
Structural, Morphological, and Optical Characterizations of Mo, CrN and Mo:CrN Sputtered Coatings for Potential Solar Selective Applications

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Abstract

Mo, CrN, and Mo:CrN sputtered coatings synthesized onto silicon Si(100) substrates were investigated as solar selective surfaces and their potential applications in optical devices. These coatings were characterized using XRD, SEM, UV-Vis, and FTIR techniques. XRD investigation, showed a change in CrN thin film crystallite characteristic due to Mo doping. Compared to the CrN coating, the Mo:CrN film has a higher lattice parameter and lower grain size of 4.19 nm and 106.18 nm, respectively. FESEM morphology confirmed the decrement in Mo:CrN crystal size due to Mo doping. Optical analysis showed that in the visible range of the solar spectrum, the CrN coatings exhibit the highest solar absorptance of 66% while the lowest thermal emittance value of 5.67 was recorded for the CrN coating doped with Mo. Consequently, the highest solar selectivity of 9.6, and the energy band-gap of 2.88 eV were achieved with the Mo-doped CrN coatings. Various optical coefficients such as optical absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constants, and energy loss functions of these coatings were also estimated from the optical reflectance data recorded in the wavelength range of 190 – 2300 nm.
Keywords: Magnetron sputtering, metal nitride, coatings, solar absorptance, thermal emittance, solar selective surface, dielectric constant.

1. Introduction

Metal nitride-based compounds have been widely used as ceramic coatings since the 1980’s due to their superior hardness, excellent wear resistance, low friction coefficient, superior thermal stability, and corrosion resistance behaviours under detrimental environmental conditions [1-4]. Compared with other types of similar binary and ternary coatings, TiN or Ti–C–N, CrN ceramic coatings exhibit superior thermal stability [5]. In tribological applications, CrN coatings also demonstrate better performance than TiN coatings under dry and lubricated conditions. As such, CrN coatings are typically used as protective coatings for several tribological forming and casting applications, such as drawing dies, and moulds [5]. Perovskite CrMeN coatings, where Me = Ti, Si, Al, Ta, Nb, Ni, B, and Mo have been explored to improve physical, mechanical and other characteristics of CrN matrix. The ternary CrMeN coatings usually form cation solid solution (Ti, Al, Ta, Nb, Ni, and Mo) or anion solid solution (in cases of B or C). These solid solution-based coatings have received less attention than conventional coatings and as such, investigation of ternary Cr–Mo–N coatings would be timely [5].

Transition metal nitride-based coatings such as TiN, CrN, MoN, and ZrN have been previously characterized using XRD, and electron microscopy and hardness measurements via indentation method. The formation of cubic crystal lattice structures under non-equilibrium conditions was detected via XRD studies while greater hardness and superior resistance tolerance behaviours were acquired by those coatings [6]. Surface microstructures of Mo-based coatings studied via AFM technique indicated the grain size reduction with subsequent increase in acetylene flow rate [7]. Nanostructured Mo-based coatings deposited onto steel and hard metal substrates by magnetron sputtering technique exhibited a hardness of ~20 GPa together with very fine grains (~2 nm). Annealing in the range from 500 to 1000°C significantly improved the hardness and elastic modulus of these coatings along with a higher resistance to plastic deformation ratio [8]. Higher ductility of these coatings was also recorded for the samples annealed up to 600 °C.
The solar absorptance and thermal stability of Mo–SiO$_2$ double cermet solar selective coating via simulation-based work using standard optical constants within the wavelength range of 0.25–2.5 μm was reported. The Mo–SiO$_2$ double cermet absorber showed a high singular absorption of 0.945 while a dramatic increase in the reflectance spectra was observed at an incident angle above 60° [9]. The simulated data was well-consistent with the experimental results. The Mo-black solar selective coatings prepared by chemical methods from an aqueous solution of ammonium paramolybdate and nickel sulphate were studied for their optical band-gap and refractive index [10]. A high value of solar absorptance and lower value of thermal emittance were reported together with the suitable optical band-gap and refractive index values. Computer simulation was carried out to analyze the optical constants such as refractive index, dielectric constants and extinction coefficient of Mo/Al$_2$O$_3$ solar selective coatings by means of Maxwell-Garnett effective medium theory in the wavelength range of 200-2500 nm [11]. An optimal coatings thickness of 200 nm for the absorption layer was proposed in the visible region of the solar spectra where the absorption was recorded to be invariant with the coating’s thickness.

Surface-textured magnetron sputtered single-layer Mo coatings synthesised through the adjustment of deposition parameters onto the silicon Si(100) and stainless steel substrates characterized via XRD, SEM, AFM and optical studies exhibited a high solar absorptance and low emittance. It was reported that the controlled surface roughness and larger aspect ratio improves the solar absorption and reduces the thermal emittance values of this coating [12]. Tauc-Lorentz and Drude free-electron theories were used to model the optical constants and the dielectric nature of the coatings was reported. The annealing temperature effect on the microstructure and spectral selectivity of single layer Mo solar selective coatings was carried out by Xinkang and co-workers [13] in order to establish the mechanism for the degradation of optical properties. After annealing, notable changes in microstructure and compositions were observed. However, the optical properties of the coatings and their thermal stability significantly improved.

Mo/Mo–SiO$_2$/SiO$_2$ spectral selective absorbers deposited onto quartz substrate via co-sputtering method for high temperature applications showed high absorptance in the visible range and low thermal emittance in the infra-red range of the solar spectra [14]. After annealing at 800 °C, the thermal emittance of such absorber coatings was significantly reduced from 9.7% to 7.5%. However, the normal reflectance of the absorbers remained
almost unchanged in the UV–Vis range of the solar spectrum and increased slightly in the IR region after being annealed at 1073 K in vacuum. Novel Mo/ZrSiN/ZrSiON/SiO₂ solar selective absorbers prepared through magnetron sputtering on the stainless steel substrates were investigated for their temperature dependent solar selective performance. Systematic reduction of the thicknesses of the ZrSiN, ZrSiON and SiO₂ layers, significantly reduced the thermal emittance at 500 °C while the solar absorptance was unaffected. On the other, the high thermal stability up to 500 °C in vacuum, indicated that these absorber coatings could be a viable candidate for high temperature concentrated solar power applications [15].

Experimental studies and computer simulation-based analysis of transition metal nitride based-coatings have been conducted to investigate their structural, microstructural, morphological, mechanical and general optical studies [11, 12, 16-20]. Recently, many researches have been reported on the effect of Mo-doping on CrN film coating in order to investigate their local electronic bonding states, mechanical, and tribological properties [5, 21-23]. Detailed optical analysis in conjunction with the structural and morphological features of these kinds of coatings are extensively discussed in earlier reports [24-29], though we find that a holistic approach integrating other pertinent analyses such as FESEM imaging, XRD analysis and band-gap calculations in tandem with single oscillator model optical dispersion analysis, dielectric characterizations, and energy loss mechanisms analysis are relatively lacking. This motivates us to therefore incorporate these value-added analyses into the present study so that a clearer all-inclusive understanding of the crystallographic structures, morphological features and optical parameters could be established for Mo, CrN, and Mo:CrN thin film coatings.

2. Experimental

2.1 Film preparation

The UDP650 closed field unbalanced magnetron sputtering ion plating system (Teer Coatings Ltd, UK) was employed to prepare Mo, CrN, and Mo:CrN thin film coatings. The silicon Si(1000 , with 50 mm diameter and 3.0 or 1.5 mm thick, were used as substrates. A rotating sample holder which could provide a uniform exposure for growing the film was surrounded by four vertically mounted pure metallic targets (Cr, Mo). Two chromium targets and one molybdenum target (Cr, Mo, purity 99.9 %, size 345 mm × 145 mm × 8 mm) were used. The background pressure and working pressure during sputtering were 4 × 10⁻⁴ Pa and 15 × 10⁻²
Pa, respectively. Mixed Ar (99.999 %; flow rate at 50 sccm, used as working gas for sputtering) and N\textsubscript{2} (99.999 %) was used as reactive gas to form nitrides. The optical emission monitor (OEM) was used to control the N\textsubscript{2} reactive gas injected near the substrate holder. The entire synthesis process was carried out without any external heating to maintain the target to a substrate distance of 17 cm. Advanced Energy Pinnacle plus 5 kW, at a frequency of 250 kHz voltage mode was used to control the bias voltage while 6 kW DC current mode was used to control the target current supply. To coat the Mo:CrN films, 0.2 micron chromium adhesive layers was applied to promote the coating adhesion with a bias voltage of -80 V [30, 31].

2.2 XRD analysis

The XRD measurements of the coatings were carried out using a Bruker AXS D8 Advance (Germany) with Cu-\(K_a\) radiation (\(\lambda = 1.54\) Å). The XRD machine was operated at 40 kV and 40 mA coupled with a Lynx-eyed detector. The scan parameters used were: \(2\theta\) scan range 30°-90°, step size (degree): 0.01°, time/step: 0.15 s and total scan time/sample was ~15 minutes. Phase identification of the films was confirmed by matching the diffraction peaks with those of JCPDS database. The lattice parameters of the defined structures were estimated from the XRD peaks using standard Cohen–Wagner’s plot for cubic crystal structure and Cohen procedure for hexagonal crystal structure [32].

2.3 FESEM analysis

The morphological analysis of the sputtered coatings was performed by a field-emission scanning electron microscope (FESEM) using Zeiss Neon 40EsB FIBSEM, an Oxford Instruments Inca X-act SDD X-ray detector. 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 coatings were glued with double sided carbon tape affixed to the sample holders.

2.4 UV-Vis studies

The UV–Vis reflectance spectroscopy of the coatings was conducted to explore various optical parameters. A UV–Vis double beam spectrophotometer with 60 mm integrating sphere (Model: UV-670 UV-Vis spectrophotometer, JASCO, USA) was used to obtain UV-Vis reflectance spectra in the wavelength range from 190 to 2300 nm. For a given wavelength
range, the solar absorptance \( (\alpha) \) is defined as the weighted fraction between absorbed radiation and incoming solar radiation \( (I_{sol}) \) (popularly known as the Beckman-Duffie method) [33-35]:

\[
\alpha = \frac{\int_{0.19}^{2.5} I_{sol}(\lambda)(1-R(\lambda))d\lambda}{\int_{0.19}^{2.5} I_{sol}(\lambda)d\lambda}
\]

The UV-Vis reflectance spectroscopic data was also used to calculate and determine the other optical constants, such as solar absorptance, band-gap, refractive index, dielectric constants and energy loss functions of Mo, CrN and Mo:CrN sputtered coatings.

### 2.5 FTIR studies

Infrared analysis of the coatings was conducted using FTIR spectrometer (Perkin Elmer Spectrum 100 FTIR Spectrometer, USA). The wavelength from 2.5 to 14.5 μm was used to estimate their thermal emittance in the infrared ranges of the solar spectrum. The FTIR reflectance data collected in the range of 650–4000 cm\(^{-1}\) was converted to the corresponding wavelengths. A bare glass substrate was used for baseline correction of the system before recording the FTIR spectra of the coatings [36]. The thermal emittance \( (\varepsilon) \) is defined as the weighted fraction between emitted radiation and the Planck black-body distribution \( (I_p) \) and can be calculated using Eq. (2) [33, 37]:

\[
\varepsilon = \frac{\int_{2.5}^{15.36} I_p(\lambda)(1-R(\lambda))d\lambda}{\int_{2.5}^{15.36} I_p(\lambda)d\lambda}
\]

### 2.6 Solar selectivity

The solar selectivity, \( (s) \) is the key parameter of a selective surface which is defined as a ratio of solar absorptance, \( \alpha \) to the thermal emittance, \( \varepsilon \) and can be expressed by the following Eq. (3) [38]:

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

where \( \alpha \) is the solar absorptance of the coatings estimated in a wavelength range of 190 nm and 2300 nm while \( \varepsilon \) is the thermal emittance in the wavelength range between 2.5 μm and 14.5 μm. The air mass (AM) of solar spectrum, \( I_{sol} \) is 1.5 according to the ISO standard 9845-1 (1992).
3. Results and Discussion

3.1 XRD analysis of Mo, CrN and Mo:CrN coatings

The XRD patterns of the Mo, CrN and Mo:CrN coatings sputtered on silicon Si (100) substrates are presented in Figure 1. From Figure 1, broadened peaks were observed at (111), (002), (022) and (311) reflection planes. CrN, and γ-Mo₂N phases were seen at (111), and (200) crystal planes while (110) reflection plane confirms the presence of Mo phase. The broadened peaks for Mo phases observed at (110) and (220) crystal planes are centred at approximately $2\theta = 40.5^\circ$ and $2\theta = 87.6^\circ$ and the strongest peak of Mo phase was observed at (110) crystal plane. The characteristic Mo thin film peaks were believed to be broadened as a result of the nano-sized agglomerations around the film surfaces [31, 39]. In the case of Mo₂N and CrN in the first two bottom graphs (see Figure 1), a strong peak centred at $2\theta = 37.525^\circ$ corresponds to the (111) crystal planes in both graphs. The peaks centred at $2\theta = 43.6^\circ$ were for CrN and γ-Mo₂N phases at (002) and (200) reflection planes, respectively, are less intense from the previously discussed peaks. Other two peaks assigned as (022) and (311) reflection planes are due to the presence of CrN phase. However, there is no clear indication of the occurrence of CrMoN phase that might be attributed to the very small crystallite size or amorphous state of the solid solution of CrMoN matrix [31]. The broadening and shifting nature of the diffraction peaks is believed to be associated with the development of internal stress and change of inter-planar spacing, which arise from the formation of a substitutional solid solution structure [40, 41]. In the case of Mo:CrN structure, its peaks are shifted towards the lower Bragg angle sides is due to the result of the substitution of Cr atoms by Mo atoms. It is believed that the Mo atom are dissolved into CrN matrix and larger Mo atoms (201 Å) replaces the Cr atoms (185 Å) [5]. Consequently, the lattice parameters, inter-planar spacing, and grain sizes are changed, as seen from Table 1. A similar effect was also observed by other studies [42-45]. This is in accordance with Bragg's equation $2d\sin\theta = n\lambda$ (where $\lambda$ and $n$ are constants while $2\theta$ is inversely proportional with lattice distance $d$), the peaks end up with a certain peak shift [2]. In addition, the substrate negative bias voltage also can alter the preferred orientation of the growth plane of the coatings during the sputtering progression [46]. In sputtered coatings, the residual stress primarily arises from the working environment and elementary potentials of two sources: thermal and intrinsic stresses. Thermal discrepancy results in thermal stresses between the
coating and substrate during final cooling from deposition to room temperature. The thermal effect becomes more exaggerated when multilayer films are coated via sputtering [47].

XRD data were used to estimate the average crystallite size of CrN, Mo, and Mo:CrN phases via Debye–Scherrer equation,

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (4)

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width at half maximum (FWHM) and \( \theta \) is the diffraction angle. Estimated crystallite sizes are listed in Table 1. Table 1 shows that compared to the CrN matrix, the Mo:CrN films have higher lattice parameter and higher grain sizes. This is due to the formation of MoN phases via Mo interaction with N around the grain boundaries of CrN phase [31]. It is also assumed that the enlargement of both the lattice parameter and grain size of Mo-doped CrN coatings is due to the fact that the Mo atoms may not only replace the Cr on their sites, but they coalesce and agglomerate around the grain boundaries of the coating matrix. This supports the idea of the presence of the Mo phase in the coating structure.

The development of intrinsic stresses and its magnitude depends on the deposition conditions, sputtering gases working pressures, substrate to target distance, reference potential on substrate, coating’s thickness and stoichiometry [48, 49]. Mohammadpour et al. and Yousaf et al. have investigated the effect of metallic Al-doped TiN coatings on their physical and mechanical characteristics [50, 51]. CrN (111) phase observed at \( 2\theta = 37.53^\circ \) has a lattice parameter of 4.14 Å is in good agreement with other literatures [41, 43, 52]. The lattice parameters of CrN and Mo:CrN phases were also found to be in good agreement with other reports [41, 43].

3.2 Morphological features of Mo, CrN and Mo:CrN coatings via FESEM studies

In order to investigate the surface morphology of Mo, CrN, and Mo:CrN coatings sputtered on silicon substrates, the samples were analysed using FESEM technique and results are shown in Figure 2. Figure 2(a) shows that the surface morphology of Mo/Si coating is markedly different from those of CrN and Mo:CrN. The Mo/Si coating displays uniform, fine, smooth, dense and compact surface structure the grain sizes seemed to be relatively
smaller than the other two coatings. CrN/Si and Mo:CrN/Si coatings exhibit uniform structured films with larger grains and “loose” structures which are caused by a non-reactive nucleation. The CrN FESEM morphology indicates irregular, rougher grain with sharp edges. The Mo-dopant to the CrN system exhibited refined edged and slightly increased grain sizes. This means that due to the Mo-doping, both the surface morphology and grain shapes are reformed with regular mould-like structures seen around the surface of the coatings. At the same time, surface roughness seems to dissipate in the Mo:CrN coatings. This may suggest that the Mo atoms are diffused around the CrN matrix during the sputtering processes and thereby stimulated grain growth is eventually acting as the nucleation site for lattice distortions. This is in good agreement with the XRD results that the substitution of Cr atoms by Mo atoms help to coalescence and agglomeration of the Mo particles to form larger grains. These features were supported in a previous study by Hones et al. [23]. They showed that CrN structures consist of a combination of larger elongated rhombohedral and small cubic crystallites while the Mo-doped CrN structure has grains with an average size of 100 nm. At a closer look, a substructure of these grains appears with a crystallite size of about 25 nm [23].

The dense and closely packed structures of Mo:CrN morphology would exhibit more stability as a selective surface at high temperatures. On the other side, such coatings are more mechanically reliable than the CrN coatings without doping [31]. The surface roughness would produce a gradient in the optical constants rather than a sharp discontinuity at the interface. Kang and Kim [53] indicated that the gradient in the optical constants strengthen the optical behaviour of such kind of coatings. The higher solar absorptance with the CrN coatings might be related to the fact that higher surface roughness gives lower dissipation of incident solar radiation. However, a better solar selectivity was attained by the Mo-doped CrN surface because the lower roughness leads to diminish the thermal emissivity, and then enhance the solar selectivity feature.

EDS analysis gives the elemental chemical compositions, and the atomic concentrations Mo, CrN and Mo:CrN coatings. The EDS data collected at different surface areas of these coatings are tabulated in Table 2.

3.3 Optical characterizations of Mo, CrN and Mo:CrN coatings

3.3.1 UV-Vis investigations
The solar absorptance of Mo, CrN and Mo:CrN coatings, measured from the UV-Vis reflectance data, as a function of wavelength within the range of 190-2300 nm, shown in Figure 3, is displayed in Table 3. Beckman-Duffie method described in equation (1) was used to calculate the solar absorptance values of these coatings [38, 54]. From Figure 3, it can be concluded that among the three coatings, in the visible range of solar spectrum, the CrN coating shows the lowest reflection of the solar radiation while Mo coating (being the sample with the highest Mo concentration) exhibits the highest reflection due to its metallic nature. On the other hand, Mo-doped CrN coating shows a reflectivity above CrN coating because Mo atoms agglomerate in the CrN structure and acting as scattering centres and traps for the incident light [55]. It is believed that Mo-doping in CrN matrix affects its band structure which clearly influences the solar selective characteristic of Mo:CrN system as seen in Figure 3. This behaviour confirms that the solar absorptance of CrN coating has been slightly dropped while Mo was doped to form Mo:CrN system.

### 3.3.2 FTIR results

Optical reflectance data measured via FTIR spectroscopy in the wavelength range from 2.5 to 14.5 µm shown in the following Figure 4, was utilized to estimate the thermal emittance values of Mo, CrN, Mo:CrN coatings using the Beckmann-Duffie method described in Eq. (2) [38, 54]. The estimated thermal emittance values of Mo, CrN, and Mo:CrN coatings are presented in Table 3. The Mo-doped CrN coating has the lowest thermal emittance than that of CrN coating (in the infrared range) suggesting that the addition of Mo and subsequent interactions of Mo atoms with that of the CrN lead to modify its band structures.

### 3.3.3 Solar selectivity results

The solar selectivity of Mo, CrN, and Mo:CrN coatings are presented in Table 3. From Table 3, it is seen that, among the three studied coatings, Mo:CrN system shows the highest selectivity. Since the band structures of Mo:CrN matrix is modified with Mo-dopant, it clearly influences the solar selective as seen from Table 3. The solar selectivity of Mo:CrN has improved from 8.5 to 9.6 due to the improvement of coating’s thermal emissivity from 7.1 to 5.6. This indicates a good potential for these materials to be used in solar selective absorber applications.
3.3.4 Optical band-gap analysis

The optical characteristics of absorber materials strongly depend on the wavelength of the incident solar radiation. When solar radiation is brought onto a certain material, a portion of the incoming light is absorbed as a result of excitations of molecular and atomic motions to a specific energy level. The photon energy of visible spectrum is sufficiently high for the absorption such atoms. A linear relationship between the solar absorption coefficient and photon energy facilitates investigation of the band structure and the type of transitions involved in absorption process, and reflected in the following equation [56]:

\[ \beta = 2.3026 \frac{A}{d} \]  

(5)

where \( \beta \), \( A \), and \( d \) are the absorption coefficient, optical absorbance expressed as percentage in terms of UV-Vis reflectance data (calculated as \( A = 100\% - R\% \)), and the coating’s thickness, respectively.

The absorption coefficient of as-deposited Mo, CrN, and Mo:CrN sputtered coatings as a function of incident photon energy is shown in Figure 5. Figure 5 clearly shows that CrN coatings possess the highest absorption coefficient while the absorption coefficient of Mo:CrN is intermediate between Mo and CrN coatings. The solar absorption of materials, at a specific wavelength, is related with the excitation of electrons in atoms and molecules to higher energy states.

Tauc relation is useful in studying the band structure and the type of electronic transitions involved during the absorption of solar radiation in crystalline and amorphous materials [56-58]:

\[ \beta h\nu = A(h\nu - E_g)^z \]  

(6)

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

Using the Tauc plots of \((\beta h\nu)^2\) vs \(h\nu\), for Mo, CrN and Mo:CrN coatings, the energy band-gaps estimated from the intercepts of the linear portion of the curves and extrapolating them to zero along the energy axis are presented in Table 4. Energy band-gap data show that Mo coating has the highest value of 3.78 eV and the CrN coating has the lowest value for the
band-gap energy. We conclude that the higher band-gap of Mo/Si coating is related to the surface oxidation of the coating (a very thin MoO$_3$ layer) during the synthesis process. The dielectric behavior of CrN coating was improved from 2.67 eV to 2.88 eV when doped by Mo-metal. As discussed previously, Mo-doping on CrN coating leads to enhance the agglomeration along the preferred orientation, enlarges the grain size and thereby reduces the density of grain boundaries. All these factors eventually lead to release the trapped free electrons in the grain boundaries, when an incident photon with specific energy interacts with the coating; some portion of the incident energy is absorbed by the electrons resulting to excite them to a higher energy level if the absorbed energy is $\geq E_g$. The enhancement of optical band gap can also be explained through the ($\Delta E_g^{BM}$) Burstein-Moss relation [59]:

$$\Delta E_g^{BM} = \frac{1}{2m_{vc}} (3\pi^2 n)^{2/3}$$

(7)

where $m_{vc}^*$ is the electron effective mass estimated from $m_v$ (effective electron mass in valance band) and $m_c$ (effective electron mass in conduction band), $n$ is the carrier concentration.

### 3.3.5 Refractive index and extinction coefficient analysis

The refractive index, $n$ and extinction coefficient, $k$ of Mo, CrN and Mo:CrN coatings calculated using the UV-Vis reflectance data in the wavelength range of 190 to 2300 nm are shown in Figures 7 and 8, respectively. The complex refractive index of materials is defined by,

$$n^* = n + ik$$

(7)

The extinction coefficient, $k$ could be directly calculated using the absorption coefficient, $\beta$ via following relation,

$$k = \frac{\beta\lambda}{4\pi}$$

(8)

In terms of the reflectance data, $R$ and extinction coefficient, $k$ real part of the complex refractive index is defined using the following equation,

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}$$

(9)
Figures 7 and 8 show that CrN coatings have the highest values for the refractive index and extinction coefficient within the observed wavelength range. The significant dispersion behaviors of CrN coating, which affects the $n$ and $k$ values, are arisen from the resonance effect between the incoming solar radiation and electronic polarizability. Our findings were consistent with earlier reported results [60]. These optical results indicate that CrN coating has better homogeneity and less porosity.

3.3.6 Dielectric characterizations

Figures 9 and 10 show the real and imaginary parts of dielectric constants, of Mo, CrN and Mo:CrN coatings, as a function of wavelength of the incident solar radiation. The frequency dependence of electron excitation spectra of a solid material can be defined in terms of complex dielectric function,

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = (n(\omega) + ik(\omega))^2$$

(10)

where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of the complex dielectric constant, respectively and are given by the following relations [61],

$$\varepsilon_1 = n^2 - k^2$$

and

$$\varepsilon_2 = 2nk$$

(11)

where $\varepsilon_1$ represents the amount of polarization energy stored in dielectric medium and $\varepsilon_2$ characterizes the energy loss of those media. The power loss in terms of heat as a loss factor, generally, produced from inelastic scattering process during the charge transfer and charge conduction mechanisms of a dielectric medium. In specified light frequency range of interest, thin film coatings having a low energy-loss nature, when they have a greater $\varepsilon_1$ to $\varepsilon_2$ ratio, this is due to the increase in the electron density of the films. The improvement in crystallinity of the film can decrease the degree of electron scattering and increase the free-electron density [62, 63].

3.3.7 Energy loss analysis

The ratio of the real to imaginary part of the dielectric constants defines the power loss (loss tangent) of a material,

$$\tan\delta = \frac{\varepsilon_2}{\varepsilon_1}$$

(10)
The loss tangent demonstrates the optical power loss in mechanical and oscillatory dissipative systems. Figure 11 shows the variation of $\tan \delta$ of Mo, CrN and Mo:CrN coatings as a function of photon energy. As seen from Figure 11, it can be noted that the variation of loss tangent of these coatings resembles the same behavior of the imaginary part of the dielectric constant. It also indicates that the tangent values of these coatings are significantly low. This applauds some valuable optical qualities of these films due to lower energy losses and lower scattering of the incident solar radiation. Figure 11 also confirms the fact that energy loss has improved for the Mo-doped CrN composite.

The other energy loss functions associated with the inelastic scattering of electrons in solid thin film coatings are known as volume energy loss function, $V_{el}$ and surface energy loss function, $S_{el}$ [64].

\[
V_{el} = \text{Im} \left( -\frac{1}{\varepsilon(\omega)} \right) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \quad (11)
\]
\[
S_{el} = \text{Im} \left( -\frac{1}{\varepsilon(\omega) + 1} \right) = \frac{\varepsilon_2}{(1+\varepsilon_1)^2 + \varepsilon_2^2} \quad (12)
\]

The $V_{el}$ and $S_{el}$ values were obtained from the real and imaginary parts of the dielectric constant of the Mo, CrN and Mo:CrN coatings using equations (11) and (12). The volume and surface energy loss functions of investigated coatings, as a function of $h\nu$, are shown in Figures 12 and 13. As observed in these Figures, the $V_{el}$ and $S_{el}$ decrease rapidly with the increase in incident photon energy and no significant changes either in volume energy or surface energy losses are detected above 3.65 eV of the incident photon energies. It was also seen that as the incident photon energy reaches to above 1.65 eV, for CrN coatings, both $V_{el}$ and $S_{el}$ values were slightly dropped. This confirms CrN coatings are optically better than the other two coatings. Further investigation also reveal that surface energy loss of the coatings is considerably lower compared to the value of the volume energy loss functions ($V_{el} > S_{el}$) for any incident photon energies. This indicates that the loss of energy of a free charge carrier when passing through the bulk of the film is much larger than that when traveling through to the exterior surface of such coatings. These findings are in good agreement with those obtained in dielectric studies of other coatings [65, 66]. It is also assumed that while passing through a medium, as a result of the excitation energy of the plasma oscillations of conduction electrons, some energies are lost by the wild moving charge carriers [67].
4. **Conclusions**

Mo, CrN and Mo-doped chromium nitride coatings fabricated using magnetron sputtering system were studied by means of structural, surface morphological and optical/dielectric studies in order to establish their phase forming behavior, microstructural changes and electromagnetic response upon exposure to the sunlight. XRD studies confirmed that the addition of Mo into the CrN matrix led to the formation of solid solution phases including Mo$_2$N, CrMoN$_x$, and Cr$_2$N. Improvement in the film crystallinity was observed upon the Mo-doping. FESEM images showed the homogeneity of the coating’s surface. CrN films demonstrated the highest value of solar absorptance 62% while a significant reduction in the thermal emittance from 31.5% (for CrN phase) to 5.6% (for Mo:CrN phase) was observed. Consequently, CrN films exhibited the highest solar selectivity value of 11.1. In a similar fashion, CrN films showed superior values for other optical parameters such as refractive index, extinction coefficient, and dielectric functions. Findings from this study would provide opportunity for future development of metal nitride-based Mo, CrN, and Mo:CrN thin film coatings for various industrial applications, especially in the area of solar selective absorbers.

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**References**


Figure 1. XRD spectra of the as-deposited Mo, CrN, and Mo:CrN sputtered coatings synthesized on silicon substrates.

Figure 2. FEMSEM images of: (a) Mo, (b) CrN, and (c) Mo:CrN sputtered coatings.
Figure 3. UV-Vis reflectance spectra of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of wavelength.

Figure 4. FTIR reflectance spectra of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of wavelength.
**Figure 5.** Absorption coefficient of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of photon energy.

**Figure 6.** Plots of $(\beta hv)^2$ vs $hv$ of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of wavelength.
Figure 7. Refractive index of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of wavelength.

Figure 8. Extinction coefficient of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of wavelength.
Figure 9. Real part of dielectric constant of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of wavelength.

Figure 10. Imaginary part of dielectric constant of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of wavelength.
Figure 11. Loss tangent of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of photon energy.

Figure 12. Volume energy loss of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of photon energy.
Figure 13. Surface energy loss of Mo, CrN, and Mo:CrN sputtered coatings deposited onto silicon substrates as a function of photon energy.
Table 1. Lattice parameters and grain size of Mo, CrN and Mo:CrN sputtered coatings.

<table>
<thead>
<tr>
<th>Coatings name</th>
<th>Lattice parameter, (a) (Å)</th>
<th>Grain size (±10%), (D) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>3.17</td>
<td>106.18</td>
</tr>
<tr>
<td>CrN</td>
<td>4.14</td>
<td>112.73</td>
</tr>
<tr>
<td>Mo:CrN</td>
<td>4.19</td>
<td>161.45</td>
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</table>

Table 2. EDS analysis of the as-deposited \(\text{Cr}_x\text{Mo}_{1-x}\text{N}_y\) magnetron sputtered films.

<table>
<thead>
<tr>
<th>Coatings name</th>
<th>Mo (at.%)</th>
<th>Cr (at.%)</th>
<th>N (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CrN</td>
<td>-</td>
<td>92.42</td>
<td>7.58</td>
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<tr>
<td>Mo:CrN</td>
<td>24.35</td>
<td>70.12</td>
<td>5.53</td>
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</table>

Table 3. Solar absorptance, thermal emittance and solar selectivity values of Mo, CrN and Mo:CrN sputtered films.

<table>
<thead>
<tr>
<th>Coatings name</th>
<th>Solar absorptance, (\alpha) (%)</th>
<th>Thermal emittance, (\varepsilon) (%)</th>
<th>Solar selectivity, (s = \alpha/\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>44.7</td>
<td>31.5</td>
<td>1.4</td>
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<tr>
<td>CrN</td>
<td>62</td>
<td>7.1</td>
<td>8.5</td>
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<tr>
<td>Mo:CrN</td>
<td>53.5</td>
<td>5.6</td>
<td>9.6</td>
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Table 4. Energy band-gap values of Mo, CrN and Mo:CrN sputtered films.

<table>
<thead>
<tr>
<th>Coatings name</th>
<th>Band-gap energy, (E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>3.78</td>
</tr>
<tr>
<td>CrN</td>
<td>2.67</td>
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<tr>
<td>Mo:CrN</td>
<td>2.88</td>
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</table>
Highlights

1. Mo, CrN, and Mo:CrN sputtered coatings were investigated for solar selective surface and optical applications.

2. Changes in crystallite characteristics of CrN films were observed due to Mo doping.

3. Lattice parameters and lower grain sizes of the films were modified due to the Mo-content.

4. Normal and anomalous dispersion behaviors of the coatings were detected.

5. CrN coatings have better homogeneity and less porosities.