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Spectral properties and thermal stability of CrN/CrON/Al_2O_3 spectrally selective coating

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ABSTRACT

Multilayered CrN(H)/CrN(L)/CrON/Al_2O_3 spectrally selective coatings, designed with a gradually decreasing refractive index from the base layer to the top layer, were deposited on stainless steel substrates by reactive DC magnetron sputtering. The thicknesses of the CrN(H), CrN(L), CrON, and Al_2O_3 layers were optimized to achieve the best spectral properties. The thermal stability test was carried out at 300–500 °C in air. An absorptance of 0.93 and a thermal emittance of 0.14 were obtained when the CrN(H)/CrN(L)/CrON/Al_2O_3 multilayer coating comprised 60 nm-thick CrN(H), 50 nm-thick CrN(L), 40 nm-thick CrON, and 40 nm-thick Al_2O_3 layers. The CrN (H)/CrN(L)/CrON/Al_2O_3 was thermally stable up to 400 °C in air. Oxidation of the CrN(L) layer and phase transformation of the CrON layer destroyed the multilayered structure and degraded the spectral properties when the CrN(H)/CrN(L)/CrON/Al_2O_3 was heated at 500 °C in air.

1. Introduction

Spectrally selective absorbers utilized for solar photo-thermal conversion have been extensively studied for several decades [1–3]. The spectrally selective absorber must have a specific spectral selectivity, i.e., high absorptance (α) in the solar irradiation region (0.3 μm to 2.5 μm) and low thermal emittance (ε) in the infrared region (>2.5 μm). Several spectrally selective absorbers have been proposed to meet these optical characteristics. Among these, the absorber/reflector tandem absorber is potentially commercialized because the layers in the tandem absorber exhibit excellent spectral selectivity [4–6]. Generally, an absorber/reflector tandem absorber comprises a spectrally selective coating to absorb solar radiation and transmit infrared (IR) radiation and a highly IR-reflective metal substrate to reflect IR radiation. This can be achieved using a grade metal multilayer structure, the refractive index (n) and extinction coefficient (k) decrease gradually from the base layer to the top layer, to yield high conversion efficiency (α/ε) [7–9]. Moreover, an antireflective (AR) layer is usually deposited on the surface of spectrally selective coating to reduce the reflection from the front surface.

Thermal stability is crucial for the spectrally selective coating. Conversion efficiency of the coating gradually degrades when operating at an elevated temperature, and, thus, eventually fails. The thermal stable and intrinsic absorption in the solar region have been the subject of few studies on the constituent layer of spectrally selective coatings [10–12]. Transition metal nitrides/oxides have excellent thermal stabilities and outstanding resistance against oxidation, making them applicable in a strict environment [13,14]. Additionally, optical properties of the transition metal-based nitrides/oxides can be tailored by varying the stoichiometry because free electron density in the d band changes with composition of the transition metal [15]. Fan et al. found that the rf-sputtered Ni/Cr-Cr_2O_3 tandem absorber is thermally stable up to 300 °C in air [16]. Barshilia et al. prepared Cr_xO_y/Cr/Cr_2O_3 spectrally selective coatings by pulsed sputtering and found that the coatings are stable in air up to 250 °C for 250 h [17]. Chromium oxynitrides have also been developed as the spectrally selective coatings in a tandem structure. Selvakumar et al. prepared CrMoN(H)/CrMoN(L)/CrON multilayer coatings on stainless steel (SS) substrate and aluminum substrate for mid-temperature solar thermal applications. The CrMoN (H) contains more metal than CrMoN(L) in their study, and the refractive index decreases gradually from the base layer (CrMoN(H)) to the top layer (CrMoN(L)) [18]. Wu et al. deposited CrN_xO_y spectrally selective coatings on Cu substrate and Si substrate by reactive DC magnetron sputtering and found that the coating on Cu substrate is stable at 278 °C in air for 300 h [19].

In this work, the CrN(H)/CrN(L)/CrON/Al_2O_3 spectrally selective coating, designed to achieve a gradual decreasing refractive index from the base layer to the top layer, was deposited on a SS substrate

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by reactive DC magnetron sputtering. The structure and optical properties of the CrN(H), CrN(L), CrON, and Al_2O_3 layers were determined. The aim of this paper is to investigate the effects of the thickness of CrN(H)/CrN(L)/CrON/Al_2O_3 constituent layers on the spectral properties and thermal stability. The results reported here could be beneficial to industry attempting to design more effective solar absorbers.

2. Experimental

CrN(H), CrN(L), CrON, and Al_2O_3 films were deposited on well-cleaned silicon wafers and SS substrates using a reactive DC magnetron sputtering system. High purity Cr (99.95%) and Al (99.999%) targets (diameter = 0.0508 m) were used for the sputtering deposition. Prior to deposition, the targets were sputter-cleaned for 10 min to remove the surface contaminants. The CrN(H) and CrN(L) were prepared using the Cr target at 150 W in a mixture of Ar and N_2. The N_2 flow rate was 8 sccm for the CrN(H) and 16 sccm for the CrN(L), and the Ar flow rate was fixed at 40 sccm. The CrON was deposited using the Cr target at 150 W in an Ar (40 sccm), N_2 (12 sccm), and O_2 (4 sccm) mixed gas. The Al_2O_3 was prepared using the Al target at 200 W in an Ar (40 sccm) and O_2 (4 sccm) mixed gas. The base pressure in the chamber was 4×10^{-4} Pa and the working pressure was 0.5 Pa. The deposition rates of CrN(H), CrN(L), CrON, and Al_2O_3 were approximately 28.3, 24.8, 5.9, and 3.8 nm/min, respectively. The low deposition rate of Al_2O_3 was due to the severe poison of Al target in the sputtering process. The CrN(H)/CrN(L)/CrON/Al_2O_3 multilayer coatings with various thicknesses of CrN(H), CrN(L), CrON, and Al_2O_3 were prepared on the cleaned SS substrate by adjusting the respective deposition time. Single-layer coatings were deposited on silicon substrates to examine the refractive index (n) and extinction coefficient (k). The thermal stability testing was carried out on the as-deposited multilayer coatings in a furnace at 300–500 °C for 2 h.

The n and k spectra of the studied coatings were measured using an ellipsometer (M-2000; J. A. Woollam) in the wavelength range from 300 nm to 1700 nm. The optical constants of the studied layers were determined by fitting the model function to the measured data using J. A. Woollam Corporation developed WVASE 32 program. The CrN(H) was fitted using the B-spline dispersion model. The general oscillator model (Gen-Osc) combined with Cody-Lorentz model and Lorentz model was used to fit the measured curves of CrN(L) and CrON. The Al_2O_3 was fitted using the Cauchy model. The normal reflectance was measured in the wavelength interval of 300–20,000 nm. An Ultraviolet/visible/near-infrared spectrophotometer (V-570; JASCO) embedded with a $BaSO_4$-coated integrating sphere was applied for the region of 300–2500 nm. A Fourier-transform infrared spectrophotometer (Nexus 470; Thermo Nicolet) with an integrating sphere was used for the region of 2500–20,000 nm. An evaporated gold mirror on glass was used as reference. The normal solar absorptance (α) and the normal thermal emittance (ε) were calculated from the reflectance measurements according to the Duffie and Beckman methodology using the following equations: [20]

$$\alpha = \int_{300nm}^{2500nm} \frac{I_{sol}(\lambda)(1-R(\lambda))d\lambda}{I_{sol}(\lambda)d\lambda} \tag{1}$$

$$\varepsilon = \int_{2500nm}^{20000nm} \frac{I_p(\lambda)(1-R(\lambda))d\lambda}{I_p(\lambda)d\lambda} \tag{2}$$

where I_{sol} is the AM 1.5 normal solar irradiance and I_P is the Plank black body distribution at 100 °C. The structure of the studied samples was characterized by glancing incidence X-ray diffraction at a 1-degree incident angle in an X-ray diffractometer (XRD, D8 Advance; Bruker) using Cu Kα radiation (40 kV, 40 mA). The microstructure of the multilayered coatings was investigated with a transmission electron microscope (TEM, JEM-2010; JEOL) operated at 200 kV. TEM samples were prepared using a focused ion beam system (Nova 200; FEI) with Ga^+ ion in the range of 5–30 kV. Elemental analysis was carried out using a TEM equipped with an energy dispersive X-ray spectrum (EDS, INCA Energy TEM; Oxford). The Cliff-Lorimer ratio technique was employed as the chemical composition quantification method.

3. Results and discussion

3.1. Characteristics of CrN(H), CrN(L), CrON, and Al_2O_3 layers

Table 1 presents the compositions of CrN(H), CrN(L), CrON, and Al_2O_3 layers. The CrN(L) had a lower Cr content than that of CrN(H), and close to the stoichiometric ratio of CrN. The composition of Al_2O_3 was also close to that of the stoichiometric Al_2O_3 compound. Fig. 1 shows the XRD patterns of respective CrN(H), CrN(L), CrON, and Al_2O_3 layer. In the pattern of CrN(H), the two peaks at 2θ values of 40.2° and 42.6° corresponded to the Cr_2N (002) and (111) planes (JCPDF 35-0803), respectively, and the peak at 43.7° was identified as the CrN (200) plane (JCPDF 65-9001). The results showed that the CrN(H) herein consisted of a mixture of Cr_2N and CrN. The CrN(L) yielded three peaks, at 37.5°, 43.7°, and 63.5°, which were identified as CrN (111), (200), and (220) planes (JCPDF 65-9001), respectively. No peak was obtained for CrON and Al_2O_3 in Fig. 1. Suzuki et al. reported that the CrON film has a non-metal substituted CrN structure, which consists of a $Cr(N_x,O_y)$ phase with different oxygen contents and the maximum oxygen concentration of 37 at.% could be incorporated in the B1-NaCl crystal structure [21]. Arvinte et al. found that a sputtered CrO_xN_y film consists of an over-stoichiometric Cr(O,N) crystalline phase when the C_{O+N}/C_{Cr} ratio was between 1 and 1.3 and an amorphous Cr_2O_3 or CrO_2 structures when the C_O/C_{Cr} and the C_{O+N}/C_{Cr} ratios were 1.7 and 2, respectively. The amorphous structure arisen from excess nitrogen was probably incorporated into the lattice or the interstitial positions within the oxide phase [22]. As shown in Table 2, the oxygen concentration of CrON were 50.6 at.%, and the C_O/C_{Cr} and C_{O+N}/C_{Cr} ratios were 1.6 and 2.1, respectively. Thus, the studied CrON can be referred to an amorphous structure of chromium-based oxides. The Al_2O_3 with the amorphous structure was characterized in our earlier study [23].

Fig. 2a and b plot the refractive indices and extinction coefficients of CrN(H), CrN(L), CrON, and Al_2O_3 layer as a function of wavelength. As presented in Fig. 2a and b, both n and k decreased in order of CrN(H)>CrN(L)>CrON>Al_2O_3. The n and k values of the CrN(H) increased with increase in wavelength, which is a characteristic behavior of metallic films. The n value of CrN(L) increased initially exhibiting a maximum around 500 nm and then decreased with increasing wavelength, while the k value rapidly decreased to 0.25 around 1000 nm and then kept constant at higher wavelengths. The results reveal the semiconductor behavior of CrN(L). However, the n and k values of CrON declined continuously as the wavelength increased because of the dielectric characteristics. The n value of the Al_2O_3 was 1.67 and the k value was zero over the measurement range also due to the characteristic of a typical dielectric. The obtained optical constants suggest that the CrN(H), CrN(L), CrON, and Al_2O_3 could be deposited sequentially to form a multilayered CrN(H)/CrN(L)/CrON/Al_2O_3 spectrally selective coating in which the refractive index decreased gradually from the base layer to the top layer. The CrN(H) and CrN(L), with a high n and k values, can act as absorbing layers in the spectrally selective coating. The CrON and Al_2O_3 with lower

Table 1
The compositions of the CrN(H), CrN(L), CrON, and Al_2O_3 layers.

Element (at.%)	CrN(H)	CrN(L)	CrON	Al_2O_3
Cr	62.8	50.4	32.1	
Al				38.6
N	37.2	49.6	17.3	
O			50.6	61.4