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Microstructure, optical and electrical properties of CrAlN film as a novel material for high temperature solar selective absorber applications

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ABSTRACT

The microstructure, optical and electrical properties of CrAlN and (Cr, Al) films synthesized by DC reactive magnetron sputtering method have been comparatively investigated. The results show that CrAlN film crystallizes in B1 NaCl-typed CrN structure with the preferred growth orientations of (1 1 1) and (2 2 0) and CrAlN grains show perfectly crystalline pyramid-like shape. The CrAlN film is determined as Al-doped CrN phase with the chemical formula of $Cr_{0.9136}Al_{0.0864}N_{0.8999}$. It shows similar reflectance and absorptance characteristics to those of TiN based films in the solar spectrum region (300–2600 nm) and exhibits semiconductor nature with a sheet resistance of 38 kΩ/sq. Hence CrAlN can be used as a novel candidate material for high-temperature solar selective absorber coatings with good thermal stability and oxidation resistance.

1. Introduction

Solar energy is one of the most environmentally friendly energy sources and the simplest method for solar energy utilization is photothermal conversion with solar absorbers. Solar selective coatings, which require high absorptance (α) in the solar spectral range (0.3–2.5 μm) and low thermal emittance (ε) in the deep infrared region (2.5–30 μm), are critical components of solar absorbers [1]. Presently, the most widely used high-temperature solar selective coatings, which are thermally stable above 400 °C, are cermets such as Pt–Al_2O_3, V–Al_2O_3, Mo–Al_2O_3, W–Al_2O_3, Mo–SiO_2, Ni–SiO_2, etc [2]. However, the coatings heat-treated in air at high-temperatures (>400 °C) usually degrade due to oxidation or diffusion of the metal component into the coatings at high temperature [3]. Thus, it is necessary to develop novel high-temperature solar selective coatings with higher thermal stability and oxidation resistance.

In recent years, transition metal nitride or oxynitride coatings have attracted considerable interests due to their exotic mechanical, chemical, electrical and optical properties. Moreover, their optical properties can be tailored by controlling the stoichiometry, which affects the density of free electrons in the transition metal ‘d’ band. It is known that transition metal nitrides such as TiN exhibit metallic characteristic. It has been reported that TiN, TiAlN and TiAlON displayed high absorptance in the solar spectral range and low emittance in the deep infrared region [4–9]. Cubic CrN has a similar crystal structure with cubic TiN and also exhibits good electrical conductivity, high oxidation resistance and thermal stability. It has been reported that the activation energies for the oxidation of TiN, CrN and TiAlN were 136, 225 and 471 kJ/mol,respectively [10]. As reported in the literature, the oxidation resistance of CrN was up to 650 °C (vs. 500 °C, TiN) [11]; Kawate et al. have reported that CrAlN films were stable up to 900 °C (vs. 750 °C, TiAlN) [12]. Otherwise, it is well known that CrN and CrAlN films have been widely used as hard, protective and wear coatings for cutting and forming tools due to their high hardness, good wear resistance, chemical inertness, and good thermal stability [10–16]. However, until now there are very few reports on the optical and electrical properties of CrN and CrAlN films. In this work, CrAlN and (Cr, Al) metal films were synthesized by DC reactive magnetron sputtering technology and their microstructure, optical and electrical properties were comparatively investigated.

2. Experimental details

The films were synthesized using a multi-target reactive DC magnetron sputtering system (JZCK-450, China). The Cr (99.9%) and Al (99.9%) targets were sputtered in Ar (99.99%) and N_2 (99.99%) mixed gas. The films were deposited under a base pressure of 8.0×10^{-3} Pa and a total Ar+N_2 mixed gas pressure of 0.5 Pa. The substrate to target distance, the substrate temperature and the

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depositing time were fixed at 100 mm, 500 °C, 2 h, respectively, and the other conditions were shown Table 1. In order to better understand the nature of CrAlN materials, amorphous soda lime glass was chosen instead of stainless steel as the substrates.

The crystallographic characterization was investigated by an X-ray diffractometer (XRD, D/Max-rA, Japan). The micrograph and chemical compositions were observed by field emission scanning electron micrographs (FESEM, JSM-6700F, Japan) with an energy dispersive X-ray spectrometer (EDX). The bonding structure of the CrAlN film was characterized by X-ray photoelectron spectroscopy (XPS) using a K-Alpha 1063 system (Thermo Fisher Scientific, England). The optical transmittance and the sheet resistance were tested by a UV–vis spectrophotometer (Hitachi U-4100, Japan) and a 4-terminal measurement (SX1934-SZ-82, China), respectively.

3. Results and discussion

The XRD patterns of as-deposited films are shown in Fig. 1. As for sample a, a high intensity peak centered at $2\theta=43.65^\circ$ and other weaker peaks at $2\theta=39.13^\circ$, 48.02°, 79.52° can be seen in Fig. 1(a). The strong peak of $2\theta=43.65^\circ$ can be attributed to the overlapping peak of the $AlCr_2$(1 0 3) plane at $2\theta=43.52^\circ$ and the Cr(2 1 0) plane at $2\theta=44.16^\circ$, and other peaks are due to Cr(2 0 0), Cr(2 1 1) and Cr(3 2 1), respectively, as identified in Fig. 1(a). As observed from Fig. 1(b), sample b crystallizes in B1 NaCl-typed CrN structure with high intensity (1 1 1) peak centered at $2\theta=37.98^\circ$ and (2 2 0) peak at $2\theta=63.87^\circ$ while other angle reflections have not been observed, indicating that the film is oriented along (1 1 1) and (2 2 0). Moreover, relative to stoichiometric CrN phase, the 2θ values of (1 1 1) and (2 2 0) peaks increase from 37.57° to 37.98° and from 63.60° to 63.87°, respectively. This shift in 2θ can be attributed to a decrease in lattice parameter according to the Bragg formula ($n\lambda=2d\sin\theta$). Otherwise, no peaks related to (Cr, Al) metal or oxide phases have been observed. So we deduced that sample b may be CrAlN film with Al atoms substituting some of Cr atoms in the CrN lattice, resulting in a decrease in lattice parameter, which is also in agreement with the literature [10]. The chemical bonding states are evaluated by XPS technique for sample b and it also reveals the presence of CrAlN.

Table 1
Procedure conditions for depositing Cr–Al–N films.

Sample	Cr target power/ W	Al target power/ W	Ar flow rate/ sccm	N_2 flow rate/ sccm
a	120	80	10	10
b	105	80	10	20

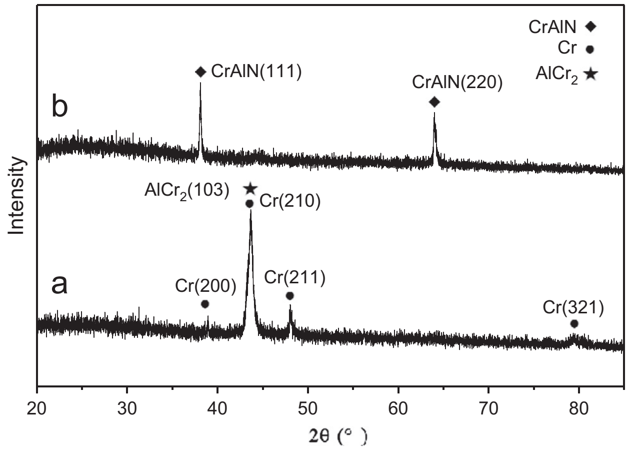

Fig. 1. XRD patterns of as-deposited films (with XPS anlysis): (a) Cr, Al film and (b) CrAlN film.

Fig. 2(a) and (c) shows SEM micrographs of as-deposited films. It can be observed that sample a shows majority of large irregular coarse particles (~500 nm) and sample b exhibits perfectly crystalline pyramid-like grains, which can be attributed to the preferred growth along (1 1 1) and (2 2 0) directions. The chemical compositions are analyzed by EDX analysis as shown in Fig. 2 (b) and (d). N, Al and Cr peaks have been confirmed in actual compositions of sample b, while N element has not been detected for sample a. So it can be concluded that, for sample a, Al and Cr have not been nitridized at a low N_2 flow rate and they exist in metal phase; for sample b, the pyramid-like grains are CrAlN crystals. The chemical composition of sample b was further measured by electron probe microanalysis (EPMA). It can be found that the atomic ratio of Cr, Al and N is 48.09 at%: 4.55 at%: 47.37 at %. The Al/(Cr+Al) atomic ratio by calculation is 8.64%, which is close to the EDX result (8.97%). Hence the chemical formula can be determined as $Cr_{0.9136}Al_{0.0864}N_{0.8999}$.

Fig. 3 shows the transmittance, reflectance and absorptance spectra of both samples at the wavelength range of 300–2600 nm. The absorptance A is deduced according to

$$A=1-R-T \qquad (1)$$

where R and T are the measured reflectance and transmittance values. It can be found that the transmittance characteristics of sample a and b are similar and the absorptance values are very high (>98.8%). However, the reflectance and absorptance characteristics are different, i.e., for CrAlN film, the reflectance and absorptance spectra show a rising and falling trend respectively with the increase of wavelength, which are similar to those of TiN based films such as TiAlN, TiAlNO and TiAlSiN films [5,7], while those of (Cr, Al) film show relatively stable. From this point of view, CrAlN can be used as a novel candidate material for high-temperature solar selective absorber coatings as TiAlN [4–9]. Furthermore, the thermal stability and oxidation resistance of CrAlN were superior to TiN and TiAlN as reported in the literature [12].

The electrical resistivity measurements indicate that the sheet resistance of (Cr, Al) film (sample a) is 4 Ω/sq, which proving its metallic nature, while the $Cr_{0.9136}Al_{0.0864}N_{0.8999}$ film exhibits a sheet resistance of 38 kΩ/sq, which suggesting its semiconducting behavior. It is in agreement with the literature which reported that the electronic properties of CrN films strongly depend on their chemical composition; small variations in N content and addition of other elements such as Al, Si, V, Nb, etc. to the Cr–N system would lead to changes in the electronic physical properties [17]. Hence, this makes it possible that the optical and electrical properties of Cr–Al–N system can be tuned by controlling the chemical composition to be suitable for high-temperature solar selective absorber coating requirements.

Otherwise, in this experiment, 3 samples for CrAlN films were prepared and they had similar chemical composition, microstructure, morphology and properties, which confirmed that the experiment reproducibility was reliable.

4. Conclusion

In this study, CrAlN film was synthesized using DC reactive magnetron sputtering method. The CrAlN film crystallizes in B1 NaCl-typed CrN structure with the preferred growth orientations of (1 1 1) and (2 2 0) and CrAlN grains show pyramid-like shape. XRD, EPMA and XPS analysis results indicate that the CrAlN film