Spectral Selectivity of unbalanced Magnetron Sputtered TiN, TiAlN and TiAlSiN Coatings: XRD, SEM and Optical Analyses

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Abstract

TiN, TiAlN (Al concentrations vary from low to high atomic %) and TiAlSiN coatings synthesized on AISI M2 steel substrate via unbalanced magnetron sputtered technology were developed for selective solar surface applications. XRD, SEM, UV-Vis and FTIR spectroscopies were used to characterise the crystalline structure, surface morphology, and optical selectivity of the coatings. Optical studies showed that the optical absorptance, in the visible range, of the TiN coatings was improved significantly from 25% to 74% with increase of Al-doping. However, an increase of optical absorptance of up to 50% resulted from coatings doped simultaneously with Al and Si. With the high Al-content, the optical emittance, in the IR range, of TiN coatings decreased from 4.5% to 3.4% whereas simultaneous addition of Al and Si to the TiN coatings resulted in a reduction of the emittance down to 4%. The highest optical selectivity of 21.76 was achieved with Al only doping and 12.50 with simultaneous Al and Si doping to the TiN matrix.

Objectives

In this study we investigated the potential development of magnetron sputtered TiN, TiAlN and TiAlSiN coatings for solar selective surfaces applications.

Materials and Characterisation Techniques

- TiN, TiAlN (Al concentrations vary from 15% to 25% and TiAlSiN coatings synthesized on AISI M2 steel substrate via unbalanced magnetron sputtered technique
- XRD measurements
- SEM and EDAX measurements
- Double beams UV-Vis spectrophotometer (UV-670 UV-Vis, JASCO, USA)
- FTIR spectrometer (PERKIN Elmer Spectrum 100)

Optical Properties

Optical properties of the coatings were analysed by measuring the optical reflectance as function of wavelength via UV-Vis and FTIR spectrometers in the range of IR ~ far IR, respectively. Using the reflectance data, R(λ), the solar absorptance (α) and the solar emittance (ε) of these coatings were calculated using the following equations.

$$\alpha(\lambda) = \frac{\int_{0.19}^{25} I_{Sol}(\lambda)\,(1-R(\lambda))d\lambda}{\int_{0.19}^{25} I_{Sol}(\lambda)\,d\lambda} \quad (1)$$

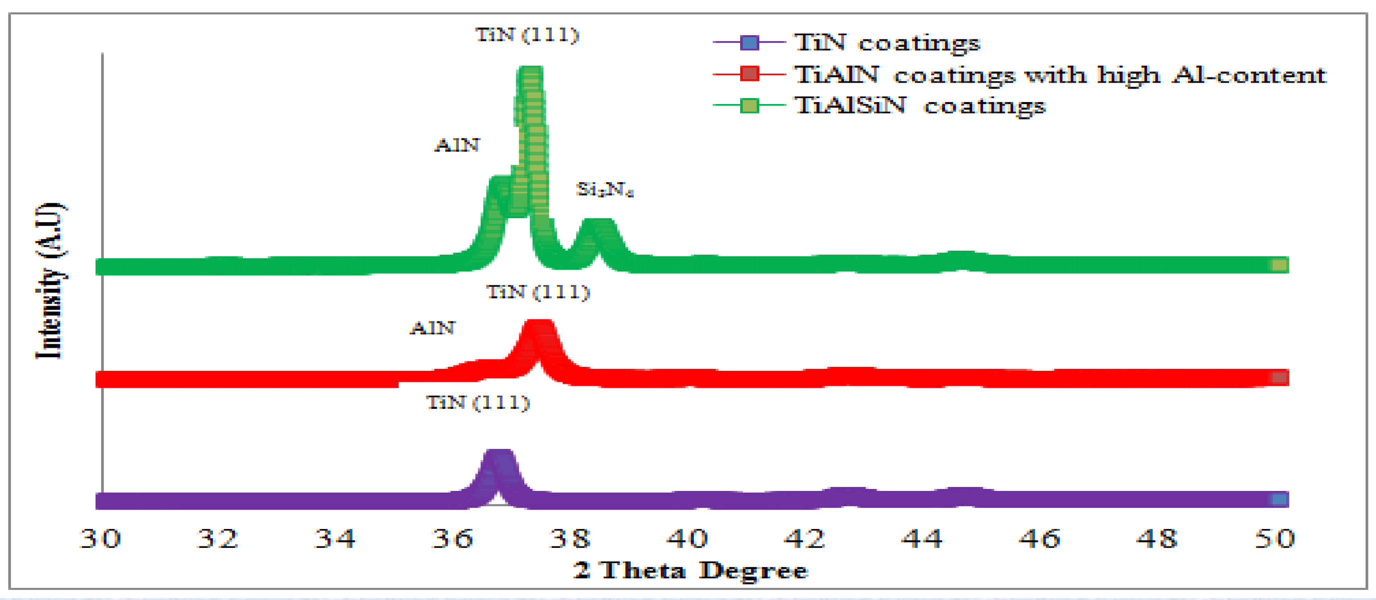
$$\varepsilon(\lambda) = \frac{\int_{2.5}^{15} I_P(\lambda)\,(1-R(\lambda))d\lambda}{\int_{2.5}^{15} I_P(\lambda)\,d\lambda} \quad (2)$$

The solar selectivity (s) is the ratio of absorptance (in UV-Vis range) and emittance (in IR range).

$$s = \frac{\alpha(\lambda)}{\varepsilon(\lambda)} \quad (3)$$

Results are summarised in Table 3.

XRD Studies



- All three coatings show the TiN phase with (111) orientation. This (TiN (111)) peak is observed to be shifted towards higher Bragg angles as the dopants (Al or Si) are added. This peak shift indicates contraction of lattice unit cell size by the substitution of larger Ti (0.147 nm) doping atoms with smaller Al (0.143 nm) and Si (0.134 nm) doping atoms.

- Due to spinoidal decompositions of TiAlN and TiAlSiN coatings, h-AlN and h-Si_3N_4 are formed in TiAlN and TiAlSiN coatings [1].
- These decompositions are based on the rise of free energy of TiAlN and TiAlSiN coatings compared to their constituents. Some sort of possible retarding forces might be also responsible for such decomposition processes [1-2]

SEM & EDAX Studies

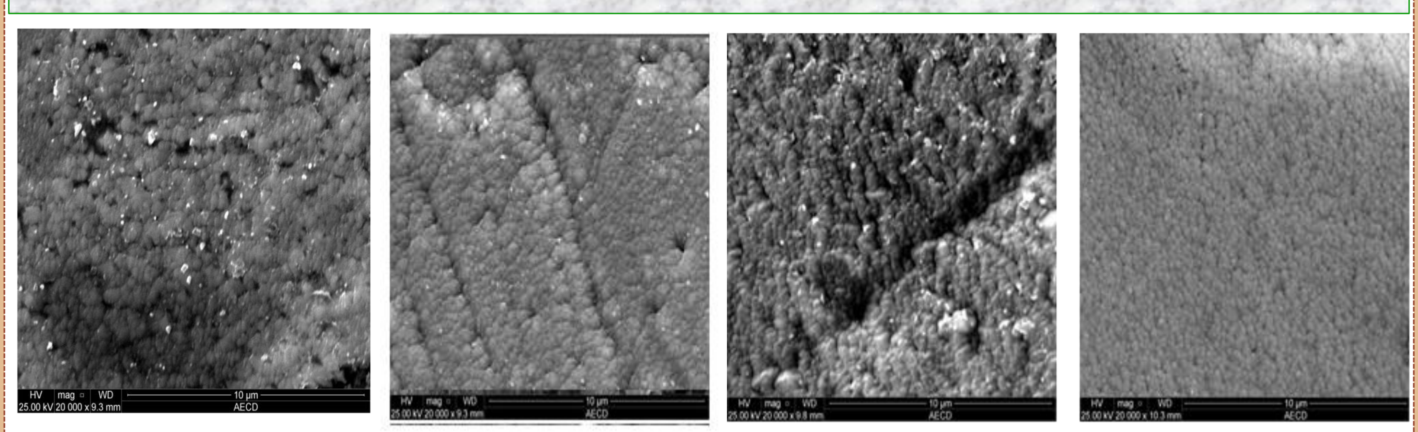
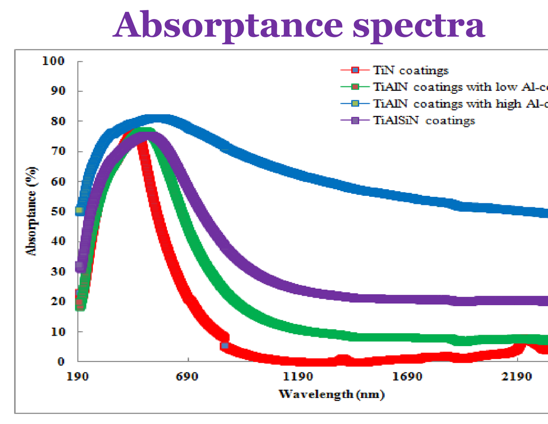


Table 1: EDAX analysis for the atomic compositions of TiN, TiAlN and TiAlSiN magnetron sputtered coatings.

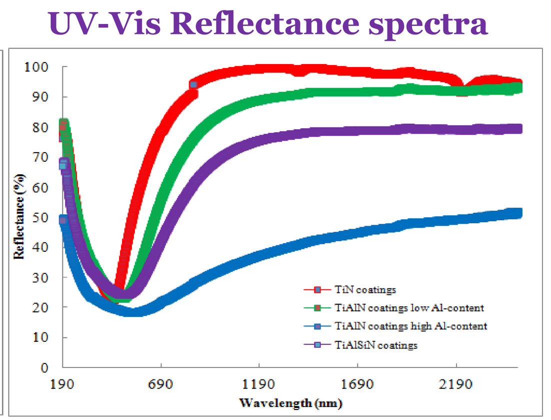
Sample	[Al]	Ti %	N %	Al %	Si %
TiN	-	88.43	11.57	-	-
TiAlN	Low	49.36	15.62	35.02	-
	High	32.47	17.50	50.03	-
TiAlSiN	-	60.86	15.21	18.80	5.13

Optical Selectivity

Absorptance spectra



UV-Vis Reflectance spectra



FTIR Reflectance spectra

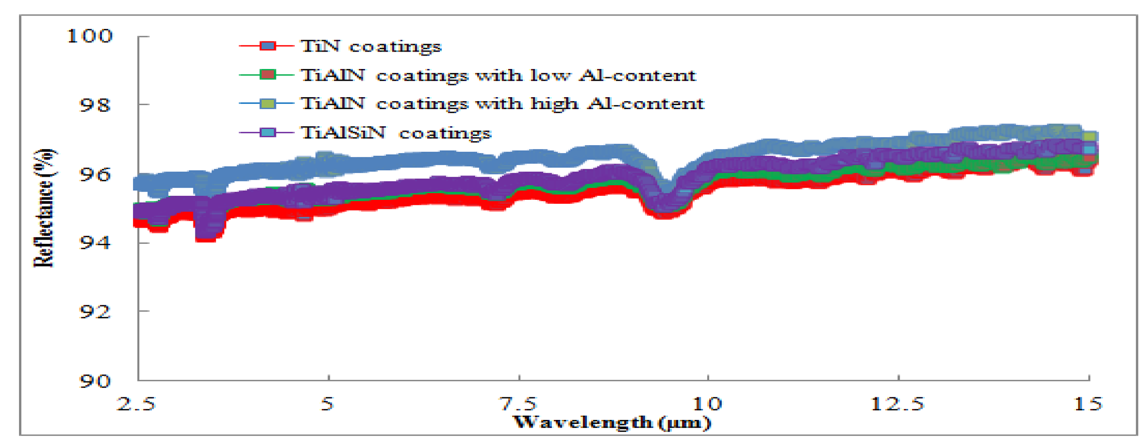


Table 2: Solar absorptance, and solar emittance values of our coatings

Sample	[Al]	Solar absorptance (α)	Solar emittance (ε)
TiN	-	0.25	0.045
TiAlN	Low	0.38	0.041
	High	0.74	0.034
TiAlSiN	-	0.50	0.040

Table 3: Optical selectivity of various transition metal nitride coatings

Sample	[Al] or x	Substrate	Deposition method	Absorptance (α) and emittance (ε) calculation method	Selectivity (α/ε) value
TiN	-	Steel	Sputtering	UV-Vis and FTIR reflectivity	5.55 [This work]
TiAlN	Low	Steel	Sputtering	UV-Vis and FTIR reflectivity	9.26 [This work]
	High	Steel	Sputtering	UV-Vis and FTIR reflectivity	21.76 [This work]
TiAlSiN	-	Steel	Sputtering	UV-Vis and FTIR reflectivity	12.50 [This work]
TiAlN	-	Copper	Sputtering	Solar spectrum reflectometer and emissometer	12.9 [3]
TiAlN/TiAlON	-	Copper	Sputtering	Solar spectrum reflectometer and emissometer	15.2 [3]
$Ti_{1-x}Al_xN$	0.21	Copper	Sputtering	UV-Vis and FTIR reflectivity	5.4 [4]
	0.58	Copper	Sputtering	UV-Vis and FTIR reflectivity	5.0 [4]
TiAlN/TiAlON/Si_3N_4	-	Copper	Sputtering	Solar spectrum reflectometer and emissometer	13.6 [3,5,6]
TiAlN/TiAlON/Si_3N_4	-	Glass	Sputtering	Solar spectrum reflectometer and emissometer	13.3 [3]
TiAlN/TiAlON/Si_3N_4	-	Stainless steel	Sputtering	Solar spectrum reflectometer and emissometer	7.4 [3]
TiAlN/TiAlON/Si_3N_4	-	Nickel	Sputtering	Solar spectrum reflectometer and emissometer	6.7 [3]

- α_{max} (TiN coatings) = 77.30%
- α_{max} (TiAlN coatings with low Al-content) = 77.10%
- α_{max} (TiAlN coatings with high Al-content) = 81.52%
- α_{max} (TiAlSiN coatings) = 77.71%

Conclusions

- Optical selectivity of unbalanced magnetron sputtered TiN coatings, doped with Al and Si, improved significantly .
- Optical selectivity (α/ε) increased from 5.55 to maximum of 21.76 for coatings with high Al-content.
- Homogeneous, dense and uniform surface microstructure of these 3d transition metal nitride based coatings was induced with addition of Al and Si dopants.

References

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