

TiAlSiN films were deposited onto AISI M2 tool steel substrates via a closed field unbalanced magnetron sputtering system (UDP650, Teer Coating Limited, Droitwich, Worcestershire, UK). The magnetron sputtered system is equipped with a four-target configuration. Before coating, the substrates were ultrasonically cleaned in an acetone and methanol solution and then dried using high purity nitrogen gas. A pressure of $2.67 \times 10^{-4}$ Pa was maintained in the chamber throughout the deposition process. Prior to synthesizing the samples, all of the targets were cleaned properly and the steel substrates were safeguarded by shutters through the magnetrons. In order to achieve a homogeneous film thickness, the substrate was rotated at a speed of 10 rpm throughout the synthesis process. The substrates were sputter cleaned with Ar plasma at a bias of -450 V for 30 minutes. The coatings were deposited in an Ar+N\textsubscript{2} mixed gas atmosphere. The partial pressure of Ar and N\textsubscript{2} were 0.133 Pa and 0.106 Pa throughout the deposition processes. The bias currents for Ti, Al and Si target were 5 A, 7 A, and 5 A, respectively. The final products were then annealed at 500, 600, 700 and 800 °C. Further details of the deposition conditions of TiAlSiN coatings are discussed in Table 9 (Chapter 4).
8.2.1 Characterizations of the TiAlSiN Coatings

Scanning electron microscopy (SEM) was conducted to realize the surface morphology of the thin film coatings with a high resolution microscope (SEM, PHILIPS XL 20, Eindhoven, The Netherlands). A secondary electron (SEI) detector was used to characterize the overall surface morphology of thin film structures. The SEM machine was operated at 25 kV. The samples were glued with double sided carbon tape affixed to the sample holders.

A depth-sensing indentation system (Ultra-Micro Indentation System, UMIS-2000, CSIRO, Australia) equipped with a Berkovich indenter was used to measure the Young’s modulus and hardness of the coatings. The indenter tip was calibrated by conducting single-cycling indentation tests on fused silica (a standard material having a known modulus of 72 GPa) at different loads. Load–unload tests were run in a closed-loop under load control to determine the mechanical properties of the samples. A maximum load of 20 mN was applied in 10 increments. The loading rate set to 2.5 mN/s represents the static response of the materials. Following each increment there were 10 decrements, from which the Young's modulus and hardness were calculated. Five indentation tests were performed on each specimen. The load vs displacement response obtained by nanoindentation is a very powerful technique for analyzing mechanical properties. The elastic behavior of, and deformation mechanisms within, the coating systems can be realized by analyzing the nanoindentation data. In order to investigate the thermal stability of the sputtered films, mechanical hardness of the coatings was tested with the samples before annealing and after being annealed between 500 °C and 800 °C in steps of 100 °C in air atmosphere.

The XPS data will reveal information on chemical structure, elemental compositions and bonding states in the outermost 5 nm surface of the films. The XPS measurements of the TiAlSiN coatings were taken using an XPS (Kratos Axis Ultra XPS spectrometer, Manchester, UK) machine operating with an Al-Kα monochromatic radiation (\( h\nu = 1486.6 \text{ eV} \)) source at a power of \(~10 \text{ mA} \) and \(~15 \text{ kV} \). The XPS machine was also equipped with a cold stage, and an Ar ion gun for etching the coatings. The samples were mounted on a steel sample holder and put in the analysis chamber where the pressure was reduced to \( 2.9 \times 10^{-9} \text{ Pa} \) and maintained at that level during the analysis. The XPS survey spectra were collected before etching, and after 6 minutes etching. Ar ion sputtering was used for etching the films. Etching was done to remove any surface oxide layers and to
reduce the Ti\(^{4+}\) ions in order to lower oxidation states. The high resolution XPS data was recorded after a 6 minute Ar\(^+\) sputtering. The typical high resolution XPS core level spectra of TiAlSiN samples before and after annealing show Ti2\(p\), Al2\(p\), Si2\(p\), N1\(s\) and O1\(s\) energy regions. Information on the existence of various chemical bonding states was acquired by subtracting the background with the Shirley’s method and deconvoluting the spectra with curve-fitting methods using CASA XPS software (version 2.3.1.5) [448].

The optical properties of the thin film coatings were analyzed by measuring the optical reflectance as a function of wavelength from ultraviolet through the visible to infrared range of the solar spectrum via UV-Vis and FTIR spectrometers. A double-beam UV–Vis spectrophotometer (Model: UV-670 UV-Vis spectrophotometer, JASCO, USA) equipped with a unique, single monochromator design covering a wavelength range from 250 to 2500 nm was used to measure the solar absorptance of the coatings. The monochromator itself was designed with 1200 grooves/mm grating and a photo multiplier tube (PMT) detector. A PERKIN Elmer Spectrum 100 FTIR Spectrometer (USA) was used for measuring the reflectance, \(R(\lambda)\), of the coatings in the wavelength range of 2.5 to 15 \(\mu\)m. Using the \(R(\lambda)\) data the solar absorptance (\(\alpha\)) and the solar emittance (\(\varepsilon\)) of a material can be conveniently estimated [452]. For a range of solar wavelengths, the total solar absorptance, \(\alpha\) is defined as a weighted fraction between absorbed radiation and incoming solar radiation (\(I_{sol}\)), while thermal emittance, \(\varepsilon\) is defined as a weighted fraction between emitted radiation and the Planck black-body distribution (\(I_p\)). The figure of merit of a selective surface is expressed in term of a parameter known as the selectivity, \(s\). The solar selectivity of a material is defined by the ratio of the solar absorptance, \(\alpha\) to the thermal emittance, \(\varepsilon\), with expression (\(s\)) given in Ref. [349]. Mathematical expressions of the solar absorptance, thermal emittance and solar selectivity are presented in Chapters 6, and 7.

The SR-XRD measurements of the TiAlSiN coatings were carried out with the powder diffraction (PD) beamline 10-BM-1 at the Australian Synchrotron, in Melbourne. The PD beamline operated at 2.5 GeV and used a bending magnet source. A continuous spectrum of photons were generated in the range 5–30 keV with a maximum flux of about \(10^{13}\) photons/sec and a beam size of 1 mm (W) \(\times\) 8 mm (L) \(\times\) 1 mm (H). The general beam size of the sample for the focused and unfocussed beam arrangements was 0.5 mm \(\times\) 0.5 mm and 5 mm \(\times\) 2 mm respectively. An X-ray wavelength of 0.8265 Å, estimated with a LaB6 standard NIST 660a, was used for the measurements. The high temperature system
was an Anton Parr HTK20 furnace. The furnace was calibrated and monitored by a thermocouple and the heating and cooling cycles were remotely controlled via a computer interface. The high resolution XRD data was acquired at room temperature, 500 °C, 600 °C, 700 °C, and 800 °C. A MYTHEN II microstrip detector system was used to record the high resolution XRD data in the range of 2θ = 15° to 35° in steps of 0.02°. At each detector setting SR-XRD data was acquired for a period of 5 minutes. Data collection was started after a 3 min thermal equilibration period at which the control sensor had reached the set temperature. The acquired data was processed with PDViPeR software for further analysis.

8.3 Results and Discussion

8.3.1 Temperature Dependent Surface Morphology of the TiAlSiN Coatings

SEM images of sputtered TiAlSiN coatings before annealing and after being annealed at 500-800 °C in steps of 100 °C are presented in Fig. 43. SEM examination of the microstructure showed nanocomposite-like structure deformed by formation of an amorphous phase and facilitated by fine grains. As the annealing temperature progresses from 500 to 600 °C, there originated some random pores around the surface of the coatings together with non-uniform grains. At the same time, the surface morphology and shape of the grains of the films were altered together with the rise in irregular mound like structures around the film’s surfaces. Further inspection confirms that the higher surface roughness is attained by the coatings as the annealing temperature is increased. This surface roughness hinders the diffusion of titanium and nitrogen atoms and slows down their diffusions, helps to grain growth and develop amorphous like structures around the grain boundaries. However, the new phase is extremely small in size and cannot be detected by either XRD or SEM. Because of this lower mobility, the crystallization process is disrupted and disordering is enhanced for further amorphization by Si₃N₄ phases around the boundaries. This amorphous grain boundaries influence the optical properties of these coatings [446]. The annealed films exhibited nanolayers which are observed as darker and lighter contrasts in the SEM micrographs together with the fine-grained structure of the coatings. This is due to the systematic increase on the oxide thickness growing on top of the coating with the rise in annealing temperatures. The oxides layers which are observed are composed of Al₂O₃ and SiO₂ at the outermost layer of the coating followed by TiO₂ layers (as seen in XPS studies). These nano-sized protective layer formed on the nitride film hinders the diffusion of oxygen into the
coating due to their small size and polycrystalline nature. These nanolayers did not vanish or alter their structure as a consequence of the heat treatment; rather, they seem to be very stable [466]. The dense and closely packed structures show more stability as selective surfaces at high temperatures. These kind of sputtered coatings are more reliable than similar coatings with large columns and open pores [447]. These microstructural features have substantial impacts on the residual stress and deformation mechanisms in the coatings and could assist with the interpretation of mechanical hardness of these coatings.
Figure 43. SEM micrographs of: (a) TiAlSiN coating before annealing and annealed at (b) 500 °C, (c) 600 °C, (d) 700 °C, and (e) 800 °C, temperatures respectively.
8.3.2 Mechanical Properties of TiAlSiN Coatings

The hardness, $H$ and Young’s modulus, $E$ values of the sputtered TiAlSiN coatings before annealing and after annealing are presented in Fig. 44.

![Graph showing mechanical properties of TiAlSiN coating before and after annealing](image)

**Figure 44.** Mechanical parameters of TiAlSiN coating before annealing and after being annealed at 500-800 °C in steps of 100 °C.

Table 23 represents the hardness, elastic modulus, Yield strength and corresponding plastic deformation resistance of the TiAlSiN coatings as acquired from the nanoindentation measurements. Before annealing, the TiAlSiN coating showed a hardness of 28.12 ± 0.6 GPa and an elastic modulus of 369 ± 9 GPa. Similar values for hardness and modulus have been reported in other studies [467-469].

**Table 23.** Mechanical characteristics of sputtered TiAlSiN films before annealing and after being annealed at different temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Hardness, $H$ (GPa)</th>
<th>Young’s modulus, $E$ (GPa)</th>
<th>Yield strength, $\frac{H}{E}$</th>
<th>Plastic deformation factor, $\frac{H^3}{E^2}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before annealing</td>
<td>28.12 ± 0.6</td>
<td>369 ± 9</td>
<td>0.08</td>
<td>0.16</td>
</tr>
<tr>
<td>500</td>
<td>26.76 ± 0.5</td>
<td>360.6 ± 7</td>
<td>0.08</td>
<td>0.15</td>
</tr>
<tr>
<td>600</td>
<td>24.4 ± 0.3</td>
<td>341.2 ± 8</td>
<td>0.07</td>
<td>0.13</td>
</tr>
<tr>
<td>700</td>
<td>23.06 ± 0.3</td>
<td>328 ± 8</td>
<td>0.07</td>
<td>0.12</td>
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<tr>
<td>800</td>
<td>22.16 ± 0.4</td>
<td>312.8 ± 12</td>
<td>0.07</td>
<td>0.11</td>
</tr>
</tbody>
</table>
The high hardness and high elastic modulus of TiAlSiN coatings before annealing arises due to the biaxial compressive stress developed by high energetic ions bombardment during the coating deposition. Effects of biaxial compressive stress on the hardness of superhard multilayer coatings were examined by Veprek et al [274, 470, 471]. An increase in the development of the intergranular amorphous phase in the nanocomposite matrix leads to a definite enhancement of the hardness of the coatings. This is also true of the elastic modulus values. At nano-scale level, the obstruction of dislocation movements and the nonappearance of dislocations also contribute to enhance the hardness of the coatings [472]. The dissolution of Al and Si atoms in the TiN crystallites produce solid solutions that are also responsible for the greater hardness of these coatings [473, 474]. In addition, the grain boundary strengthening at interphase boundaries also predominate to a higher hardness in the films [468, 475]. According to Veprek [274, 470, 471], a superhard microstructure with high elasticity and thermal stability can be formed by fine nanocrystallites (<10 nm) enclosed by a thin amorphous phase (<1 nm) along with a strong boundary between the amorphous and crystalline phases. This interface successfully hinders the grain boundary sliding’s, the formation of dislocations and their movements, and the spread of cracks. Generally a hard material has high wear resistance. The material’s hardness and elastic modulus are also related to the wear behavior [401]. It is known that the wear of a material is coupled with the elastic limit of materials that define the ability of a material to deform under an applied stress and regain its initial state without being deformed permanently [401]. Experimental value of the elastic limit is expressed by the $H/E$ ratio. The $H^3/E^2$ ratio, which is known as the plastic deformation factor, indicates the coating’s resistance to plastic flow [476]. Each of the parameters play an essential role in the coating wear behaviors. The linear decrease of $H$, $H/E$ and $H^3/E^2$ are well correlated with the reduction of wear resistance of TiAlSiN coatings during high temperature annealing. A high value of the $H^3/E^2$ ratio of a coating means that it offers high resistance to plastic deformation. This high value of the $H^3/E^2$ ratio is also associated with hindering dislocation formation or movement due to nano-grains and the solid impeding of the crack dissemination in the amorphous Si$_3$N$_4$ phase [477]. From an engineering application viewpoint, coating hardness must be accompanied by appropriate toughness and the ability of a material to absorb energy under an applied stress until fracture [478]. Musil and Jirout [479] reported their findings that resistance against crack formation of thin film coatings increases with increasing $H^3/E^2$ ratio. From Table 23, it can be seen that both the hardness and elastic modulus strongly depend on the annealing temperatures. The hardness decrement of the TiAlSiN coatings at elevated annealing
temperatures may result from diverse mechanisms. Since the coatings were heated in air, the composition at the surface is expected to change due to oxidation, and therefore, it is reasonable to have lower hardness as the annealing temperature is enhanced. At high temperature annealing, the reduction in hardness and elastic modulus values of TiAlSiN coatings may be also ascribed to the softening of steel substrates, changes in composition of the films due to the diffusion, formation of new phases and stress relaxations. High temperature annealing causes grain refinement, and when combined with the formation of point defects, interstitials, biaxial compressive stress, and other effects of the ion bombardment may result in a reduction of hardness and elastic modulus as the temperature is increased. According to Petrov et al. and Barna et al., oxygen and other impurities can lead to the grain refinement and alter the grain morphology of the coatings which also results to grain boundary embrittlement [480, 481]. Thus, the precise mechanism of the decrease of hardness with the rise in annealing temperature is not clear.

8.3.3 Atomic Compositions and Surface Chemical Bonding States of TiAlSiN Coatings at Various Annealing Temperatures

The elemental compositions of the TiAlSiN coatings were determined via XPS survey scans shown in Fig. 45. The detailed atomic compositions of these coatings, before annealing and after annealing at 500, 600, 700 and 800 °C, extracted from XPS survey spectra are outlined in Table 24. The existence of Ti, Al, Si, N, and O were identified following repeated XPS measurements of the deposited films.

The results show that annealing significantly affects the elemental compositions of these coatings. The atomic percentages of the constituent elements (Ti, Al, Si, N) are decreasing as the annealing temperature is increased; however the oxygen contents of the coatings were increased linearly. At 800 °C the Si2p and N1s signal were completely lost. This indicates that surface oxidation occurred at high temperatures. Since the oxygen content is higher at high annealing temperature, the oxidation layer may be thicker and more predominant at the surface. The specimens were etched with Ar+ for 6 minutes in order to remove the contamination. The XPS data acquired from these tests was calibrated with respect to the C1s peak at a standard binding energy of 284.6 eV, in order to make a correction for the charge shift.
Figure 45. XPS survey scans of magnetron sputtered TiAlSiN coatings before annealing and after being annealed at 500-800 °C in steps of 100 °C.

Table 24. Details of the elemental compositions of the as deposited-TiAlSiN and after being annealed unbalanced magnetron sputtered coatings acquired via XPS survey scans.

<table>
<thead>
<tr>
<th>Annealing temperatures (°C)</th>
<th>Atomic percentages of the elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>Ti 20.31 Al 18.23 Si 2.57 N 25.64 C 13.13 O 20.12</td>
</tr>
<tr>
<td>500</td>
<td>Ti 17.21 Al 15.37 Si 2.38 N 7.86 C 14.06 O 43.12</td>
</tr>
<tr>
<td>600</td>
<td>Ti 17.17 Al 10.71 Si 1.51 N 5.05 C 13.41 O 52.15</td>
</tr>
<tr>
<td>700</td>
<td>Ti 14.27 Al 7.05 Si 0.67 N 3.84 C 27.72 O 46.45</td>
</tr>
<tr>
<td>800</td>
<td>Ti 6.75 Al 6.15 Si 00 N 2.27 C 34.57 O 50.26</td>
</tr>
</tbody>
</table>

The surface chemical bonding states of films were characterized by curve fitting of high resolution XPS data which were recorded after 6 minutes of etching. High resolution XPS spectra of the characteristic Ti2p, Al2p, Si2p, N1s, and O1s peaks before annealing and after being annealed at 500-800 °C in steps of 100 °C are shown in Figs. 46-50. The existence of oxygen peaks exposes the existence of residual oxygen in the vacuum chamber and subsequent oxidation followed by the annealing in air atmosphere. High resolution Ti2p, Al2p, Si2p, N1s, and O1s peaks were deconvoluted to approximate the relative contributions of metal nitride and metal oxide related components to the coatings. The photoelectron lines, bonding states and their corresponding binding energy positions, FWHM values, and percentages of the components present in the coatings before
annealing and being annealed at various temperatures as assessed from XPS curve fittings are displayed Table 25.

The deconvolution curves of the high resolution XPS spectra of Ti2p3/2 photoelectron lines are presented in Fig. 46. In TiAlSiN coatings the deconvolution of Ti2p3/2 spectrum can be allocated to three bonding states in the energy range of 455.1-458.6 eV. The peaks seen at 455.1-455.2 eV (labelled ‘i’) correspond to Ti-N/TiAlN/TiSiN/TiAlSiN phase, the peak at 456.6 eV (labelled ‘ii’) is related to Ti2O3 bonds and another peak at 458.6 eV (labelled ‘iii’) may be attributed to suboxides based on Ti2AlO5 or TiO2 compounds. This reveals that the surface oxidation is initiated in these coatings while the peak broadening at higher annealing temperature confirms the appearance of reduced Ti ions. As a result of these peak broadenings, formation of bonding states of Ti-Al(N) and Ti-AiSi(N) phases are also predicted. It is also expected that some Ti may occur as Ti3+ ions in the form of TiN.
Figure 46. Typical fitting curves of Ti2p3/2 XPS spectra of sputtered TiAlSiN coatings before annealing and after being annealed at various temperatures. Red color stands for raw data black color stands for fitting envelope.
The deconvolution of Al$2p$ spectra (Fig. 47) demonstrates two sub-peaks in the energy range of 72.6-75.3 eV. The first components are observed within 74.0-74.6 eV (labelled ‘i’), the second components were seen around 75.0-75.3 eV (labelled ‘ii’). The first features detected in the binding energy range of 74.0-74.6 eV are assumed to be the contribution of AlN structure. The second contribution is due to the occurrence of Al$_2$O$_3$ phase [451]. From the XPS fitting curves of these spectra it is revealed that the major portion of the Al$2p$ spectrum is occupied by AlN phase.

![Typical fitting curves of Al$2p$ XPS spectra of sputtered TiAlSiN coatings before annealing and after being annealed at various temperatures. Red color stands for raw data black color stands for fitting envelope.](image)

**Figure 47.** Typical fitting curves of Al$2p$ XPS spectra of sputtered TiAlSiN coatings before annealing and after being annealed at various temperatures. Red color stands for raw data black color stands for fitting envelope.
Fig. 48 shows the Si$2p$ core level photoelectron lines of TiAlSiN thin film coatings. Deconvoluting the Si$2p$ core-level spectra by the curve-fitting method, we assessed the relative contributions of various phases to the total photoelectron signals in the sputtered coatings before and after annealing. The Si$2p$ core level XPS spectra are fixed with two fragments within the energy range of 101.5-102.7 eV. The first segments at 101.5-101.8 eV (labelled ‘i’) are due to Si$_3$N$_4$ structure while the second peaks detected around 102.5-102.7 eV (labelled ‘ii’) are from O$_2$/Si or SiO$_2$ phase. Throughout the observations, all the Si atoms were bonded smoothly and demonstrated stoichiometric compositions with various stable structures.

**Figure 48.** Typical fitting curves of Si$2p$ XPS spectra of sputtered TiAlSiN coatings before annealing and after being annealed at various temperatures. Red color stands for raw data orange color stands for fitting envelope.
The N1s photoelectron lines of TiAlSiN films before and after annealing are shown in Fig. 49. The curve fitting of N1s core level XPS spectra exhibited three constituents in the energy range of 396.5-398.5 eV. The first components in the binding energy range of 396.5-396.7 eV (labelled ‘i’) are related to nitrogen in TiN via TiN/TiAlN bonds, the second fragment at 397.3-397.6 eV (labelled ‘ii’) arise from the AlN phase and the relatively low intense third peak centred at 398.3-398.5 eV (labelled ‘iii’) are due to the presence of TiO_{x}N_{y} and/or the Ti(Al/Si)O_{x}N_{y} phase.

**Figure 49.** Typical fitting curves of N1s XPS spectra of sputtered TiAlSiN coatings before annealing and after being annealed at various temperatures. Red color stands for raw data light green color stands for fitting envelope.
Fig. 50 shows the O1s core level XPS spectra before and after annealing. Fitting the O1s XPS spectra consisted of three components in the binding energy range of 530.4-532.7 eV. The first features seen at 530.4-530.7 eV (labelled ‘i’) are applicable to the O2/Ti or the TiO2 phase, the second component detected within the binding energy positions of 531.2-531.7 eV (labelled ‘ii’) are apportioned as O2/Ti or O2/Al or O2/Si phases while the third fragment observed around 532.3-532.7 eV (labelled ‘iii’) originated from the TiON or SiO2 phases.

**Figure 50.** Typical fitting curves of O1s XPS spectra of sputtered TiAlSiN coatings before annealing and after being annealed at various temperatures.
The deconvoluted XPS spectra of Ti\(2p_{3/2}\), Al\(2p\), Si\(2p\), N\(1s\) and O\(1s\) photoelectron lines reflect the fact that no significant changes in the binding energy features of these photoelectron lines were detected with respect to the increase in annealing temperatures. Accordingly, good structural and chemical stability of these films were achieved at high temperature annealing which is responsible for superior optical behaviors.

**Table 25.** Fitting results of the XPS data of TiAlSiN sputtered coatings for the core level binding energies.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Photoelectron lines</th>
<th>Bonding states</th>
<th>Binding energy (eV)</th>
<th>FWHM (eV)</th>
<th>Percentages of the component (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Ti2p}_{3/2})</td>
<td>TiN/TiAlN/TiSiN/TiAlSiN</td>
<td>455.1</td>
<td>1.1</td>
<td>35.0</td>
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<tr>
<td></td>
<td>Ti2O3</td>
<td></td>
<td>456.6</td>
<td>1.5</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>Al2TiOx or TiO2</td>
<td></td>
<td>458.6</td>
<td>1.7</td>
<td>15.3</td>
</tr>
<tr>
<td>Before annealing</td>
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<td>AlN</td>
<td>74.2</td>
<td>1.0</td>
<td>60.6</td>
</tr>
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<td>Al2O3</td>
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<td>75.0</td>
<td>1.0</td>
<td>39.4</td>
</tr>
<tr>
<td></td>
<td>Si2p</td>
<td>Si3N4</td>
<td>101.5</td>
<td>1.2</td>
<td>40.5</td>
</tr>
<tr>
<td></td>
<td>O2/Si or SiO2</td>
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<td>102.6</td>
<td>1.2</td>
<td>59.5</td>
</tr>
<tr>
<td></td>
<td>N1s</td>
<td>TiN/TiAlN/TiSiN/TiAlSiN</td>
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<td>1.2</td>
<td>39.9</td>
</tr>
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<td>1.7</td>
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<td>531.7</td>
<td>1.9</td>
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</tr>
<tr>
<td></td>
<td>TiON or SiO2</td>
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<td>532.7</td>
<td>1.7</td>
<td>15.2</td>
</tr>
<tr>
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<td>Ti2p_{3/2}</td>
<td>TiN/TiAlN/TiSiN/TiAlSiN</td>
<td>455.1</td>
<td>1.2</td>
<td>27.6</td>
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<tr>
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<td>Ti2O3</td>
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<td>456.7</td>
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<td>456.4</td>
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<td>O₂/Si or SiO₂</td>
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<td>52.7</td>
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<tr>
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<td>52.7</td>
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<tr>
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<td>TiON or SiO₂</td>
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<td>532.3</td>
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</table>
8.3.4 Solar Selectivity Sputtered TiAlSiN Thin Films at Various Annealing Temperatures

The UV-Vis reflectance spectra of the TiAlSiN coatings before annealing and after being annealed at 500-800 °C in steps of 100 °C are demonstrated in Fig. 51. In the visible spectrum range, the solar absorptance, $\alpha$ of these coatings was estimated by the Duffie and Beckman method [452]. In the Duffie-Beckman method, the estimated solar absorptance is an average value calculated from 20 values corresponding to the solar spectrum range between 190 nm and 2500 nm.

![UV-Vis reflectance spectra of sputtered TiAlSiN coatings before annealing and after being annealed at 500-800 °C in steps of 100 °C.](image)

**Figure 51.** UV-Vis reflectance spectra of sputtered TiAlSiN coatings before annealing and after being annealed at 500-800 °C in steps of 100 °C.

The UV-Vis spectra reveals that all of the films demonstrate moderate reflectance up to 60 % to UV light, high absorptance above 90 % in the visible spectrum and exceptionally high reflectance (>98 %) in the infrared-far-infrared region of the solar spectrum. In the 400-650 nm range, all of the coatings display sharp absorption edges. It was also seen that the reflectivity of the coatings is decreased systematically as the annealing reaches up to 700 °C and then increased at 800 °C. Above the visible range, the reflectance was enhanced gradually over the infrared range up to 2500 nm. The highest absorption of solar radiation was documented in the visible spectrum and the lowest absorptance in the infrared region. Similar absorptance features on TiN-based sputtered coatings were reported by Brogren *et al.* [482]. The high absorptance of the coating makes it an ideal candidate for selective solar surfaces to be used in the solar thermal collectors. The
increase in solar absorption at high temperature annealing may be also associated with the gradual increase in the refractive index of the films from the surface to the substrate. In the case of single layered films on steel substrates, we achieved the highest solar absorptance of just over 84% and we believe that this can be substantially enhanced by designing multilayered transition metal nitride coatings. The addition of an antireflection layer on the top of film surface can also increase the light absorption ability of these coatings.

The FTIR reflectance spectra of the TiAlSiN thin film coatings before annealing and after annealing are demonstrated in Fig. 5.2. The solar absorptance, emittance and their before and after annealing are shown in Table 26.

![FTIR reflectance spectra](image)

**Figure 52.** FTIR reflectance spectra of sputtered TiAlSiN coatings before annealing and after being annealed at 500-800 °C in steps of 100 °C.

The results show the thermal emittance of the coatings decrease with the rise in annealing temperatures up to 600 °C while a significant declination of emittance was recorded for the coatings annealed at 700 and 800 °C. The absorptance values of the coatings were found to be increasing up to 700 °C while the emittance values were decreasing until 600 °C. Accordingly, the coatings have very high thermal stability in air up to 600 °C together with a high solar selectivity value of 24.63. (See Table 27). The high thermal stability of these coatings in air up to 600 °C is due to several factors. Firstly, TiAlN works as a diffusion hurdle for steel. The formation of various metal oxides and nitrides phases (e.g., Ti$_2$O$_3$, Al$_2$TiO$_5$, TiN, AlN, and Si$_3$N$_4$ as seen in XPS results) at high
temperatures conveniently stops the diffusion pathways for steel and thus acts as ideal diffusion barrier [483]. Thermal emittance is dependent on the surface oxide layers of these coatings. Higher infrared reflectivity of aluminium contributes to strengthen the oxidation behaviour of Al as observed around the Al2p spectrum. TiON with a stable phase and a very high melting point also acts as a diffusion barrier. In view of the above features, the TiAlSiN sputtered coatings display good thermal stability and preserve their optical properties even at higher annealing temperatures. At the same time, other factors such as the microstructure and the surface roughness of the films also influence the scattering, and the reflection of light. As annealing progresses from 600 °C to 800 °C, the emittance values decline because of the formation of the thick surface oxide layers that result in high infrared reflectivity [453].

**Table 26.** Solar absorptance and thermal emittance of sputtered TiAlSiN coatings before annealing and annealed at 500, 600, 700, and 800 °C.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Solar absorptance, ( \alpha ) before annealing</th>
<th>Solar absorptance, ( \alpha ) after annealing</th>
<th>( \Delta \alpha )</th>
<th>Thermal emittance, ( \varepsilon ) before annealing</th>
<th>Thermal emittance, ( \varepsilon ) after annealing</th>
<th>( \Delta \varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.810</td>
<td>0.822</td>
<td>+0.012</td>
<td>0.0358</td>
<td>0.0344</td>
<td>+0.0014</td>
</tr>
<tr>
<td>600</td>
<td>0.830</td>
<td>0.830</td>
<td>+0.020</td>
<td>0.0337</td>
<td>0.0337</td>
<td>+0.0021</td>
</tr>
<tr>
<td>700</td>
<td>0.844</td>
<td>0.844</td>
<td>+0.034</td>
<td>0.0488</td>
<td>0.0488</td>
<td>-0.0130</td>
</tr>
<tr>
<td>800</td>
<td>0.798</td>
<td>0.798</td>
<td>-0.012</td>
<td>0.0528</td>
<td>0.0528</td>
<td>-0.0170</td>
</tr>
</tbody>
</table>

**Table 27.** Solar selectivity of sputtered TiAlSiN coatings before annealing and annealed at 500, 600, 700, and 800 °C.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Solar absorptance, ( \alpha )</th>
<th>Thermal emittance, ( \varepsilon )</th>
<th>Solar selectivity, ( s = \alpha /\varepsilon )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before annealing</td>
<td>0.810</td>
<td>0.0358</td>
<td>22.63</td>
</tr>
<tr>
<td>500</td>
<td>0.822</td>
<td>0.0344</td>
<td>23.90</td>
</tr>
<tr>
<td>600</td>
<td>0.830</td>
<td>0.0337</td>
<td>24.63</td>
</tr>
<tr>
<td>700</td>
<td>0.844</td>
<td>0.0488</td>
<td>17.30</td>
</tr>
<tr>
<td>800</td>
<td>0.798</td>
<td>0.0528</td>
<td>15.11</td>
</tr>
</tbody>
</table>

The \( \alpha/\varepsilon \) ratio is known as the solar selectivity, \( s \). It characterizes the spectral features of a selective solar surface and is used in many solar thermal collector devices. The solar selectivity values of our coatings before and after annealing at various temperatures are set out in Table 27. The solar selectivity of TiAlSiN coatings is enriched significantly with the increase in annealing temperature up to 600 °C. The solar selectivity values of these coatings depend on a number of factors such as the thicknesses of the films, their
structure, chemical compositions, relative content of individual phases, materials used, processing techniques, processing conditions, and the reflective nature of the substrate used. Thus, high temperature annealing effectively helps the formation of stable multiple crystalline and non-crystalline structures as seen in SR-XRD and XPS studies, stable chemical bonding states (as observed in XPS results) and thereby enhances the solar selectivity of these films. Moreover, the variation in structural morphology and elemental compositions might also help the surface roughness of the films to enhance their selectivity values. Consequently, the overall solar selectivity of these coatings is boosted up to annealing of 600 °C.
8.3.5  *In Situ* Synchrotron Radiation X-ray Diffraction (SR-XRD) Analysis

The TiAlSiN sputtered coatings were analysed by SR-XDR from room temperature then 500-800 °C in steps of 100 °C. The scan diffraction angle was between $2\theta = 15^\circ$ and $35^\circ$. The SR-XRD analysis results are presented in Fig. 53.

![Figure 53. Synchrotron radiation X-ray diffraction data of TiAlSiN thin film coatings at different temperatures acquired in the powder diffraction beamline at Australian synchrotron, Melbourne.](image)

Figure 53. Synchrotron radiation X-ray diffraction data of TiAlSiN thin film coatings at different temperatures acquired in the powder diffraction beamline at Australian synchrotron, Melbourne.

As seen in Fig. 53, there is no apparent change in the patterns from room temperature up to 600 °C. However from 700 °C between $2\theta = 22$ and $35^\circ$, new peaks appear and some peaks disappear. Furthermore, the intensities of the peaks were also modified and peak widths were decreased. Gradual sharp and insignificant shifting of the peak positions at higher annealing temperatures indicate the formation of stable microstructures resulting from isostructural decomposition to form Ti-rich, Al-rich and Si-rich phases via spinodal decompositions [484, 485]. This also demonstrates the fact that TiAlSiN coatings retain decent structural and chemical stability within the operating temperature up to 800 °C. Analysis of the SR-XRD data established that the sputtered TiAlSiN coatings were made up of crystalline TiN, AlN, $\text{Si}_3\text{N}_4$, $\text{Al}_2\text{O}_3$, and Fe (substrate) phases. The $2\theta$ positions,
crystal phases, Miller indices and space groups of sputtered TiAlSiN coatings from SR-XRD are set out in Table 28. The 2θ positions of the existing phases are very close to each other at all temperatures. The formations of h-AlN and h-Si$_3$N$_4$ phases are evidence of the spinodal decomposition of these coatings. This spinodal decomposition [442] is responsible for the grain refinement and modifications of microstresses within AlN and Si$_3$N$_4$ domains. The modification of peak intensities suggests that a higher degree of crystallinity is achieved when the films are annealed at high temperatures. At 800 °C two of the Fe based peaks (due to the substrate) disappear indicating that a phase transition has occurred in the substrate. This is not unexpected as the Fe phase diagrams show phase changes above 600 °C.

Generally the formation of an Al$_2$O$_3$ layer on the surface of coatings prevents the penetration of oxygen into the specimen as temperature is raised, thereby increasing the crystal stability at high temperature working environments [486]. These features are also associated with the difference in atomic radii of the constituent elements together with the bond coordination, and the preferred crystallographic network of the films. The compact Al$_2$O$_3$ layer obstructs the inward diffusion of oxygen and the outward diffusion of Ti, Al and Si and thereby improves the oxidation resistance of TiAlSiN coatings. According to Chen et al. [487], in TiN and TiAlN coatings surface oxidations were detected at 700 and 800 °C and the substrate started to oxidize at 800 and 900 °C respectively. However, TiAlSiN coatings can prevent oxidization up to 900 °C. This is probably due to the formation of thin dense oxide layers around the surfaces of the films that protects them from being further oxidized. The influence of temperature is not only related to the formation of stable phases and oxygen contamination but also to the morphology and growth mode of the films that it also affects the solar selectivity of the films.
Table 28. 2θ Positions, crystal phases, Miller indices and space groups of sputtered TiAlSiN coatings as observed from synchrotron radiation X-ray diffraction (SR-XRD) studies.

<table>
<thead>
<tr>
<th>2θ position at room temperature</th>
<th>2θ position at 500°C</th>
<th>2θ position at 600°C</th>
<th>2θ position at 700°C</th>
<th>2θ position at 800°C</th>
<th>Crystal structure</th>
<th>Miller Index</th>
<th>Space group</th>
<th>JCPDS reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.33 (A)</td>
<td>19.35</td>
<td>19.32</td>
<td>19.32</td>
<td>19.30</td>
<td>TiN$_{0.6}$/Tetragonal</td>
<td>(112)</td>
<td>I4$_1$/amd(141)</td>
<td>76-1834</td>
</tr>
<tr>
<td>20.18 (C)</td>
<td>20.20</td>
<td>20.19</td>
<td>20.18</td>
<td>20.21</td>
<td></td>
<td>(103)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.09 (G)</td>
<td>26.10</td>
<td>26.11</td>
<td>26.13</td>
<td>26.09</td>
<td></td>
<td>(211)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.14 (I)</td>
<td>33.12</td>
<td>33.10</td>
<td>33.10</td>
<td>33.10</td>
<td></td>
<td>(220)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.55 (B)</td>
<td>19.58</td>
<td>19.54</td>
<td>19.52</td>
<td>19.51</td>
<td>TiN/Cubic</td>
<td>(111)</td>
<td>Fm-3m(225)</td>
<td>87-0633</td>
</tr>
<tr>
<td>22.26 (D)</td>
<td>22.28</td>
<td>22.28</td>
<td>22.26</td>
<td>22.25</td>
<td></td>
<td>(200)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.18 (H)</td>
<td>32.22</td>
<td>32.18</td>
<td>32.15</td>
<td>32.16</td>
<td></td>
<td>(222)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.33 (A)</td>
<td>19.34</td>
<td>19.33</td>
<td>19.32</td>
<td>19.30</td>
<td>AlN/Hexagonal</td>
<td>(002)</td>
<td>P6$_3$mc(186)</td>
<td>88-2360</td>
</tr>
<tr>
<td>20.18 (C)</td>
<td>20.18</td>
<td>20.19</td>
<td>20.20</td>
<td>20.18</td>
<td></td>
<td>(101)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.33 (A)</td>
<td>19.32</td>
<td>19.33</td>
<td>19.34</td>
<td>19.33</td>
<td>Si$_3$N$_4$/Hexagonal</td>
<td>(120)</td>
<td>P6$_3$(173)</td>
<td>82-0705</td>
</tr>
<tr>
<td>21.08 (B)</td>
<td>21.09</td>
<td>21.08</td>
<td>21.10</td>
<td>21.10</td>
<td></td>
<td>(310)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.09 (G)</td>
<td>26.09</td>
<td>26.08</td>
<td>26.11</td>
<td>26.12</td>
<td></td>
<td>(111)</td>
<td>P6$_3$(173)</td>
<td>82-0705</td>
</tr>
<tr>
<td>19.33 (A)</td>
<td>19.34</td>
<td>19.35</td>
<td>19.32</td>
<td>19.30</td>
<td>Al$_2$O$_3$/Rhombohedral</td>
<td>(104)</td>
<td>R-3c(167)</td>
<td>88-0826</td>
</tr>
<tr>
<td>22.59 (E)</td>
<td>22.58</td>
<td>22.57</td>
<td>22.55</td>
<td>22.55</td>
<td></td>
<td>(113)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.26 (F)</td>
<td>23.25</td>
<td>23.25</td>
<td>23.23</td>
<td>23.20</td>
<td>Fe/Cubic</td>
<td>(110)</td>
<td>Im-3m(229)</td>
<td>85-1410</td>
</tr>
<tr>
<td>33.14 (I)</td>
<td>33.13</td>
<td>33.12</td>
<td>33.10</td>
<td>33.10</td>
<td></td>
<td>(211)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Data from XRD are from the bulk substrate/film as the x-rays penetrate through thickness of many micrometers (μm) while the XPS data is from penetration of only a few nanometres (nm). At 800 °C, combining the XPS and XRD results together, it is certain that the top layer of the sample consists of Ti and Al oxides and no nitrides while the rest of the film consists of Ti, Al and Si oxides and nitrides. Fig. 54 is a schematic diagram showing the general region of the oxide and nitride phases at this temperature. At temperatures below 800 °C the entire thin film consists of oxide and nitride phases as listed in Table 25 and Table 28.
Figure 54. Schematic diagram of XPS and XRD penetration region on samples at 800 °C. Also shown is the general type of phase compositions [488].

8.4 Conclusions

State-of-the-art magnetron sputtered TiAlSiN thin films, on a M2 steel substrate, were investigated, before and after annealing over temperature range of 500 °C to 800 °C, for their structural, microstructural morphology, mechanical properties, surface chemical bonding states and solar selective behaviours. Images from SEM analysis show nanolayers forming dense and closely packed structures with amorphous grain boundaries. Increasing annealing temperature results in higher surface roughness of the thin films. These indicate the sputtered films have good stability and increased reliability than similar coatings with large columns and open pores. Mechanical studies show a decrease of hardness, Young’s modulus, plastic deformation and constant yield strength, in the above temperature range, for the coatings. These displayed good wear resistance which is dependent on better oxidation and thermal stability initiated from amorphous boundaries to slow down the interface reaction and recrystallization in the annealing cycle. No significant changes in the binding energies of the Ti2p, Al2p, Si2p, N1s and O1s photoelectron lines were detected from the XPS studies of the films. The XPS results indicate mixed Ti, Al and Si nitrides and oxides as main film components but at 800 °C the top layer, of the thin film, is clearly composed of Ti and Al oxides. The solar selectivity increased a maximum of 24.6, at 600 °C, and then substantially decreased at higher temperatures due to formation of oxide phases at the top layer of the thin film coatings. This is in accordance with the general rule that solar selective coatings are
affected by the stoichiometric compositions, and the annealing temperature. XRD analysis showed various Ti, Al and Si nitride and oxide phases, for the above annealing temperature range, with isostructural development of cubic Ti-rich, Al-rich and Si-rich domains. From 700 °C there are strong indications that a phase change is occurring with the Fe component in the substrate. Transition metal nitride based materials exhibited a variety of interesting structural, mechanical and optical properties and are expected to play growing roles in energy related applications, such as solar energy harnessing as solar selective surface. The XPS results obtained from the coating surface can not reveal the composition inside the coatings because; high temperature annealing was in air atmosphere, whereas oxygen is more prominent at the surface. Depth profile studies along the film thickness direction, will afford better understanding of the oxidation mechanisms as well as the possible diffusion and distribution of different elements of the sputtered coatings. The studies may even clarify any phase changes occurring in the substrate.
CHAPTER NINE: MECHANICAL CHARACTERISTICS AND NEAR-EDGE ABSORPTION STRUCTURES OF SPUTTERED Cr$_{1-x}$M$_x$N COATINGS

9.1 Introduction

Over the past decade, scientists and engineers around the world have shown significant interest in the investigations of metallic nitrides (e.g., GaN, AlN, InN, CrN, TiN [59-63]) with dopants such as Si [59], Al [64], Mn, C [64] and Cr [61-63] owing to their unique properties, e.g., large band-gap [60, 65-67], high surface acoustic velocity [60], corrosion resistance [60], oxidation resistance [68], excellent chemical and thermal stability as well as mechanical robustness. Recently, superhardness (hardness, or H > 40 GPa) has been obtained in TiN, and CrN by Si doping [288, 489, 490]. It is believed that the addition of Si changes the microstructures of the binary compounds from closely-packed columnar grains into nanocrystalline structures integrated in a Si$_3$N$_4$ amorphous matrix [288, 489]. Superhardness has also been reported in CrN with a suitable amount of Al-doping [281]. Al atoms are found to be segregated around the grain boundaries to form an amorphous AlN structure. The measured superhardness of CrSiN and CrAlN is due to the combination of the fine grain size together with a strong interfacial bonding between the nanocrystalline and amorphous structures. It is well-established that the hardness of CrN coatings is mainly governed by grain size and boundary structure [278]. Generally, the hardness of a material increases with a decrease in its grain size [280]. With infusion of Si, Al or Ti into CrN, the grain size within the material has been found to reduce to a nanoscale that results in an increase in hardness of the coating [281]. At nanoscale grains, the formation of dislocations becomes tough and the hardness of the coatings can be controlled by changing the grains size [277]. Recently, a high resolution transmission electron microscopy (HRTEM) study showed that Cr$_{1-x}$M$_x$N coatings consist of nanocrystalline grains surrounded by amorphous boundaries [283]. The impact of these amorphous boundaries on the material hardness has yet to be studied. Thus, it is important to tailor the structure of the amorphous boundary for enhancement of coating properties.

Introduction of a suitable amount of dopant has been found to enhance the physical properties by inducing various defects such as vacancy, atom substitution, cluster formation and deformation [64]. X-ray absorption near-edge structure (XANES) has been previously used to study the structural properties of Al-incorporated titanium nitride
In this study, the bonding structural evolution of the TiN thin films with an increase in Al-addition was discussed and the spectral changes were correlated and ultimately afforded a complete understanding about the local atomic structure. Meanwhile, attempts at producing new doping materials and research on improving their novel properties are still ongoing [491]. More recently, carbon doping on CrAlN has been performed by Zeng et al. [64] to study the effect of the dopant on a material’s electromagnetic properties. At the end of their investigations, authors concluded that carbon-doped dispersed clusters enhanced resistivity at the low frequency while high rate of carbon doping induced disorder, thereby resulting in weakened magnetic coupling [64]. Hirai et al. [492, 493] reported that, above 75 at.% of Cr-doping, AlN thin films demonstrate a structural phase transition from rock salt crystalline phase to a wurtzite structure.

During the period of volcanic eruption in Chile in 2011, planes were grounded all over Australia, which prompted scientists and technologists to design and test novel coatings that can prevent mechanical damage to jet engines due to intrusion of volcanic ash [494]. Chromium nitride (CrN) is a prominent material which can be engineered onto the surface of metals as a protective layer to enhance mechanical performances and durability of coated metals [495]. Even though CrN has been found to show good wear and corrosion resistance, nonetheless the extension of such coatings is hindered by its relatively low hardness and poor oxidation resistance nature [496]. Moreover, the oxidation resistance of materials at high temperatures is typically controlled by surface chemistry and the construction of grain boundaries [497]. In Cr$_{1-x}$M$_x$N coatings, native oxide layers are generally formed on the surface of the coatings [285], leading to a substantial increase in their heat-resistance. Addition of Si, Al or Ti generally hinders the penetration of oxygen along the grain boundaries which may diminish the hardness of the coatings. Thus, a detailed study of the structural and compositional characteristics of the oxide layer will provide us with more information pertaining to the impact on Cr$_{1-x}$M$_x$N coatings.

Over the past decades, scientists have used the synchrotron radiation facilities to characterize the electronic structure of homogeneous alloys in virgin and doped states. Owing to the unique advantages of synchrotron radiation facilities such as polarization control, coherence, high brightness and photon-energy tunability, they are widely used in the identification of the atoms, molecules and compounds [498]. Up to the 1990s, the extended X-ray absorption fine structure (EXAFS) spectroscopy has received more
attention than NEXAFS due to the correlation between EXAFS oscillations and the local crystallographic structure about the central excited atom [499]. It has been well-established that in the range of 30-50 eV above the absorption edge of NEXAFS and EXAFS, regions match nicely. Since then, the development and utilization of EXAFS have made great strides in the understanding of near-edge structure of molecules, ordered and disordered solids, inorganic complexes and biological systems [394]. Generally, XANES technique is used for the structural investigations of solids and inorganic complexes while NEXAFS is employed more for surface studies. NEXAFS technology is widely used in understanding complex systems and identifying the co-existence of various phases either in ordered (crystalline) or in disordered (amorphous) form. In previous investigations [68], it was observed that the addition of silicon could remarkably improve physical hardness of the material such as toughness, as well as oxidation resistance. As the silicon content increased, the sample was found to ‘lose’ its crystallinity by exhibiting peak broadening. Furthermore, it was noticed that silicon appeared in the form of silicon nitride with the addition of 9 to 14 at.% of silicon, (Si3N4) [59].

Electronic structures of nitride based materials can be successfully studied through various techniques e.g., X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES). XAS and XES techniques probe the unoccupied and occupied densities of states of a material on an element and orbital angular momentum based dipole selection rules [60]. NEXAFS spectroscopy essentially provides a unique opportunity to probe differences in the electronic structure as the composition of transition metal nitride (CrN) changes as seen in shifts in the Al K-, Cr L-, and Si K-edge absorption energies. Here we will focus on establishing the bonding structural evolution in Cr1-xMxN upon progressive incorporation of Al and Si. The effects of aluminum and silicon doping to CrN from 14.3 to 28.5 at.%% have been investigated by measuring the Al K-, Cr L-, and Si K-edge NEXAFS spectra using the Synchrotron radiation. This study aims to gain novel insights into the roles of dopants (Si, Al) in tailoring the structure of the grain boundary within Cr1-xMxN coatings through NEXAFS experiments, as well as the surface chemistry of the oxide layer. The results will lead to the development of extremely hard, oxidation-resistant coatings by means of surface and grain boundary engineering.
9.2 Experimental Details

9.2.1 Specimen Preparation Technology

Aluminum and silicon-doped chromium nitrides with the composition Cr$_{1-x}$M$_x$N, where M is Al and Si, and x was varied from 14.3 to 28.5 at.% had been coated on AISI M2 tool steel substrates at the City University of Hong Kong using a TEER UDP 650/4 closed field unbalanced magnetron sputtering system. A four-target configuration manufactured by Teer Coatings Ltd., Droitwich, Worcestershire, UK, had been used for this purpose. Low, medium and high amounts of doping had been added to all the samples. In addition, the reference samples of CrN, AlN, Si$_3$N$_4$ were prepared as well. Surfaces of samples were mechanically cleaned in ultra-high vacuum by means of a diamond needle file and tungsten-wire brush. Special care has been taken in ultrasonic cleaning of the samples for NEXAFS study. Table 29 indicates the at.% of Al/Si content as of low, medium and high doping elements in CrN coatings.

**Table 29.** Chemical compositions of Cr$_{1-x}$M$_x$N with different Al/Si contents.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Amount of Al/Si</th>
<th>At% ration of Al/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_{1-x}$M$_x$N</td>
<td>Low</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>28.5</td>
</tr>
</tbody>
</table>

9.2.2 Structural Characterization of CrAlN and CrSiN Thin Film Coatings

Structural characterizations of CrSiN and CrAlN films has been previously performed by means of cross-sectional bright field TEM (XTEM), high resolution X-ray photoelectron spectroscopy (HRXPS), XRD and nanoindentation techniques. The XTEM method was used to observe the factors influencing the mechanical properties of CrSiN coatings with the progressive addition of Si-content while XPS and nanoindentation methods elucidated the surface chemical composition and physical hardness, elastic modulus and residual stress, respectively. Grazing incidence X-ray diffraction (GIXRD) patterns of CrN coatings had been reported to be unaffected with the Al-doping [286]. Undoped samples and samples doped with low, medium and high amounts of Al were identified to be cubic structure; however, other studies reported the existence of wurtzite structure of CrN with Al-doping. XPS study [286] found the existence of an amorphous phase of AlN at the grain boundaries. Preferred orientations have been found to be altered by the Al-substitutions. According to the GIXRD data, it had been observed that (200) preferred
orientation was reduced monotonically with the increase in Al-content while a linear increase in the intensity was observed on (111) and (220) reflection planes.

9.2.3 Hardness Test of CrAlN and CrSiN Coatings

In the past few years, CrNs have been widely studied owing to their good combination of mechanical and thermal properties in comparison with other transition metal nitrides [500-502]. Transition metal nitrides (i.e., CrN, TiN etc) have been found to show superhardness (hardness > 40 GPa) with suitable doping (i.e., Si, Al etc.) [286, 288, 489, 490]. The Si or Al dopant significantly modifies the microstructures of the binary compounds from closely-packed columnar grains into nanocrystalline structures embedded in an amorphous matrix [286, 489]. In addition to the exceptionally high hardness, improved oxidation resistance and higher thermal stability of binary CrN coatings were also reported [503, 504]. The mechanical properties of CrAlN and CrSiN sputtered coatings have been carried out via nanoindentation system equipped with a Berkovich indenter (Ultra-Micro Indentation System 2000) that measures the hardness and elastic modulus of the films via Oliver-Pharr method [403]. In order to minimize the substrate effect, a maximum load of 5 mN was applied and indentation depths smaller than 10% of the coating thickness were confirmed. Twenty indentations (20 incremental and 20 decremental) were conducted on each of the samples. Prior to the measurements, the area function of the indenter tip was calibrated using a standard fused silica specimen.

9.2.4 Synchrotron Radiation Near-edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

NEXAFS measurements of the coatings were performed using the soft X-ray spectroscopy at the Australian Synchrotron facility based in Melbourne. The storage ring was operated at 3 GeV. In the top-up mode operation, the beam current was 200 ± 1 mA. A collimated light plane grating monochromator (SX700), with a grating of 1200 lines/mm was used to monochromatize the X-ray beam coming out of the storage ring. A minimum pressure of 1×10⁻⁷ Pa was maintained in the analysis chamber throughout the NEXAFS measurements. The hemispherical analyzer is mounted in the horizontal plane at a glancing incidence of 55° (the magic angle [398]) with the X-ray beam (the magic angle is to do with the photoemission and the asymmetry parameter which becomes zero for all electron energy orbital quantum numbers e.g., 2p3/2, 4f7/2 etc.). NEXAFS spectra were collected at Si K-edge (1820-1920 eV), Al K-edge (1520-1620 eV) as well as Cr L-
edge (670–730eV) by using the Auger electron yield (AEY) and total fluorescence yield (TFY) modes. Electrons strongly interact with matter, as the incidence X-rays pass into the sample, electrons will be generated throughout the depth of the material, however only those electrons generated close to the sample surface can escape and be detected. Hence electron yield methods are always strongly surface sensitive. The fluorescence yield, likewise to the electron emission will be generated throughout the depth of the material, but as these fluorescent X-rays pass relatively easily through matter the sampling depth is always much deeper than that of electron yield methods. The fluorescent yield signal is therefore indicative of the bulk of the samples are always free of artifacts produced by self-absorption however this is not always the case for fluorescent yield. AEY investigated the surface oxide layer and probed the interaction of oxides with underlying materials while the TFY revealed the bulk structure of materials e.g., chemical bonding at the grain boundary. The spectra obtained in AEY and TFY were normalized with respect to the incidental photon flux. This has been accomplished by dividing the samples signal $I_{\text{sample}}$ by the incident photon flux $I_0$. Since the grain boundaries are amorphous in nature, it was believed that TFY and AEY of metal K-edges in the grain boundaries might be shifted or broadened with the enhancement of dopant concentrations. The shifts have been compared with the reference materials spectra. In this study, NEXAFS measurements were performed by AEY mode and TFY mode with a channeltron facing sample positioned 30° above the incoming beam. All the samples were well grounded and mounted on adhesive carbon tapes to avoid the surface charging. Prior to analysis the NEXAFS spectra were normalized to the primary beam current.

9.3 Results

9.3.1 Mechanical Properties of the CrAlN and CrSiN Coatings

The mechanical properties such as hardness, elastic modulus, yield strength and plastic deformation parameter of CrN coatings doped with low, medium and high amount of Al and Si-contents are recorded in Table 30. From Table 30, it is clearly seen that in the case of CrAlN coatings, both the hardness and young’s modulus of the coatings were found to be increased linearly with subsequent addition of Al to the binary CrN system. Similar features were recorded for the yield strength and plastic deformation factors as well. However, in the case of CrSiN coatings highest hardness and elastic modulus values were recorded for coating doped with medium amount of Si while the hardness was reduced as the silicon content in the films was increased to 28.5 at.%. The yield strength and plastic
deformation ratio were found to follow the same trend. It is believed that the Si or Al dopant significantly modifies the microstructures of the binary compounds from closely-packed columnar grains into nanocrystalline structures embedded in an amorphous matrix [288, 489]. Compressive residual stress of CrN coatings is increased about ~52% with the increase of Al-dopant up to ~28.5 at.%. In a similar fashion, the mechanical hardness and Young’s modulus of the CrN thin film coatings have been noticed to increase ~48% and ~16% respectively with the addition of ~28.5 at.% of Al-content [286]. Furthermore, the yield strength, \( \frac{H}{E} \) [505] and plastic deformation factor, \( \frac{H^3}{E^2} \) [506] increase ~29% and ~140% respectively with the highest amount Al-doping to the binary CrN coatings reflecting a potential increase in the wear resistance. Al atoms are assumed to be segregated around the grain boundaries to form an amorphous AlN structure. In the case of CrSiN coatings, the hardness reduction might be associated with occurrence of high volume fraction of amorphous Si\(_3\)N\(_4\) phase segregated around the grain boundaries. A combination of good hardness and good elastic modulus in CrN with Si and Al substitutions reveal the combination of the fine-grain size together with the strong interfacial bonding between the nanocrystalline and amorphous phases.

**Table 30.** Mechanical properties of Cr\(_{1-x}\)M\(_x\)N sputtered coatings with different Al/Si contents.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Amount of Al/Si</th>
<th>Hardness, ( H ) (GPa)</th>
<th>Young’s modulus, ( E ) (GPa)</th>
<th>Yield strength, ( \frac{H}{E} )</th>
<th>Plastic deformation factor, ( \frac{H^3}{E^2} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(_{1-x})Al(_x)N</td>
<td>Low</td>
<td>35.3</td>
<td>401.2</td>
<td>0.087</td>
<td>0.273</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>38.9</td>
<td>421.3</td>
<td>0.092</td>
<td>0.331</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>42.3</td>
<td>438.3</td>
<td>0.097</td>
<td>0.393</td>
</tr>
<tr>
<td>Cr(_{1-x})Si(_x)N</td>
<td>Low</td>
<td>32.3</td>
<td>370.2</td>
<td>0.087</td>
<td>0.246</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>35.6</td>
<td>398.1</td>
<td>0.089</td>
<td>0.285</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>25.3</td>
<td>348.3</td>
<td>0.073</td>
<td>0.133</td>
</tr>
</tbody>
</table>

### 9.3.2 NEXAFS Spectra at Cr L-edge of CrAlN and CrSiN Coatings

Figs. 55 to 58 show the NEXAFS spectra of Cr L-edge for CrAlN and CrSiN samples doped with low, medium and high at.% of Al and Si as well as a reference CrN sample for comparison in the AEY and TFY modes. All the AEY and TFY spectra for both samples are of similar trend. The local environments of Cr are of similar type with the subsequent doping of either Al or Si to the CrN reference sample. For the TFY spectra of
CrSiN sample, first peak observed around $572\pm 1$ eV can be assigned to a transition from Cr1$s$ core state to the Cr3$d$ states. This peak is observed in all the compositions that reveal the fact that the local structures surround Cr atoms are $C_{3v}$ symmetry [63]. In an earlier XANES study [63], a peak in AlCrN sample has been found to split into two parts: one corresponding to the non-bonding level while the other to the anti-bonding level with a splitting range of 1.5 eV consistent with the first-principle calculations [507]. However, this splitting has not been observed in our experiment.

**Figure 55.** NEXAFS spectra of Cr $L$-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in AEY mode with progressive addition of Al-content.

**Figure 56.** NEXAFS spectra of Cr $L$-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in TFY mode with progressive addition of Al-content.
Figure 57. NEXAFS spectra of Cr $L$-edge of Cr$_x$Si$_{1-x}$N coatings and CrN reference sample in AEY mode with progressive addition of Si-content.

Figure 58. NEXAFS spectra of Cr $L$-edge of Cr$_x$Si$_{1-x}$N coatings and CrN reference sample in TFY mode with progressive addition of Si-content.

For TFY spectra of both samples, a tiny peak assigned at ~575 eV arises due to the transitions from the Cr1$s$ state to the anti-bonding state resulting from hybridizing between the Cr4$s$ and the N2$s$ states. This hybridization can also be considered as the partial mixing of the N2$p$ state because less intensity relative to the peak is observed at ~573.9 eV. The shift of the peak at lower intensity might be related to the increase in lattice constants of the samples [398]. From a comparison of AEY and TFY spectra, it
has been seen that the first spectrum in TFY mode is marginally shifted towards a lower energy position. In TFY mode, a small peak is observed to be followed by the first spectrum. However, in both modes, all the second peaks correspond at ~584.5 eV.

However, in both modes, all the second peaks correspond at ~584.5 eV. Intensities of the peaks observed at either ~577.2 eV or ~584.5 eV do not show substantial changes with the addition of Al or Si content to the CrN coatings. This feature again confirms the uniqueness of the local environments of Al and Si in the CrN sample. It is well-established that the L-edges spectra for transition metal compounds with unfilled $d$-shells can be described on the basis of multiplet and crystal field transitions from $2p^6d^n$ to $2p^5d^{n+1}$ state for an appropriate site symmetry determined by ligands [508]. Multiplet calculations for Cr ligand formed with oxygen and other transition metals in typical bonding environments are available in the literature [509-511]. These reports show the sensitivity of L-edge spectra to the oxidation state and local symmetry of the metal.

Localized excitations at Cr L-edges arise from ligand field splitting of Cr$^{3+}$d levels. As shown in Figs. 55-58, Cr L-edge absorption in AEY mode is much stronger than that in TFY mode. This feature can be attributed to the fact that the fluorescence yield in Cr L-shell decay is much lower than the corresponding Auger yield due to larger efficiency of the Auger decay process [512]. For CrAlN and CrSiN samples, in AEY mode, features observed at 577.2 eV and 584.5 eV of Cr L-edge spectrum are very similar to that of Cr$_2$O$_3$ according to the earlier investigations [512]. Both in AEY and TFY modes, it is also noticed that two principal peaks are separated by a few electron volts (from ~7.5 to ~10 eV) with additional structures. These additional fine structures might result from the multiplet effects arising from an addition of an extra electron to the $3d^3$ configuration.

The separation energy between the two main peaks is comparable to the width of the valence band [512]. Even though the experimental pin-point of Cr$^{3+}$d states is difficult, however, comparison to band structure calculations suggest that Cr$^{3+}$d states straddle most of the valence band and hybridize strongly with the O$2p$ states at the bottom of the valence band [512]. It is also assumed that the scattering at the Cr L-edge results in excitation of $3d \rightarrow 3d$ transitions arising from the ligand field splitting of the Cr$^{3+}$d states.

### 9.3.3 NEXAFS Spectra at Al K-edge of CrAlN Coatings

The Al K-edge NEXAFS spectra of CrAlN with low, medium and high at.% of Al-content and Al reference sample in AEY and TFY modes are displayed in Figs. 59 and 60, respectively. For the NEXAFS spectra of all the CrAlN samples, it is clear that all the
curves have the same trend confirming that the local environments of Al remain unchanged in this sample. This means that the local environments of Al are independent of the composition. The intensities of the peaks have been found to increase markedly with the increase in Al percentage in the coatings.

Figure 59. NEXAFS spectra of Al K-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in AEY mode with progressive addition of Al-content.

Figure 60. NEXAFS spectra of Al K-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in TFY mode with progressive addition of Al-content.
By comparing the NEXAFS data of CrAlN with that of the reference AlN in both modes, it is noticed that the edges (~1556.7 eV), tiny peak (at ~1560.1 eV) and central peak with maximum intensity (at ~1565.5 eV) and peaks at ~1568.6 eV and ~1584.6 eV are overlapped. This reflects the existence of AlN in CrAlN samples with the progressive addition of Al-content. The peak observed at ~1560.1 eV is weak, possibly due to the result of dipole forbidden 1s→a_1 (3s like) transition. The major peaks seen at ~1565.5 eV could be assigned to the allowed transition of Al1s electrons to the antibonding t_2 (3p like) transition while the peaks at ~1576.6 eV and ~1613 eV are related to the transitions of Al1s electrons to the e and t_2 (3d like) states, respectively. These peaks are known as the symmetry forbidden shape resonances [513, 514]. On the other hand, peaks at ~1568.6 eV and ~1584.6 eV might correspond to multiple scattering from more distant shell atoms [515]. The increase of intensity of Al K-edge with the progressive addition of Al-doping can be explained on the basis of the increase in coordination of Al, increase in effective charge on Al atoms and weaker Al-O bonding [516]. Barcroft et al. [516] also reported that addition of Al would increase intensity of the Al K-edge with an increase in Al-content, which is related to the increase in Al-content to the respective octahedral and tetrahedral sites. The increase of intensity also supports the fact that the absorption coefficient is proportional to the number of absorbing atoms as well as the absorption cross-section.

9.3.4 NEXAFS Spectra at Si K-edge of CrSiN coatings

Figs. 61 and 62 show the NEXAFS spectra around Si K-edge of CrSiN samples with different Si-content as well as an amorphous reference sample of Si_3N_4 for comparison in AEY and TFY modes. It is obvious that no significant changes in the spectral lineshape as a function of silicon content from low to high at.% indicating that the local environment of Si remains invariant in this sample. The intensities of peaks increase significantly with the increase in Si-content in the coatings. In both modes of measurements, all peaks are found to exist around the same energy. The increase of peak intensity with the increase in Si-content is associated with a valence increase from +3 to +4 as well as +5 or +6 [517-519]. It is also believed that the increased intensity might be related to a reduction of crystalline domains down to the nano-scale [520]. The presence of high valence Cr might have been involved in the large intensity with the increased Si at.% in the coatings. Furthermore, the increase of intensity peaks with higher Si-content may be due to the existence of chemical interactions between Cr and Si. These new
chemical interactions give rise to Cr3d Si2p hybridization [59]. Comparing the NEXAFS data of CrSiN with that of the reference Si3N4 coatings, it is evident that in all cases the spectral lineshape is of the same trend with Si3N4. A tiny peak at ~1861 eV has been observed for all samples in both modes as well. Edge positions around ~1840 eV has been observed for all samples in both modes as well.

Figure 61. NEXAFS spectra of Si K-edge of CrxSi1-xN coatings and reference Si3N4 sample in AEY mode with progressive addition of Si-content.

Figure 62. NEXAFS spectra of Si K-edge of CrxSi1-xN coatings and reference Si3N4 sample in TFY mode with progressive addition of Si-content.
Edge positions around ~1840 eV and features observed at ~1847 and ~1862 eV typical of Si$_3$N$_4$ are clearly seen in all CrSiN samples without marked changes with the progressive addition of Si-doping. Thus, the indication of the formation of amorphous type Si$_3$N$_4$ compound in the CrSiN coatings with the progressive addition of Si-content is clear. Our results have been found to be in good agreement with an earlier report of XANES spectrum of Si-doped TiN sample [59]. In that report, the researchers presented the XANES spectrum of Si-doped AlCrN sample and reported that peak observed at 1847 eV is aligned with the spectrum for SiO$_2$ single spectrum. This would imply oxygen contamination of Si in SiO$_2$ form. The edge positions along with the other features of our coatings are found to be consistent with Si$_3$N$_4$ and SiO$_2$ reference samples [521]. Our study has also been found to be in good agreement with an earlier investigation [59]. Further observation confirms that there is no evidence of the presence of any kind of complex spectral lineshape as compared to the reference Si$_3$N$_4$ sample. Thus, the formation of any kind of ternary compounds is not identified. For electron diffraction and TEM investigations, the presence of an amorphous region in the CrAlN with the addition of Si has been reported in terms of the possible formation of SiO$_x$, however, no experimental evidence for the presence of SiN$_x$ has been reported [517]. Only a trace amount of SiN$_x$ compound at nanometer scales were observed in fast Fourier transform (FFT) [517]. On the other hand, an XPS study of Wo et al. and a few other reports [490, 501, 502] found the experimental evidence of the existence of SiN$_x$ along with the presence of SiO$_x$. According to their report [490] Cr, N and O were identified on the coating surfaces of all CrSiN samples. Presence of Cr$_2$O$_3$ peak at 576.7 eV indicates the bonding of oxygen in the surface of all samples. A weaker peak of Cr-O-N at 398.9 eV was observed due to the surface oxidation as well [522]. Moreover, another component central peak at 397.4 eV due to Si$_3$N$_4$ was identified in the N1s spectra for all four CrSiN films.

9.4 Discussion

With the introduction of Al to the CrN, some Cr atoms were found to be replaced by Al atoms, because of a smaller atomic radius of Al (0.121 nm) than that of Cr (0.139 nm) [513]. As a result, the lattice parameters are lowered. Grain sizes of the CrAlN coatings were also decreased slightly with an increase of Al-substitution [286]. CrN coatings possess a columnar structure composed of vertically aligned grains that remain unaltered with an increased Al-content [286]. A very subtle variation of the grain size of the
coatings with the Al alloying indicates insignificant effect of Al on the nucleation and grains growth of CrAlN coatings. As the Al-substitution varies from a low to high amount, the amorphous structure of the coatings is noticeably enhanced and the grain boundary sliding’s become extremely tough which causes further hardening of the films [286]. XPS study of CrAlN coatings by Z. Li et al. [286] showed the existence of Cr₂O₃ and Al₂O₃ phases in the CrAlN coatings that create an oxidation layer at the surfaces of the samples which in turn improves the oxidation resistance behaviors of the coatings. This also confirms the existence of amorphous structures around the grain boundaries. The Al-rich oxide layers and Al-N bonding play significant role in the oxidation resistance behavior and thermal stability of the coatings respectively [503-505]. The hardness of the CrN coatings increases with an increase of Al doping reaching to a maximum of 42.5 GPa at 28.5 at.%. Exceptionally high hardness (hardness > 40 GPa) of the coatings can be attained by synthesizing nanocomposite structures which consist of nanograins surrounded by extremely thin amorphous matrix [295] having a thickness of typically 1-3 nm that can successfully protect the movements of grain boundaries during deformation [277].

As the Si-content is enhanced, the hardness of CrSiN coatings varies between 25.3 and 35.6 GPa. CrN coatings doped with medium Si-content shows the highest hardness and elastic modulus, while the sample having the highest Si content exhibited the lowest modulus. At low Si contents, the increase in hardness is due to the formation of a solid solution of Si in crystalline CrN [523-525] while at higher Si doping up to ~21.2 at.%, the increase in hardness is ascribed to the reduced grain size [317, 501, 523, 524, 526]. At 28.5 at.% of Si-content, the hardness of the coatings is lowered that reveals the formation of localized defects tends to be aligned parallel to the film growth direction. For this reason, coatings offer less yield strength under a stress normal to the coating surface. With the highest Si-content, compressive residual stress, hardness and elastic modulus values are reduced to a level closer to that measured in the CrN coating because of the disappearance of columnar grains, despite the apparently smaller grain size in this sample. Furthermore, a significant reduction of grain sizes results in the reduction of the lattice distortion that leads to lowering the compressive residual stress [490]. Moreover, the presence of a high volume fraction of amorphous Si₃N₄ phase disorders the crystal structure together with lowering the density and thereby reduces the compressive residual stress. Additionally, the CrN crystals are too small in size (i.e., ~50 nm, as seen in Ref.
to tolerate the higher internal stress by the creation of structural defects such as dislocations and, consequently, fine cracks emerge in the amorphous $\text{Si}_3\text{N}_4$ structures.

9.5 Conclusions

The effects of 14.3 to 28.5 at.% Al and Si doping on local electronic structure of CrAlN and CrSiN coatings deposited by a TEER UDP 650/4 closed field unbalanced magnetron sputtering system have been investigated. In CrN samples, features corresponding to AlN have been observed in all cases without any significant changes in the spectral lineshape with the gradual increase in Al-content. For CrSiN coatings, features corresponding to $\text{Si}_3\text{N}_4$ and $\text{SiO}_2$ have been observed in all cases. No remarkable changes in the spectral lineshape have been noticed with the progressive doping of Si-content as well. Thus, it is conclusive that the local environments of both Al and Si have been found to remain unchanged in these samples with an increase in either Al or Si at.%. The hardness of the CrN coatings was increased significantly due to the existence of an amorphous AlN phase at the grain boundaries and high residual stress. Amorphousity of CrN increases with the progressive addition of Al-content that toughens the coatings. The presence of chromium and aluminum oxides at the coatings surface enhances the oxidation resistance of the coatings. The highest hardness and elastic modulus of the CrN coatings have been observed with the medium Si-doping. The hardness and elastic modulus of CrN increases with an increase in Si-doping in crystalline CrN. With high Si-content, hardness, residual stress and elastic modulus decrease due to the creation of localized defects, and lattice distortion.
CHAPTER TEN: ATOMIC BONDING STATES OF $\text{Cr}_{1-y}\text{Ni}_y\text{N}$ COATINGS THROUGH SYNCHROTRON RADIATION NEXAFS SPECTROSCOPY

10.1 Introduction

Interests in transition metal nitrides have risen in the past few years due to their unique physical and mechanical properties that render them suitable for a wide range of technological applications in numerous devices [60, 63-69, 73, 490, 527, 528]. For their superior strength, high corrosion and oxidation resistance, these materials have been used in extreme pressure and temperature conditions, e.g., jet engine components. Moreover, dopants have been used to enhance their various physicochemical and mechanical properties such as hardness, oxidation resistance, inertness, diffusion resistance and reflectance by the formation of dislocations, disorder, vacancy and atom substitution [63, 64, 490, 527]. In addition, incorporation of Si, Al or Ti into the CrN matrix results in the reduction of grain sizes down to the nanoscale, which enhances the hardness of the thin films [60]. At the nanoscale, the formation of dislocations becomes difficult and the hardness of the thin coatings is thereby controlled by the grain boundary [529].

Endrino et al. [527] studied the binary (TiN) and ternary (AlCrN) metal nitride coatings with silicon doping using X-ray diffraction (XRD) and NEXAFS techniques and found that they exhibited favorable physical hardness, toughness and good oxidation resistance. The bonding structural evolution and the spectral changes were correlated in the X-ray absorption near-edge structure (XANES) studies of the aluminum incorporated titanium nitride [158] which afforded a comprehensive treatment on the local atomic structure of TiN. More recently, we [157] presented the bonding structural evolution in CrN coatings upon the progressive incorporation of Al and Si using NEXAFS spectroscopy in order to understand the change in electronic structure as the concentration of dopant varies. Evolution of the bonding structure was identified from shifts in the peaks of Al $K$-, Cr $L$-, and Si $K$-edge absorption energies. Further, the addition of Al and Si was found to play significant roles in tailoring the structure of the grain boundary within CrN coatings as well as the surface chemistry of the oxide layer, allowing the development of highly oxidation and corrosion resistant superhard coatings. In a comprehensive review, Chen [530] presented the NEXAFS investigations of transition metal nitrides, carbides, sulphides, oxides along with other interstitial materials. Meanwhile, there are many attempts at producing new doping materials and improving their novel properties based
on findings from the NEXAFS spectroscopy [157, 158, 312, 527, 531-534]. It is clearly evident that modifications of electronic and surface structures of transition metal nitrides remain a focus of research concerning thin film coatings in recent years. It should be noted that, however, the effects of Ni, Al and Si doping elements on the electronic properties and surface structural evolution and their subsequent roles in modifying the grain boundaries of chromium nitride thin film coatings remain unclear. These effects could be revealed by utilizing the capabilities of a surface sensitive spectroscopic analytical technique. To further shed light on the electronic and surface properties of the doped Cr-nitrides, we performed NEXAFS measurements in surface-sensitive Auger electron yield (AEY) and bulk-sensitive total fluorescence yield (TFY) modes to discern the differences between the surface and bulk compositions of Cr nitrides with the dopants. Our present study is aimed at utilization of synchrotron radiation NEXAFS as a fingerprint technique to explore the local atomic structure of CrN coatings around Ni and investigate their changes with respect to the progressive doping of Ni$^{2+}$ ions. The NEXAFS measurements have been carried out around Cr $L$-, Ni $L$-, N $K$-edge for Cr$_{1-y}$Ni$_y$N coatings.

10.2 Experimental Section

10.2.1 Deposition of Cr$_{1-y}$Ni$_y$N Thin Film Coatings

Cr$_{1-y}$Ni$_y$N (with $y$ varied from 10 up to 40 at.%) thin film coatings with ~2 µm thickness have been deposited on AISI M2 tool steel substrates using a TEER UDP 650/4 closed field unbalanced magnetron sputtering technique [157]. A four-target configuration manufactured by Teer Coatings Ltd., Droitwich, Worcestershire, UK installed at the City University of Hong Kong has been used for this purpose. CrN coatings with low, medium and high amount of Ni-contents and three reference samples of CrN, NiCr, Ni have been also prepared. All samples were mechanically cleaned in an ultrahigh vacuum by means of a diamond needle file and tungsten-wire brush for the NEXAFS study.

10.2.2 XRD Analysis

The structural information and phase identification of the Cr$_{1-y}$Ni$_y$N thin film coatings were analyzed using X-ray diffraction (XRD). These analyses were conducted via Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector using Cu-$K_\alpha$ radiation ($\lambda = 0.154$ nm), operated at 40 kV and 40 mA at room temperature. The XRD
scans of the Cr$_{1-y}$Ni$_y$N thin film coatings were recorded in the angular range $10^\circ \leq 2\theta \leq 60^\circ$ in steps of 0.01$^\circ$.

10.2.3 Synchrotron Radiation and NEXAFS Analysis of the Coatings

Cr$_{1-y}$Ni$_y$N coatings were characterized by NEXAFS technique using the soft X-ray spectroscopy (SXR) beam-line at the Australian Synchrotron facility in Melbourne. The storage ring was operated in the top-up mode with a beam current of $200 \pm 1$ mA at 3 GeV. A plane diffraction grating monochromator SX700 with a grating of 1200 lines/mm was used for collimating and monochromatizing the X-ray beam. For NEXAFS measurements, the samples were mounted on a stainless steel sample-holder using double-sided carbon tapes to compensate charging, and a minimum base pressure of $1 \times 10^{-10}$ mbar has been maintained in the analysis chamber throughout. The photon energy used was 1253.6 eV. Measurements were conducted at a glancing incidence of 55$^\circ$, the so-called ‘magic angle’ with the X-ray beam. At the magic angle, possible effects of the preferred molecular orientations can be minimized for samples without azimuthal order.

Two types of modes, Auger electron-yield (AEY) and total fluorescence yield (TFY) were used for the NEXAFS data record. For Cr$_{1-y}$Ni$_y$N thin film coatings, NEXAFS data were recorded at Cr $L$-edge (570-610 eV), Ni $L$-edge (840-890 eV) and N $K$-edge (380-450 eV) in both modes with a channeltron facing the sample positioned 30$^\circ$ above the incoming beam and by monitoring drain current. The NEXAFS data recorded in AEY and TFY modes were normalized with respect to the incident photon flux by dividing the samples signal $I_s$ with the incident photon flux $I_o$ monitored using a gold grid with high transmissivity positioned in front of the sample. The linear background was subtracted from the spectra by fitting the pre-edge region. The data was processed using SPECSLAB (V2.75-R25274) software.

10.3 Results and Discussion

10.3.1 Structural Characterization of Cr$_{1-y}$Ni$_y$N Thin Film Coatings

Fig. 63 exhibits the XRD patterns of CrN and Cr$_{1-y}$Ni$_y$N thin film coatings deposited by magnetron sputtered technique. In Fig. 63, CrN (111) and (200) can be identified at about 37.2$^\circ$ (Peak-A) and 43.2$^\circ$ (Peak-B) $2\theta$, respectively, based on (JCPDS 77–0047; space group 225). The (200) becomes broader, as well as decreases in intensity, as the Ni
concentration is increased indicating the grain size crystallites of the CrN phase become smaller. This is consistent with the previous observation by Wo et al. [535].

![Figure 63. XRD pattern of Cr$_{1-y}$Ni$_y$N thin film coatings, where Ni varies from about 15 to 29 at.%.](image)

The peak (C) at $2\theta = 44.7^\circ$ is due to (1) the iron based substrate ((JCPDS 87-0721); space group 229; (110)), (2) Ni$_3$N crystalline ((JCPDS 89-5144); space group 182; (111)), and (3) metallic Ni ((JCPDS 88-2326); space group 225; (111)). The iron (110) is seen in all the coating samples. The intensity of the peak at this position increases with addition of Ni atoms indicating the appearance of the new Ni$_3$N and metallic Ni phases in the CrN matrix. The existence of Ni-N and metallic Ni bonds have been confirmed via XPS and reported in [535]. The XPS results clearly showed elemental Ni bonding state dominating Ni-N bonding state (approximately 80%:20%). The broadening of base of the peak at 44.7° towards high $2\theta$ may indicate the wide Ni$_3$N composition distribution in the sample. The NEXAFS study below will give further discussion of the possible bonding states existing in the coatings.

### 10.3.2 Evolution of Cr and N in the Nickel-doped Cr$_{1-y}$Ni$_y$N Thin Films

Typically, X-ray absorption and/or emission spectroscopy probe the unoccupied and occupied densities of states of any compound on an element and orbital angular momentum based dipole selection rules. Generally, the NEXAFS of transition metal compounds are very sensitive to local ligand symmetry and d-shell electron occupancy.
Due to the localized nature of $p \rightarrow d$ transitions for first-row transition elements, the multiplet phenomenological theory can be successfully applied for the interpretation of $L_{3,2}$-edge spectra of Cr and other transition elements [509]. The absorption around $L_{3,2}$-edges in transition metals originates from the transition of electrons from the $2p$ state to empty $3d$ states above the Fermi level. The two principal peaks with sharp intensities, the so-called white lines observed in the NEXAFS spectra (See Figs. 62 and 63) correspond to the two transitions: $2p_{3/2} \rightarrow s_{1/2}, d_{3/2}, d_{5/2} (L_3)$ and $2p_{1/2} \rightarrow s_{1/2}, d_{3/2} (L_2)$, respectively. The Cr $L_{3,2}$-edges originated from the spin-orbit coupling of the initial states and separated by an energy of ~9 eV. In addition to the atomic and molecular electronic structures, the quantification of intensities of $L_{3,2}$-edges also provides information about the momentum, spin and valance state.

Figs. 64 and 65 show the Cr $L$-edge NEXAFS spectra of Cr$_{1-y}$Ni$_y$N thin films in pure state and doped with varying nickel content in the AEY and TFY mode. The NEXAFS spectra show that the local environments of nickel are of similar type with the progressive doping of nickel to the pure chromium nitride sample. In both modes, the first and second peaks are found at photon energies around ~576.5 and ~585 eV, respectively. Their intensities do not show any significant variation with the progressive Ni-content to the pure chromium nitrides, which in turn reveal the invariant nature of the local environments of Ni in the coatings. Comparing the NEXAFS data of Cr$_{1-y}$Ni$_y$N with that of the Cr and NiCr reference coatings, it can be clearly seen that the spectral lineshape are of the same trend for the two reference samples. All the peak and edge positions of the two reference samples are matched with that of Cr$_{1-y}$Ni$_y$N thin film coatings without any changes with the variation of Ni-content. Thus, the existence of Cr and formation of NiCr is evident with the addition of Ni-content to the pure CrN matrix. Two main peaks around the Cr $L_{3,2}$-edges are observed at ~576.5 and 585 eV both in AEY and TFY modes. The absorption of Cr $L$-edge in AEY mode is much stronger than that in TFY mode, which may be attributed to the fact that the decay of the fluorescence yield in Cr L shell is less than the corresponding Auger yield. In Auger mode, the features found around 577 and 584 eV are similar to that of Cr$_2$O$_3$ [512]. A small peak observed at ~575 eV originates due to the transformations of Cr1$s$ state to the anti-bonding state arising from hybridizing between the Cr4$s$ and the N2$s$ states.
Figure 64. NEXAFS spectra of CrN, Cr$_{1-y}$Ni$_y$N, Cr reference, and NiCr reference coatings at Cr $L$-edge in AEY mode.

Figure 65. NEXAFS spectra of CrN, Cr$_{1-y}$Ni$_y$N, Cr reference, and NiCr reference coatings at Cr $L$-edge in TFY mode.

This happens for the partial mixing of the N$2p$ state. The first peak which is observed around 576.5 eV can be assigned to a transition from Cr$1s$ core state to 3$d$ states which reveals that the local structures around Cr atoms are $C_{3v}$ symmetry. The small intensity and-relative energy level of the peak is due to the transitions from Cr$1s$ state to anti-bonding state originating from the hybridization between Cr$4s$ state and N$2s$ state (forbidden transition) with the partial mixing of N$2p$ state. The separation between the $L_3$
and $L_2$ components is about 8.5 eV with some additional fine features arising from the multiplet effects. This separation energy is comparable with the width of the valance band. Additional fine structures basically arise from the addition of an extra electron to the $3d^1$ configuration [512]. The scattering of electrons at the Cr $L_{3,2}$-edge stimulates the $3d \rightarrow 3d$ transformations originating from the ligand field separation of the Cr$3d$ states. Furthermore, the $L_{3,2}$-edges absorption spectra of transition metal nitrides with unfilled $d$-shells may be explained on the basis of multiplet calculations and crystal field transformations from $2p^5d^6$ to $2p^5d^{n+1}$ state for an appropriate site symmetry determined by ligands. On the basis of multiplet calculations formation of Cr ligand with oxygen and other transition metals in normal bonding environments, there was a previous study that showed the sensitivity of $L$-edge spectra to the oxidation state and local symmetry of the metal [510]. It is well known that the experimental identification of the Cr$3d$ states is complex, however the band-structures suggest that the Cr$3d$ states are comprised most of the valence band and at the bottom of the valance band there is strong hybridization with the O$2p$ states. In contrast to the AEY spectrum, Cr $L_{3}$- and $L_2$-edges spectrum is approximately equally intense in the TFY mode. This is attributed to the fact that the fluorescence yield of chromium strongly depends upon the incident photon energy. This feature has been predicted by de Groot and co-researchers [536]. It is interesting to note that the Cr L-edge spectrum in CrN shows a slight difference at the energy position compared to Cr$_{1-y}$Ni$_y$N with different Ni concentration. A chemical shift of 0.40 eV to a high energy position in CrN is observed which is due to the different binding energy of the coating with the doping content.

Figs. 66 to 67 represent the N $K$-edge NEXAFS spectra of Cr$_{1-y}$Ni$_y$N thin film coatings in AEY and TFY modes recorded in a vacuum analysis chamber. The same shape of the N $K$-edges spectra in all samples indicates that the materials possess the same purity level, homogeneous structure and zones with same type of elemental atomic ratios. Likewise, in the previous two cases, no obvious variations in the spectral lineshape was detected with variation of Ni content to the CrN suggesting that the local environment of Ni remains unchanged in CrN coatings. Both in AEY and TFY modes, the presence of the principal maxima and other peaks were almost at the same energy positions. The features seen at 398 and 401 eV are assigned to unoccupied N$2p$ states hybridized with Cr $3d$ orbital’s, while the features around ~409 eV to unoccupied N$2p$ states hybridized with Cr$4sp$ orbitals. The characteristic peak appearing at 398 eV is observed in all the NEXAFS spectra of our coatings which demonstrate that the Cr atoms are in the center of a
tetrahedron while the N atoms are at the corners. It was also observed that the intensity of
the second main peak is lower than that of the first main peak in both modes. Our results
show good consistency with previous report [537]. As the doping content is increased, a
small shift in the second peak (from \( \sim 0.5 \) to \( \sim 1 \) eV) is noted along with the broadening of
the N2p feature. This could be related to the significant changes in spectral weight in the
NEXAFS spectra of nitrogen 2p partial density of states observed around the valence
band due to higher doping content. Similar features have been reported for GaN with Cr
doping [538]. The modifications of intensity, observed with substantial addition of Ni, are
associated with possible factors, such as variation in valence and alternation of the
crystalline domains down to the nanoscale.

![Figure 66. NEXAFS spectra of CrN, and Cr_{1-x}Ni_xN coatings at N K-edge in AEY mode.](image-url)
Figure 67. NEXAFS spectra of CrN, and Cr$_{1-y}$Ni$_y$N coatings at N K-edge in TFY mode.

10.3.3 Significance of Dopant Ni in Cr$_{1-y}$Ni$_y$N Thin Films

The $L_{3,2}$- absorption edges NEXAFS spectra of transition metal compounds provide information on the unoccupied orbitals associated with the oxidation state, spin state and bond covalence. The Cr/Ni $L_{3,2}$-edge represents the dipole-allowed transition of a 2$p$ electron into empty 3$d$ and possibly 4$s$ states (with $\Delta l = \pm 1$). The spin–orbit coupling results in a splitting of the metal $L_3$-edge ($2p_{3/2} \rightarrow 3d$) and $L_2$-edge ($2p_{1/2} \rightarrow 3d$). Figs. 68 and 69 are NEXAFS spectra of the Ni $L_{3,2}$-edges for Cr$_{1-y}$Ni$_y$N ternary compound with varying Ni contents, as well as a NiCr reference sample for comparison. The intensities of the peaks have been found to be substantially enhanced with an increase in atomic percentages of Ni in the CrN coatings. However, no special features have been found on the NiCr reference sample at this absorption energy. This suggests that there is no clear evidence of the formation of NiCr at the Ni $L$-edge of the Cr$_{1-y}$Ni$_y$N coatings. The increase of the peak intensities of Ni $L$-edge spectrum, with increase of Ni, is associated with the increase in coordination and effective charge of Ni atoms. It is expected that, with an increase in Ni doping to the CrN matrix, the additional Ni will be located at octahedral positions in the phase. Since the absorption coefficient is proportional to the number of absorbing atoms and the absorption cross-section, the intensity is eventually increased. In AEY and TFY modes, two main peaks are observed at positions ~852.2 and ~869.5 eV, respectively, along with a relatively marginal peak observed at ~858 eV.
peak positions and profiles of the spectra at ~852.2 and ~858 eV are similar to those of NiO$_2$ [539]. In general, the $L_3$-edge absorption of NEXAFS spectra is sharper and more prominent because of the longer lifetime of the excited state.

**Figure 68.** NEXAFS spectra of Cr$_{1-y}$Ni$_y$N (with progressive addition of Ni-content), and NiCr reference coatings at Ni $L$-edge in AEY mode.

**Figure 69.** NEXAFS spectra of Cr$_{1-y}$Ni$_y$N (with progressive addition of Ni-content), and NiCr reference coatings at Ni $L$-edge in TFY mode.

The lineshape and intensity of a spectrum is affected by the metal coordination environment and the number of conduction states. The intensity of the Ni $L_{3,2}$-edge absorption gradually increases with the progressive addition of Ni due to the presence of
a large number of Ni based conduction states and higher positively-charged Ni atoms, e.g. Ni\(^{2+}\). The Ni L-edges absorption in all the coatings is found to be at the same photon energy. This suggests that the binding energy of the Ni\(^{2+}\) level is the same in all the coatings and the electron density of empty Ni d-states is the same as the Fermi level in all the samples. The near-edge absorption structure of \(L_{3,2}\)-edge for 3d metals is governed mainly by that of the empty 3d states [394, 540]. The intensity of the Ni \(L_{2,3}\)-edges for 3d metals depends on the number of the valence d-shell electrons, i.e., by the d-shell occupancy [530]. This indicates that the occupancy of the Ni d-shell in the Cr\(_{1-y}\)Ni\(_y\)N becomes higher with increase in Ni content. In addition, higher electron transfer takes place with a marked difference in electronegativity between Cr and Ni. The symmetric Ni \(L_{2,3}\)-absorption edges of the NEXAFS spectra can be designated to the structure of the density of empty d-states of Ni, which does not change with the gradual increase of Ni-content. This confirms the invariant nature of the Ni into the coatings. We also believe that with the increase in Ni, in the Cr\(_{1-y}\)Ni\(_y\)N coatings, the direct bonds are formed by additional nickel Ni d-shell electrons. The generations of the direct d-bonds in the compound leads to the increase in resistance against crystal deformation, oxidation resistance and wear resistance during the structural transformation. The NEXAFS measurements indicate that the absorption energy does not show any appreciable shift. In a previous study [541], it was reported that the partial electron yield (PEY) and fluorescence electron yield (FEY) spectra were quite different from each other; however, in the present study the AEY and TFY spectra are found to be identical.

### 10.3.4 Implications of Electronic Configurations on Materials Properties of Cr\(_{1-y}\)Ni\(_y\)N Coatings

The physico-mechanical properties of nanocomposite coatings, consisting of nanocrystalline and/or amorphous phases, are a function of volume fractions of the mixing components, and also influenced by the grain boundary configuration and size of the constituent phases. Owing to their very small grain sizes and abundant boundary zones surrounding individual grains, nanocomposite coating materials exhibit unique properties, e.g. superhardness and good toughness [542]. Superhardness of transition metal nitrides, e.g. CrN, has been achieved by adding various doping elements such as Si, Al [286, 543]. The doping elements altered the microstructures of the binary compounds from closely-packed columnar grains into nanocrystalline structures embedded in an amorphous matrix [489]. Doping by Al enhanced compressive stress, mechanical
hardness, Young's modulus, resistance to elastic breakdown \((H/E)\) and the plastic resistance \((H^3/E^2)\) of CrN coatings with the highest amount of Al-content. Al atoms were found to be segregated around the grain boundaries to form an amorphous AlN structure. The superhardness in CrN with Si and Al substitutions results from the combination of the fine-grain size together with the strong interfacial bonding between the nanocrystalline and amorphous phases [543]. Investigation of electrochemical behaviour of CrN/Ni hard coatings on steel substrate established that the corrosion behaviour of CrN coatings were significantly affected by the introduction of Ni as an interlayer [544, 545]. The superior thermal stability of CrNiN and ZrNiN nanocomposite thin film coatings has also been reported by Karvánková et al. [546]. In a recent study, Wo et al. [535] reported the microstructural and mechanical characterizations of CrN coatings with differing Ni-contents. The gradual increase of Ni improved the damage tolerance and found to be governed by intercolumnar shear sliding facilitated by high aspect ratio columnar grains. CrNiN coating system exhibited a good combination of high hardness and toughness with the increase of the Ni content.

High resolution XPS spectra of the synthesized Cr\(_{1-x}\)Ni\(_x\)N, in the energy region of Cr 2p, were found to be decoupled into two stoichiometric peaks: referred as CrN and Cr\(_2\)N. The occurrence of these two peaks shows a reduction of CrN phase and an increase of Cr\(_2\)N phase as Ni content was increased. This resulted in the reduction of hardness in the Ni containing coatings compared to the binary CrN system as shown in Fig. 7 of [535]. The addition of Ni content changed the deformation mechanism from grain boundary sliding in CrN to plastic deformation [535]. The NEXAFS results from the \(\text{Cr}_{1-y}\)Ni\(_y\)N coatings are able to explain the mechanical behavior of these coatings previously observed in a previous study [535]. The data in Figs. 64-69 show no significant lineshape changes, as Ni content is increased, in the near-edge spectra, suggesting that the angular character of the existing bonding are not affected by the addition of Ni. Although chemical states in the coatings changes with Ni introduction, less significant changes has been detected from the local environments of Ni, which means that the types of bonding existing in the coatings are the same in all coatings. It also appears that there are more direct \(d\)-bonds in Ni containing CrN coatings. Recent nanoindentation study on the same set of Cr\(_{1-y}\)Ni\(_y\)N coatings shows that although the hardness value of the coatings are maintained at a reasonably high level (>15 GPa), a monotonic decrease in hardness occurred as Ni content increased from 15 to ~28 at. % [535]. This could be the result of an increase in \(d\) sub-orbitals observed in the present study. In addition, an increase in peak intensities of
Cr L-edge spectra were observed in high concentration of Ni, suggesting possible variations in valence, which could result in a reduction of crystalline domains, i.e., smaller grain size. This is a plausible explanation for the narrower (finer) grains observed in the Cr$_{1-y}$Ni$_y$N from previous XTEM examinations [535]. The increase of the peak intensities of Ni L-edge spectrum, with increasing Ni concentration, indicates an increase in coordination and effective charge of Ni atoms, with stronger bonds associated with the Ni atoms. This leads to stronger grain boundaries in the crystals. This agrees with the transition of deformation mechanism from grain boundary sliding in CrN to buckling of grains in Cr$_{1-y}$Ni$_y$N as seen in previous study [535].

10.4 Conclusions

Comprehensive synchrotron radiation NEXAFS measurements were performed on Ni doped CrN coatings to obtain a fundamental understanding of the influence of addition of Ni on the electronic and structural properties, in particular occupied and unoccupied Cr3$d$, Ni3$d$ and N1$s$-states, of Cr$_{1-y}$Ni$_y$N coatings. It is shown that the chemical states in Cr$_{1-y}$Ni$_y$N with different concentration of Ni are changing, as shown with the presence of a small chemical shift and moderate change of shapes of various absorption edges. This explains the reduction in grain size as Ni content increase in Cr$_{1-y}$Ni$_y$N observed previously in a XTEM study and current XRD analysis. No significant changes in the NEXAFS spectral line shapes are detected with the progressive doping of Ni content to the CrN matrix, suggesting that the local environments of Ni remain unmodified in the samples. The higher peak intensities of Ni L-edge and Cr L-edge spectra obtained in CrN, with higher concentration of Ni, suggests an increase in valance, coordination number and effective charge of ions, and the existence of metallic Ni. The increase of Ni concentration reduces the hardness of Cr$_{1-y}$Ni$_y$N coatings. However, the toughness of the coatings is enhanced, and the overall mechanical properties of the materials are improved possibly due to an increase in coordination and effective charge of the Ni atoms as observed in NEXAFS results. In the concentration range of Ni selected in this study, NEXAFS and previous studies did not show the optimal concentration for the highest hardness of the coatings. Further investigation with a wider range of Ni concentrations could provide a clearer explanation of the optimal condition for hardness and toughness for the overall mechanical properties of the coatings.
CHAPTER ELEVEN: LOCAL BONDING STRUCTURES OF SPUTTERED Cr_{1-x}(Al/Si)_{x}N FILMS: SYNCHROTRON RADIATION NEXAFS STUDIES

11.1 Introduction

Over recent years, chromium nitride (CrN_x) has been widely used as protective coatings to enhance the mechanical performance, wear and corrosion resistance of metal components in engineering applications [547]. Both the hardness and oxidation resistance of CrN_x coatings can be improved via the introduction of doping elements such as Si, SiC, Al, and AlSi [278, 281, 283, 286, 490, 548-550]. The dopants enhance these properties by creating various defects, such as vacancies, atom substitution, cluster formation and deformation [281]. High resolution transmission electron microscopy (HRTEM) study on Cr_{1-x}M_xN coatings has shown the existence of nanocrystalline grains surrounded by amorphous grain boundaries [283]. Thus, the grain size and grain boundaries are crucial in controlling the hardness and oxidation resistance of such coatings. Integration of silicon, aluminium or titanium into the CrN_x matrix resulted in the reduction of grain sizes to the nano-scale [60]. When scaling the grain size down to the nanoscale, the formation of dislocations becomes difficult and the hardness of the coatings is thereby predominantly controlled by the grain boundary characteristics [529].

In recent years, X-ray photoelectron spectroscopy (XPS) [299], NEXAFS and extended X-ray absorption spectroscopy (EXAFS) [74], nuclear magnetic resonance (NMR) [302] and infra-red (IR) spectroscopy [307] have been used for structural characterization and phase identification of hard coatings in an attempt to understand and control various factors governing their properties [14-15]. Katsikini et al. [309] performed NEXAFS studies on binary AlN, GaN and InN nitrides and found that the energy positions of the absorption edge ($E_{abs}$) of these materials were shifted monotonically towards the higher wavelength side with the atomic number of the cation. The electronic structure of plasma assisted pulse laser deposition (PLD) grown AlN, CrN and Cr-doped AlN thin films were investigated by X-ray absorption spectroscopy (XAS) and soft X-ray emission spectroscopy at the N K-edge [60] and results were compared with that of density functional theory (DFT) models. Since, the X-ray absorption spectroscopic method probes the occupied and unoccupied densities of states of a material on an element-specific and orbital angular momentum specific basis controlled by dipole selection rules,
the spectra acquired at N K-edge represent the N2p conduction band and valence band partial density of states (PDOS). DFT calculations show that the AlN PDOS has been shifted to allow for the overlap of the main occupied 2p PDOS. An appreciable N2p PDOS was observed just above Fermi energy only for those nitrogen sites that are beside the Cr and whose 2p states hybridized with Cr unoccupied 3d levels. The hybridized unoccupied N2p density of states was seen in the TEY X-ray absorption spectra. Similar theoretical and experimental NEXAFS studies on β- and spinel SiAlON have also been performed by Tatsuni et al. [311]. The authors in that study pointed out that the local environments of Al are independent of the composition. The elastic constants of β-SiAlONs were found to decrease with the increase of Al-content, thereby causing lattice softening, which may affect mechanical performance [312]. Synchrotron radiation X-ray absorption spectroscopy was employed to realize the influence of particle size on the distributions of the metal atoms over the tetrahedral and octahedral sites of the spinels and a slight deviation from the bulk structure was noticed due to the effect of the surface on tiny particles [551].

NEXAFS technique is one of the most popular and powerful spectroscopies for the investigating the surface unoccupied electronic structure of transition metal nitrides because; (i) the NEXAFS spectra provide the density of states of the unoccupied molecular orbitals which are directly related to the structural and electronic properties of transition metal nitrides; (ii) the AEY and TFY modes of NEXAFS technique work by different detection limits that can be successfully used to distinguish the bulk and surface properties of the materials. In a previous report, NEXAFS spectroscopy was used to probe the differences in the electronic structure of CrN with Al and Si doping in terms of chemical shifts seen in the Al K-, Cr L-, and Si K-edges [157]. Incorporation of dopants was found to play a remarkable role in modifying the grain boundary morphology and surface chemistry of these coatings. In a recent work, NEXAFS data were collected to explore the electronic and surface properties of nickel doped Cr-nitrides and to elucidate the differences between the surface and bulk compositions around the absorption edges of Cr1-yNi yN coatings [159]. The appearance of direct d-bonds and an increase in peak intensities within the Cr L-edge spectra confirmed the possible variations in valence and a reduction in crystalline domains, while an enhancement of Ni L absorption edges intensity indicated an improvement in the coordination and effective charge of Ni atoms. Understanding the electronic and surface structure of transition metal nitride-based thin film coatings is therefore crucial from both an experimental and theoretical perspective.
However, there has been very limited effort toward elucidating the effects of dopant elements on the electronic and surface structural evolution, and on the tailoring of the grain boundaries. A recent review [530] provides comprehensive elaborations about the $K$-edge features of the transition metal compounds. In this study, we have conducted XRD analysis and synchrotron radiation NEXAFS measurements over the nitrogen $K$-edge ($N$ $K$-edge) for a series of $Cr_{1-z}(Al/Si)_zN$ coating samples with increasing incorporation of aluminium and silicon. Both surface sensitive Auger electron yield (AEY) and bulk sensitive total fluorescence yield (TFY) modes were used to investigate the effect of dopant elements (Al, and Si) on the crystalline phase, surface structural evolution and local electronic bonding states of the coatings.

11.2 Experimental Section

Aluminum and silicon doped CrN coatings with general formula $Cr_{1-z}A_zN$ ($A = Al$, or $Si$, and $z$ varies from 14.3 to 28.5 at.%), were prepared via magnetron sputtering approach. A TEER UDP 650/4 closed field unbalanced magnetron sputtering system with four-target configuration (Teer Coatings Ltd., UK) was used to coat the films on AISI M2 tool steel substrates (hardened to a hardness of HRC 60). Table 3 presents details pertinent to the deposition conditions for the preparation of the coatings. Four elemental targets were installed in the coating system (2 Cr + 1 Al + 1 Si). Compositions of the coatings were adjusted by controlling the sputtering power applied to each target (Cr, Al, and Si). The deposited coatings were cleaned mechanically in an ultrahigh vacuum using a diamond needle file and tungsten-wire brush. The atomic percentages of elemental compositions of $Cr_{1-z}Al_zN$ and $Cr_{1-z}Si_zN$ coating systems have been outlined elsewhere [157]. XRD was employed for the structural analysis, phase identification and homogeneity of the coatings. A Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector was used for the XRD measurements of the samples. The XRD machine used Cu-$K_\alpha$ radiation ($\lambda = 0.154$ nm), and was operated at a power of 40 kV and 40 mA at room temperature. The XRD tests of samples were performed in a 2$\theta$ geometry from 30° to 60° in steps of 0.01°. The soft X-ray (SXR) beam-line at the Australian synchrotron facility in Melbourne was utilized for the NEXAFS measurements of the coatings. Here, horizontally polarized soft x-ray radiation is produced from an undulator light source. The beamline, based around a plane diffraction grating monochromator (line spacing 1200 lines/mm) is used to collimate and monochromatize the X-ray beam. The films were mounted onto a stainless steel sample-holder using double-sided carbon tape, and
introduced into the ultra-high vacuum end-station on the beamline. The base pressure in
the system was of the order of $5 \times 10^{-10}$ Torr. The N Kedge NEXAFS data ($h\nu = 380 –
450\text{eV}$, $0.1\text{eV}$ step size) were acquired at the “magic angle”, in which the angle between
sample surface and electric field vector of the polarized x-rays is 55°. Two different,
simultaneous, detection modes were used to measure the x-ray absorption signal: surface
sensitive Auger electron yield (AEY), obtained by monitoring the sample drain current
and the more bulk sensitive Total Fluorescence Yield (TFY), achieved by using a
retarding grid detector directed toward the sample and located 30° above the incoming
beam. The NEXAFS spectra were normalized with respect to the incidental photon flux
by dividing the sample signal $I_s$ with the incident photon flux $I_o$, monitored using a 50%
transmissive gold grid located just before the sample. A linear background was subtracted
from the spectra by fitting the pre-edge region. The approximate energy resolution of the
NEXAFS spectra is around 0.1eV.

**Table 31.** Details of the deposition conditions of the Cr$_{1-z}$A$_z$N ($A =$ Al, or Si, and $z$ varies
from 14.3 to 28.5 at.%) unbalanced magnetron sputtered coatings.

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11.3 Results and Discussion

11.3.1 XRD Studies of Cr$_{1-x}$(Al/Si)$_x$N Thin Film Coatings

The XRD data of both sets of sputtered coatings are presented in Fig. 68. The main phases identified are: (i) cubic CrN phase (JCPDS 77-0047, 011-0065; space group: Fm$-3m$ (#225)) with (111) and (200) at 37° (peak A) and 43° (peak D) respectively; (ii) cubic Fe phase (JCPDS 87-0722, 87-0721, 89-4186); space group: Im$-3m$ (#229) with (110) (peak E) from the M2 steel substrate. Peaks labeled B, C and F are also related to the substrate (noting that the substrate is not pure Fe) and are also observable in the synchrotron study (see below); (iii) cubic Cr$_2$N phase (JCPDS 79-2159; space group: P$-31m$ (#162) with (-1-11) at $2\theta = 42.3°$ (peak C).

In both Cr$_{1-x}$Al$_x$N and Cr$_{1-x}$Si$_x$N, XRD spectral lines for phases with Al or Si (e.g. Al$_2$O$_3$, CrSi$_x$, Si$_x$N etc) are not observed. The Al or Si form amorphous phases or any crystalline phase is consisted of small crystallites which are undetectable by XRD. Recently we conducted in-situ high resolution Synchrotron XRD investigations of the 14.2% Al doped CrN coatings on M2 steel substrates heated up to 700 °C. Analysis of the synchrotron data for the room temperature (25 °C) samples showed crystalline CrN, c-AlN, and Al phases [552]. We surmise that for the Cr$_{1-x}$Al$_x$N coatings the crystalline c-AlN and Al phases are not seen in the XRD spectra because the crystallite size is very small and undetectable by XRD. However for the Cr$_{1-x}$Si$_x$N coatings we also assume that either the Si forms an amorphous phase or the crystallites are also very small and undetectable by XRD measurements.

The XRD data for Cr$_{1-x}$Al$_x$N (Fig. 70 (I)) shows a decrease in the CrN phase as the Al atom % is increased. It seems the Al is incorporating into the CrN matrix thereby reducing the presence of the CrN crystal structure. However, a similar increase in Si atom % reduces the CrN phase until the phase is no longer observable in the XRD spectra. Further observation also shows a continuous drop in peak intensity centered at $2\theta = 43°$ (peak D, (200)) with increasing Al or Si content for CrAlN and CrSiN coatings. This may be due to formation of amorphous solid solutions or new structures such as Si/CrN and/or Si$_3$N$_4$ that will be discussed in the NEXAFS result (see Section 11.3.2).
Figure 70. XRD pattern of: (I) Cr$_{1-z}$Al$_z$N, and (II) Cr$_{1-z}$Si$_z$N (where $z$ varies from 14.3 to 28.5 at.%) unbalanced magnetron sputtered thin film coatings.

11.3.2 Evolution of N K-edge Near-edge X-ray Absorption Spectra in Al and Si Doped CrN Coatings

X-ray absorption spectroscopic (XAS) method is widely deployed to probe the unoccupied and occupied densities of states of a material on an element-specific and orbital angular momentum specific basis governed by dipole selection rules. For NEXAFS measurements around the N K-edge the unoccupied nitrogen 2p partial density
of states of the material is probed. Due to the dipole selection rules governing the transitions, the NEXAFS spectra obtained at the N K-edges represent the nitrogen 2p conduction band with p-symmetry at nitrogen sites. The distinctive features observed in the NEXAFS spectra can be used as fingerprints to identify the corresponding bonding environments in the ternary \( \text{Cr}_{1-z} (\text{Al/Si})_z \text{N} \) coatings. Figs. 71 to 74 present NEXAFS measurements at the N K-edge of the \( \text{Cr}_{1-z} (\text{Al/Si})_z \text{N} \) and reference samples in AEY and TFY modes.

**Figure 71.** AEY NEXAFS spectra of \( \text{CrN} \), \( \text{Cr}_{1-z} \text{Al}_z \text{N} \) (with progressive addition of Al-content), and AlN reference coating at N K-edge.

**Figure 72.** TFY NEXAFS spectra of \( \text{CrN} \), \( \text{Cr}_{1-z} \text{Al}_z \text{N} \) (with progressive addition of Al-content), and AlN reference coatings at N K-edge.
Since there are no noticeable changes in the spectral lineshape with an increase in at% of either aluminum or silicon content to the chromium nitride system, hence the local environment of aluminum and silicon remains unaltered in chromium nitride matrix.

For the Cr$_{1-x}$Al$_x$N series, creation of an AlN phase is evident (Figs. 71 and 72) as the spectral lineshapes of Cr$_{1-x}$Al$_x$N are of the same trend with the AlN reference sample. Incorporation of Al results an obvious shallowing of the dip (403-405 eV region) in the NEXAFS spectra, which could be attributed to a growing impact from the wide bulge atmosphere of the AlN reference film. However, presence of the AlN phase was not detected in the XRD results indicating that the AlN phase is made of tiny crystallites or exists in an amorphous state around the grain boundaries.

For Cr$_{1-x}$Si$_x$N coatings: formation of crystalline Si$_3$N$_4$ phase was also identified (Figs. 73 and 74) as the NEXAFS data of the reference Si$_3$N$_4$ phase, both in AEY and TFY modes, align with the spectral lineshape of Cr$_{1-x}$Si$_x$N coatings. The silicon substitution is causing a noticeable shallowing of the dip (403-405 eV region) in the NEXAFS spectra, which could be ascribed to an increasing contribution from the broad hump character of the Si$_3$N$_4$ reference sample. In both modes (AEY and TFY), the principal maxima seen at ~398 and ~409 eV can be ascribed to unoccupied N2p states hybridized to Cr3d orbitals and unoccupied N2p states hybridized to Cr4sp orbitals respectively. The intensity of the maxima at 409 eV was lower than the 398 eV maxima [537]. This observation indicates that the chromium atoms are at the center of a tetrahedron while the N atoms are located at the corners. Similar to the Cr$_{1-x}$Al$_x$N films, the occurrence of the Si$_3$N$_4$ phase was not established in the XRD studies of the Cr$_{1-x}$Si$_x$N coatings reflecting that the Si$_3$N$_4$ phases possess very small crystallites or exist in an amorphous form in the vicinity of the grain boundary regions.

With the subsequent increase in the aluminum and silicon content to the CrN system, a small shift in the second maxima of ~1eV was observed together with the broadening of the N2p feature which might be due to changes in spectral weight of nitrogen 2p partial density of states [553]. High valance chromium might also initiate new chemical interactions which also give rise to Cr3d (Al2p/Si2p) types of hybridizations. This is because the unoccupied and occupied electron density of states being polarised with the Cr atoms and strongly bonded to the $e_g$ mostly empty spin up electrons in the valence band and $t_{2g}$ totally empty spin down electrons in the vicinity of the Fermi levels [60]. The degree of interactions between Cr 4sp and non-metal 2p orbitals is also related to the
difference in energy between $2t_{2g}$ and $(3a_{1g} + 4t_{1u})$ orbitals [530, 554]. The other features observed in our coatings are also consistent with the Si$_3$N$_4$, which is in good agreement with the XAS report by Endrino et al. [527]. The XPS study of Wo et al. [543] on CrSiN films also establishes experimental evidence of SiN$_x$ and SiO$_x$ species.

**Figure 73.** NEXAFS spectra of CrN, and Cr$_{1-z}$Si$_z$N (with progressive addition of Si-content), and reference Si$_3$N$_4$ coatings at N K-edge in AEY mode.

**Figure 74.** NEXAFS spectra of CrN, and Cr$_{1-z}$Si$_z$N (with progressive addition of Si-content), reference Si$_3$N$_4$ coatings at N K-edge in TFY mode.

Since chromium nitride is very close to pure metal at the surface, the N K-edge in both AEY and TFY modes show good agreement with each other [555]. For all the samples in
both modes, for the second peak at 408.4 eV, the corresponding N-K edge broadens and also decreases in intensity, which is in agreement with the previous study [556]. Between Cr$_{1-z}$Al$_z$N and Cr$_{1-z}$Si$_z$N coatings, subtle differences in the features observed at 408.4 eV are due to the different divergences of 3$d$ conduction bands in Al, and Si. These spectra also confirm the nitrogen 2$p$ partial density of states valence band hybridization of the occupied N2$p$ states with the more evident Cr3$d$ states. Incorporation of aluminum to the CrN replaces some chromium atoms, consequently initiating the formation of a Cr$_{1-z}$Al$_z$N solid solution causes strengthening of the coatings. In reference to the CrN coatings, the hardness, the compressive residual stress, elastic strain to failure ratio and plastic deformation factor of Cr$_{1-z}$Al$_z$N coatings were significantly improved together with the change in preferred orientation with the subsequent increase in Al-content. Furthermore, the formation of amorphous AlN around the columnar grain boundaries of chromium nitride also plays important role in conglomerating high mechanical hardness and damage tolerance [30]. The AlN phase potentially obstructs the migration of the grain boundaries during deformation, leading to an increase in the mechanical hardness of the films. Magnetron sputtered coatings are known to form a columnar structure along with the inter-granular shear sliding that reduces the stress concentrations, which improves the damage resistance of the coatings. A similar phenomenon was reported in a previous study during the design of superhard and self-toughening CrAlN coatings [30]. With the subsequent addition of silicon to the chromium nitride coatings, the increase of hardness was a consequence of enhancement in the compressive residual stress, grain boundary strengthening caused by amorphous Si$_3$N$_4$, and creation of a solid solution of silicon [555]. Another factor associated with the superhard behavior of CrSiN coatings might be the refinement of the grain structures by the transition of columnar grain structure to the nanocomposite phase exhibited by the amorphous Si$_3$N$_4$ matrix. Similar to the Cr$_{1-z}$Al$_z$N coatings, we also see in Cr$_{1-z}$Si$_z$N films a sturdy interfacial bonding between the nanograins and amorphous regions. A large amount of oxygen content as native oxide layers of Cr-O-N, Al$_2$O$_3$, Cr$_2$O$_3$ and SiO$_x$ phases were confirmed by previous reports on CrAlN and CrSiN coatings [543, 557]. However, as discussed in previous sections, these structures were not detected in the XRD studies due to the smaller crystallite sizes and/or amorphous nature.
11.4 Conclusions

In the present work, we have conducted XRD studies and synchrotron radiation NEXAFS N K- absorption edges measurements to better understand the electronic and structural properties of doped CrN coatings on steel substrates. Formation of crystalline CrN, Cr$_2$N, and Fe phases were confirmed by the XRD studies of these coatings. For the CrN coatings, the local environment of Al and Si was left unchanged with the subsequent increase in their at.%, as no apparent changes in the spectral lineshapes were observed. The occupied and unoccupied partial density of states (PDOS) in Cr, Al, Si and N such as, Cr3$d$-, Al3$p$-, Si3$p$ and N2$p$-states gave rise to Cr3$d$(Al3$p$/Si3$p$)N2$p$ hybridizations in Cr$_{1-z}$(Al/Si)$_z$N compositions that modified the electronic configurations and band structures of these coatings. The additional features seen above 420 eV in AEY and TFY modes are the complex structure splitting, due to spin-orbit interaction of the Cr3$d$ levels. As a result, microstructure, grain sizes and grain boundaries of the coatings are changed and thereby the chemical and electronic bonding states of the films were modified as seen in NEXAFS studies.
We have adopted the sol-gel dip coating method to synthesize 3d transition metal oxide based thin film coatings with and without the addition of graphene oxide to realize their solar structural characteristics, surface morphology, surface chemical bonding states and solar selective behaviors. In addition to the metal oxide based coatings, a few series of 3d transition metal nitride based unbalanced magnetron sputtered thin film coatings were studied for their spectral selective features associated with thermal structural stability, mechanical, near-edge absorption and local electronic bonding structures. Synchrotron radiation based XRD studies on both metal oxide and metal nitride based coatings show the presence of physically, thermally and chemically stable multiple phases. The solar absorptance was found to increase with the progressive addition of graphene oxide to the Cu,Co,O system while the optical emittance was reduced and thereby the solar selectivity was significantly increased. Hence, copper cobalt oxide thin films with the addition of graphene oxide show good potential to be a smart solar selective surface for photothermal applications. With the addition of 1.5 wt.% of graphene oxides, the Cu,Co,O thin films demonstrated a very high solar selectivity up to 29.01. Occurrence of multiple stable phases seen in synchrotron radiation X-ray diffraction studies were also confirmed via deconvolution of high resolution XPS data.

XRD studies detect the spinodal decompositions in TiAlN and TiAlSiN which confirms the existence of AlN and Si,N (arising from sp Si bonding with sp N) phases. XPS analysis is consistent with the XRD results. Unlike XPS, no peaks of SiO, Al,O phases were detected in XRD studies which tend to show that they are either in miniscule amounts or in amorphous phases. Uniform, dense and stable surface morphology of the metal nitride coatings were induced with Al and AlSi-doping to the TiN matrix. Lower reflectivity in the visible range and higher reflectivity in the infra-red to far-infrared range of the solar spectrum ensures a low thermal emittance of these coatings. The solar selectivity of AlSi doped TiN coatings improved significantly, and reaching up to 22.63 at room temperature. The amorphous assembly of SiO and Al,O phases establish among TiAlN and TiAlSiN grains cohesively to enhance their solar selectivity. Temperature dependent studies of TiAlSiN coatings exhibit a structural change near their stable components of TiN, AlN and Si,N phases prompted by an isostructural establishment of cubic Ti-rich, Al-rich and Si-rich domains. TiAlSiN films synthesized via spinodal phase
segregation and enhanced energetic ion bombardment system display substantial thermal stability. The interfacial amorphous boundaries restrain the atomic movements while Al₂O₃ and SiO₂ phases were found to prevent oxygen diffusions. Decent thermal stability originating from amorphous boundaries slows down the interface reaction and recrystallization in annealing. Good wear resistance at high annealing temperature plays an important role in improving their oxidation behaviors. Up to 700 °C, all of the coatings demonstrated high absorptance in the visible range, and a low thermal emittance in the infrared range was recorded for the coatings annealed up to 600 °C. Consequently, a high and stable solar selectivity of 24.63 was achieved by TiAlSiN coatings annealed at 600 °C. The solar absorption, thermal emittance and stability of solar selective coatings are generally affected by stoichiometry of the compositions, impurities and dopants.

The incorporation of aluminum in the CrN system causes shrinkage of the lattice parameters and the grain sizes of the films because larger Cr (0.139 nm) atoms are replaced by the smaller Al (0.121 nm) atoms. The formation of CrAlN solid solutions is responsible for the increase in the strain energy of the coatings and the lattice distortions. The fine-grain structure of these coatings reveals the formation of a large number of nucleation sites during the growth process. As the Al-content varies from a low to a high amount, the amorphous structure of the coatings has been enhanced remarkably. Due to the enhanced amorphous grain boundary, sliding becomes exceedingly difficult and this results in the hardening of the coatings. It is also assumed that increased hardness in these coatings is initiated due to the presence of the AlN phase at the grain boundaries in conjunction with the high residual stress. With gradually increased Al-content, the compressive residual stress is increased by 52 % and this helps to resist the shear sliding of the grains and results in the hardening of the films. In CrSiN coatings’ highest hardness and elastic modulus values were recorded with medium Si-doping while the highest Si-content demonstrated the lowest hardness and lowest modulus values. Solid solution formation of Si in crystalline CrN and reduction in grain sizes are responsible for hardness enhancement at low and medium silicon doping. However, at 28.5 at.% of Si-content, the hardness is lowered due to the formation of localized defects that are aligned parallel to the film growth direction. Furthermore at the highest Si-content, the formation of a high volume fraction of amorphous Si₃N₄ phase also disorders the crystal structure by lowering the density and therefore the compressive residual stress is reduced. As a result, coatings offer reduced yield strength under a stress normal to the coating surface. The dopants can alter the microstructures of the binary compounds from closely-packed
columnar grains to nanocrystalline structures surrounded by an amorphous phase. Aluminum and silicon doping enhance the mechanical hardness, Young's modulus, Yield strength ($H/E$) and the plastic deformation resistance ($H^2/E^2$) of CrN coatings. Al and Si atoms are also segregated about the grain boundaries to form amorphous structures that help to form strong interfacial bonding between the crystalline and amorphous phases. Near-edge X-ray absorption studies revealed the features corresponding to AlN (in CrAlN) and Si$_3$N$_4$ (in CrSiN) both in AEY and TFY modes without any significant changes in the spectral lineshapes with the subsequent increase in Al and Si-contents into the CrN system. This confirms the fact that the local environments of both Al and Si remained unchanged in CrN coatings with an increase in their at.%. Thus, the hardness and elastic modulus enhancement of these coatings were consistent with the NEXAFS studies. As seen from the above discussion, the structural and mechanical properties of these coatings, consisting of nanocrystalline and/or amorphous phases, are significantly affected by their grain boundary structures and crystalline phases.

A good combination of high hardness and toughness were seen in CrNiN coatings with the gradual increase in Ni-content. The existence of two stoichiometric peaks known as CrN and Cr$_2$N were observed via XPS studies of sputtered CrNiN coatings. At a higher Ni-content, the hardness reduction in CrNiN coatings was associated with the reduction of the CrN phase and the increase of the Cr$_2$N phase that changed the deformation mechanism via the grain boundary sliding. No significant lineshape changes in the near-edge absorption structures of these coatings either in AEY or TFY mode, with the gradual increase in Ni-content, indicate that the angular nature of the local bonding states remain unchanged with the higher nickel content. This shows that the types of bonding existing in these films are of same. Due to the appearance of large direct $d$-bonds in CrNiN coatings, the increase in $d$ sub-orbitals, and possible variations in valence results in the reduction of the crystalline domains and thereby the hardness of these coatings is lowered as the Ni-content is enhanced. The structural and electronic behavior analysis of the occupied and unoccupied partial density of states of CrNiN coatings with different Ni-dopant shows a subtle chemical shift and insignificant changes of lineshapes around the absorption edges. This confirms the reduction in grain sizes. Enhancement in coordination numbers, effective charge of ions, and the existence of metallic Ni were also detected via NEXAFS studies. As a result, the toughness of the films was improved, and the mechanical properties of the coatings were upgraded.
NEXAFS studies of sputtered CrAlN and CrSiN coatings around the N K-absorption edges also implying the local environments of aluminum and silicon were unmodified with the increase in their at.%. Good crystallinity, well-defined diffraction lines, and a (200) preferred orientation were shown when aluminum and silicon were incorporated into the chromium nitride system, and this also confirmed the high purity levels of the raw materials used in both series of coatings. Formation of multiple stable crystalline phases such as CrN, Cr$_2$N and Fe were established via XRD studies of these films. The appearance of these phases on the surface of these coatings is assumed to play remarkable roles in improving the structural, mechanical and local atomic bonding states of these coatings. As a consequence of spin-orbit coupling, and complex structure splitting among Cr$3d$-, Al$3p$-, Si$3p$ and N$2p$-states, the electronic and chemical bonding states of the sputtered films were altered.

3d transition metal oxide and metal nitride based materials exhibited a variety of interesting structural, mechanical and optical properties that afford them great opportunities to be utilized in many different applications. They are expected to play growing roles in energy related applications, such as solar energy harnessing as solar selective surface with reduced environmental pollutions. The solar selectivity of such coatings is dependent on the appropriate choice of a material with maximum absorptance (in the visible range) and minimum thermal emittance (in the IR range), structure of films, surface electronic bonding states, energy band-gaps, roughness of the surface and particle morphology. In order to achieve higher spectral selectivity, multilayer thin film coatings are also being developed by other researchers. In multilayer coatings, enhanced solar absorption is achieved via two mechanisms: intrinsic absorption by the individual layers and absorption due to the interference between the layers. Thus, future work could have been involved onto the development of 3d transition metal oxide and metal nitride based multilayer thin film coatings with the focus of optimized synthesis conditions to achieve an optimum solar selectivity. The addition of an anti-reflecting layer also contributes to improve the absorptance because of the anti-reflection effect without increasing the emittance. Furthermore, nanoindentation and NEXAFS studies on these films could have been also involved to realize the property-property correlation of sol-gel and sputtered thin film coatings.
APPENDIX 1

Molecular Structure, Physical Parameters and XPS Survey Scans of CuCoO Coatings with and without the Addition of GO

XRD studies reveal the spinel structure of Cu$_{75}$Co$_{2.25}$O$_4$ system without and with the addition of controlled amount of GO (graphene oxide), with space group $Fd\bar{3}m$ (227), $Z = 8$, and lattice parameter 8.122 Å. In a unit cell of Cu$_{75}$Co$_{2.25}$O$_4$ system, there are 6 copper atoms, 18 cobalt atoms and 32 oxygen atoms. Copper and cobalt atoms are shared in the tetrahedral and octahedral sites. Fig. 73 shows the spinel structure of Cu$_{75}$Co$_{2.25}$O$_4$ system drawn using GaussView 5.0.8 software. The volume of a unit cell is $5.35783 \times 10^{-28}$ m$^3$ while the weight of this spinel is $3.24478 \times 10^{-24}$ kg, which turns out to a density of 6056.15154 kg/m$^3$. Assuming the spinel grains are perfectly spherical in shape and making use of the two dimensional (2D) hexagonal lattice of GO with 60:40 carbon-to-oxygen ratio; atomic bond length = 1.42 Å; having a density $8.6256 \times 10^{-07}$ kg/m$^2$, we calculate the spinel weight per grain. Using density and wt.% of GO added, we obtain the graphene oxide area per spinel grain and GO weight respectively. Further, assuming that the spinel grains are distributed uniformly on the graphene oxides, we obtain the distance between spinel grains (GO sides per spinel grain, See Fig. 74). Results of such calculations are depicted in Table 32.

![Crystal structure of Cu$_{75}$Co$_{2.25}$O$_4$.](image)

Figure 75. Crystal structure of Cu$_{75}$Co$_{2.25}$O$_4$. 
Table 32. Physical properties of $\text{Cu}_{0.75}\text{Co}_{2.25}\text{O}_4$ with the addition of GO.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Grain diameter, $d$ (µm)</th>
<th>Spinel weight ($\times 10^{13}$ kg)</th>
<th>GO weight ($\times 10^{13}$ kg)</th>
<th>GO sides, $s$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}<em>{0.75}\text{Co}</em>{2.25}\text{O}_4$</td>
<td>4.92</td>
<td>3.78</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.75}\text{Co}</em>{2.25}\text{O}_4 + 0.1\text{wt.}%$ GO</td>
<td>4.64</td>
<td>3.17</td>
<td>0.32</td>
<td>19.17</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.75}\text{Co}</em>{2.25}\text{O}_4 + 0.5\text{wt.}%$ GO</td>
<td>4.62</td>
<td>3.13</td>
<td>1.57</td>
<td>42.68</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.75}\text{Co}</em>{2.25}\text{O}_4 + 1\text{wt.}%$ GO</td>
<td>4.00</td>
<td>2.03</td>
<td>2.05</td>
<td>48.75</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.75}\text{Co}</em>{2.25}\text{O}_4 + 1.5\text{wt.}%$ GO</td>
<td>3.90</td>
<td>1.88</td>
<td>2.86</td>
<td>57.63</td>
</tr>
</tbody>
</table>

Figure 76. Structure of typical $\text{Cu}_{0.75}\text{Co}_{2.25}\text{O}_4$ with the addition of GO, $d$ and $s$ are provided in Table 32.
Figure 77. Synchrotron radiation X-ray diffraction data of (Cu$_x$Co$_y$O$_z$ coatings at room temperature, 100 °C, 200 °C, and 300 °C acquired at the powder diffraction beamline at Australian Synchrotron, Melbourne.
Figure 78. Synchrotron radiation X-ray diffraction data of Cu$_x$Co$_y$O$_z$ thin film coatings with 1.5 wt% of graphene oxide at room temperature, 100 °C, 200 °C, and 300 °C acquired at the powder diffraction beamline at Australian Synchrotron, Melbourne.
Figure 79. XPS survey scans of sol-gel derived Cu$_x$Co$_y$O$_z$ coatings before and after etching.

Figure 80. XPS survey scans of sol-gel derived Cu$_x$Co$_y$O$_z$ + 0.1wt.%GO coatings before and after etching.
**Figure 81.** XPS survey scans of sol-gel derived Cu$_x$Co$_y$O$_z$ + 0.5wt.%GO coatings before and after etching.

**Figure 82.** XPS survey scans of sol-gel derived Cu$_x$Co$_y$O$_z$ + 1wt.%GO coatings before and after etching.
Figure 83. XPS survey scans of sol-gel derived Cu$_x$Co$_y$O$_z$ + 1wt.%GO coatings before and after etching.

Figure 84. SEM images of the sol-gel derived CuCoO thin film coatings deposited with different wt.% of GO: (a) Cu$_x$Co$_y$O$_z$, (b) Cu$_x$Co$_y$O$_z$+0.1wt.%GO, (c) Cu$_x$Co$_y$O$_z$+0.5wt.%GO, (d) Cu$_x$Co$_y$O$_z$+1wt.%GO, (e) Cu$_x$Co$_y$O$_z$+1.5wt.%GO.
Molecular Structure and Physical Parameters of Sputtered CrN and Cr(Al/Si/Ni)N Coatings

Figure 85. The crystal structure of (a) CrN and (b) Cr$_{0.75}$Ni$_{0.25}$N thin film coatings drawn via GaussView 5.0.8 software.

XRD studies reveal the structure of CrN and Cr$_{1-y}$Ni$_y$N, with space group $Fm-3m$ (225) and $Z = 4$. The lattice parameter of these coatings varies with different substituents and concentrations. In order to draw the typical crystalline structure, we assume that lattice parameter = 4.148 Å and $y = 25$ at.% (medium concentration of Ni). In a unit cell of CrN, there are 4 chromium atoms and 4 nitrogen atoms while in a unit cell of Cr$_{0.75}$Ni$_{0.25}$N, there are 3 Cr atoms, 1 atom of the substituent (Ni) and 4 N atoms. Similarly, in a unit cell of Cr$_{0.5}$Ni$_{0.5}$N ($y = 50$ at.%), there are 2 chromium atoms, 2 atoms of substituent (Ni) and 4 nitrogen atoms. Using the GaussView 5.0.8 software and aforementioned parameters, we have drawn the CrN and Cr$_{0.75}$Ni$_{0.25}$N crystal structures presented in Figs. 81. The lattice parameter calculations of CrN and Cr(Al/SiNi)N coatings were performed via NWChem 6.3 software and local density approximation (LDA) exchange-correlation potential within plane wave density functional theory framework. The simulated optimized lattice parameters are presented
From the simulated results it is observed that experimental and simulated results of CrN show good agreement with a maximum error of less than 1%.

Table 33. Lattice parameters of CrN and Cr(Al/Si/Ni)N coatings.

<table>
<thead>
<tr>
<th>Samples composition</th>
<th>Experiment</th>
<th>Simulation (accuracy = 0.027 eV)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration of dopants (Al, Si, Ni)</td>
<td>Lattice constant (Å)</td>
<td>Concentration of dopants (Al, Si, Ni)</td>
</tr>
<tr>
<td>CrN</td>
<td>-</td>
<td>4.220</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Low Al (≈ 10%)</td>
<td>4.150</td>
<td>-</td>
</tr>
<tr>
<td>CrAlN</td>
<td>Medium Al (≈ 25%)</td>
<td>4.130</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>High Al (≈ 40%)</td>
<td>4.110</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>Low Si (≈ 10%)</td>
<td>3.980</td>
<td>-</td>
</tr>
<tr>
<td>CrSiN</td>
<td>Medium Si (≈ 25%)</td>
<td>4.290</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>High Si (≈ 40%)</td>
<td>4.050</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>Low Ni (≈ 10%)</td>
<td>4.178</td>
<td>-</td>
</tr>
<tr>
<td>CrNiN</td>
<td>Medium Ni (≈ 25%)</td>
<td>4.169</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>High Ni (≈ 40%)</td>
<td>4.146</td>
<td>50%</td>
</tr>
</tbody>
</table>
Mohammad Mahbubur Rahman was born at Kishoreganj in Bangladesh on May 12, 1977. He has received his Bachelor of Science (Honors) and Master of Science (MSc) degrees in Physics from Jahangirnagar University in 1997 and 1998 respectively. Mr. Rahman completed his Master of Philosophy degree from the Department of Physics at Khulna University of Engineering & Technology (KUET) in 2007. Later Mr. M. M. Rahman has also received another Master of Science degree from the Department of Physics & Physical Oceanography at Memorial University of Newfoundland, Canada in 2009. He has been serving as a faculty in the Department of Physics at KUET from June 01, 2003 to April 09, 2010. In April 10, 2010 Mr. Rahman has joined as a faculty in the Department of Physics at Jahangirnagar University. He has published in total of 68 papers in peer-reviewed international, national journals and conferences held in different countries. Mr. Rahman has also received few national and international scholarships, awards and fellowships during his period of study and jobs at different universities. He has been holding professional memberships of 22 organizations around the world. Mr. Rahman has also significant contribution as reviewer and editorial board member in about 40 national and international journals.
REFERENCES

[15] M. Du, L. Hao, J. Mi, F. Lv, X. Liu, L. Jiang, S. Wang, Optimization design of Ti0.5Al0.5N/Ti0.25Al0.75N/AlN coating used for solar selective applications, Solar Energy Materials and Solar Cells, 95 (2011) 1193-1196.


[92] Q. Zhao, J. Jin, C. Li, Z. Wang, J. Zhang, Q. Ma, J. Cui, The preparation and study of graphene supported Co$_x$Mn$_{3-x}$O$_4$ nanocomposites as advanced oxygen reduction reaction electrocatalyst, in, 2013, pp. 348-351.


C. Feng, S. Zhu, M. Li, L. Xin, F. Wang, The effect of Hf on the oxidation and corrosion behavior of Ti 0.7Al 0.3N coating prepared by arc-ion plating, Oxidation of Metals, 71 (2009) 63-76.


[541] W.S. Yoon, M. Balasubramanian, K.Y. Chung, X.Q. Yang, J. McBreen, C.P. Grey, D.A. Fischer, Investigation of the charge compensation mechanism on the electrochemically Li-ion deintercalated Li₂₋ₓCo₁₋ₓNi₁₋ₓMn₁₋ₓO₂ electrode system by


