Optical Properties of Multi-layer TiNO/AlCrNO/Al Cermet Films Using DC Magnetron Sputtering

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Among many the oxynitrides, TiNO and AlCrNO, have diverse applications in different technological fields. We prepared TiNO/AlCrNO/Al thin films on aluminum substrates using the method of dc reactive magnetron sputtering. The reactive gas flow, gas mixture, and target potential were applied as the sputtering conditions during the deposition in order to control the chemical composition. The multi-layer films have been prepared in an Ar and O₂+N₂ gas mixture rate. The surface properties were estimated by performing scanning electron microscopy (SEM). At a wavelength range of 0.3~2.5 μ m, the exact composition and optical properties of thin films were measured by Auger electron spectroscopy (AES) and Ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometry. The optimal absorptance of multi-layer films was exhibited above 95.5% in the visible region of the electromagnetic spectrum, and the reflectance was achieved below 1.89%.

Keywords: DC magnetron sputter, Multi-layer, Optical properties, Absorptance, Reflectance

1. INTRODUCTION

Solar thermal selective coatings play a pivotal role in the construction and working of solar power systems. Solar selective absorber coatings are characterized by two important features: i) a very high absorptance and ii) a low reflectance in the solar spectral range of 0.3~2.5 μ m [1]. A solar thermal selective absorber can convert solar energy of low density to heat energy of high density, improving the efficiency of a photo-thermal conversion [2]. In general, solar selective absorber coatings can be generally categorized into six components [3]: a) intrinsic

absorber, b) semiconductor metal tandem, c) multi-layer absorber, d) multi dielectric composite, e) textured surfaces, and f) selective solar transmitting coating. An intrinsic absorber uses a material, having intrinsic properties and a requisite spectral sensitivity. The semiconductor-metal tandems absorb radiation of short wavelength, because of the semiconductor bandgap and a low thermal emittance. Multi-layer absorbers exhibit multiple reflection effect between multi layers in order to absorb solar energy. The metal dielectric composites are composed of fine metal particles, which are found in either the dielectric or ceramic host material. The textured surfaces exhibit high solar absorptance as multiple reflections occur on their needle-like or porous microstructure. Finally, the selective solar transmitting coatings are applied on an absorber that resembles a blackbody. Thus, such an absorber is functional even at low temperatures. Using these coating methods, we develop multi-layer absorber coatings with high absorption and low thermal emittance in the solar region.

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Therefore, they are stable at an elevated temperature, depending on the materials used in construction. A typical double-cermet layer of a film extends from the surface to a substrate, depicting a figure described as follows: an anti-reflection layer enhances solar absorption; an absorbing layer is composed of two homogeneous cermet layers: a low-metal-volume fraction (LMVF) cermet layer on high-metal-volume fraction (HMF) cermet layer; and a metallic infrared reflector layer that reduce emittance from the substrate [4-6].

Several multi-layer absorbers, consisting of different metals (Mo, Ag, Ni, Cr, and Ti) and dielectric layers (Al_2O_3 , SiO_2 , CeO_2 , NiO , and Cr_2O_3), have been used as solar materials [7-10]. Recently, a coating made from either transition metal nitride or oxynitrides has attracted the attention of several researchers, because the constituents of the coating have remarkable chemical, mechanical, electrical, and optical properties. Furthermore, it has been reported that TiN, TiAlN, and TiAlNO have high absorption and low emittance in the deep infrared region [11]. Cubic CrN has a similar crystal structure containing TiN, and it shows excellent electrical conductivity, high oxidation resistance, and thermal stability. It is a well-known fact that CrN and AlCrN films have been widely used as protective coatings, because they possess chemical inertness and good thermal stability [12].

A variety of techniques, such as electro-deposition, CVD, evaporation, ion plating, pulsed laser deposition, and magnetron sputtering, can produce multi-layer cermet coatings [13-17]. With the help of magnetron sputtering, we can possibly apply on a large area deposition of thin films. Therefore, they are highly suitable for use as solar selective absorbers or multi-layer films without contamination. However, presently, very few reports have described about the optical and surface properties of AlCrNO and TiNO multi-layer films. In this study, we prepared multi-layer AlCrNO and TiNO cermet films on Al substrate by conducting a dc reactive magnetron sputtering method. Thereafter, their optical properties and microstructure were investigated on the basis of a change in the rates of gas mixtures.

2. EXPERIMENTS

A dc magnetron sputtering system was used for applying a solar selective multi-layer coating. This sputtering system was of the sputter-down category. At a purity level of 99.995%, the Al:Cr(5 wt.%) and Al:Ti(10 wt.%) target was sputtered in a mixture of gases: Ar(99.99%), N_2 (99.99%), and O_2 (99.995%); these gases constituted the sputtering atmosphere. The 5-layer thin film solar selective absorbing deposition was executed subsequently on an Al substrate. An antireflection layer of Al_2O_3 was prepared at a pressure of 20 mTorr, which was exerted by a mixture of Ar and O_2 gases. In cermet films, the volume fraction of the metal component was controlled by the mixing rates of Ar:(N_2+O_2) gas. The sputtering parameters are enlisted in Table 1.

Figure 1 presents a schematic structure of $\text{Al}_2\text{O}_3/\text{AlTiNO}/\text{AlCrNO}/\text{Al}$ multi-layer cermet absorber. An Al metal acts as an

Fig. 1. Schematic structure of multi-layer solar absorber film.

infrared reflecting layer on the substrate, reducing the emittance of the substrate. The absorbing multi-layer film consists of two AlTiNO and AlCrNO cermet layers, with different volume fractions of metals. As shown in Fig. 1, in the layer (third cermet layer) near the substrate, there is a high metal volume fraction (HMF) of AlCrNO. In the next layer, there is a low metal volume fraction (LMVF). Subsequently, HMF layer of AlTiNO is located on the AlCrNO cermet layer, while LMVF of AlTiNO layer is positioned near the antireflection layer. The top antireflection layer is a transparent Al_2O_3 , which ensures higher solar absorption.

The surface micrograph of a multi-layer thin film was estimated by field emission scanning electron microscopy (FE-SEM). The exact composition and optical properties of cermet absorber films were measured by Auger electron spectroscopy (AES) and UV-Vis-NIR spectroscopy, respectively. The reflectance of absorber thin films were measured in the wavelength ranges of 0.3–2.5 μm using UH4150 UV-Vis-NIR spectrophotometer (Hitachi, Tokyo, Japan). In the multi-layer, solar absorptance was calculated using standard AM1.5 solar spectrum.

3. RESULTS AND DISCUSSION

In Fig. 2, we have presented field emission-scanning electron micrographs (FE-SEM) of multi-layer solar absorber films with different gas mixture rate of Ar and (O_2+N_2).

Table 2 elucidates the deposition conditions of cermet multi-layer coating, as shown in Fig. 2. From (a) to (c) in Fig. 2, the gas mixture rate of Ar and (O_2+N_2) was increasing in AlCrNO and AlTiNO cermet layer, respectively. All the surfaces were dark purple in color. As the gas mixture rate is increased, the grain size of cermet thin films grows up gradually in the resulting FE-SEM micrographs. In Fig. 2(c), it was observed that the surface showed large irregular particles that were pyramidal in shape. This is because the surface had not been nitridized due to low N_2 flow rate. Moreover, an additional metallic phase also existed [7].

Table 2. Sputtering conditions of multi-layer cermet films as shown in Fig. 2.

Dep. Conditions	AlCrNO layer		AlTiNO layer	
		Ar:(N_2+O_2)		Ar:(N_2+O_2)
(a)	HMF	2.5 : 1		1 : 1
	LMVF	1.25 : 1		0.86 : 1
(b)	HMF	12.5 : 1		1.2 : 1
	LMVF	6.25 : 1		1 : 1
(c)	HMF	20 : 1		1.5 : 1
	LMVF	10 : 1		1.2 : 1
DC power [W]		200	250	
T-S distance [cm]		10	10	

Table 1. Sputtering conditions of multi-layer solar absorber films.

Sputtering conditions	Values
Base pressure	3×10^{-6} Torr
Operating pressure	10–60 mTorr
Sputtering power	100–300 W
Mixed gas(for Al & Al_2O_3)	20 mTorr
Ar : (N_2+O_2) for cermet layer	0.86:1~20:1
T-S distance	8~10 cm
Total deposition time	40~50 min.
Substrate temperature	RT

Fig. 2. SEM micrographs of multi-layer absorber films at different gas mixture rates

As shown in Fig. 2(a), (b), and (c), the grain sizes were approximately 42 nm, 66 nm, and 175 nm, respectively.

Figure 3 shows FE-SEM images of multi-layer cermet films, containing an AlTiNO layer of varying dc power. The sputtering parameters of gas mixture rates are exactly same as the sample (c) conditions reported in Table 2. In the deposition process of Al-CrNO layer, the dc power was 200 W. The grain size of multi-layer cermet films increased with an increase of dc power.

Figure 4 shows the AES depth profile analysis of Al₂O₃/AlTiNO/AlCrNO/Al multi-layer cermet absorber. Table 3 presents the deposition conditions of multi-layer coating, which is depicted in Fig. 4. In Al₂O₃ that serves as an antireflection layer, the gas mixture rate of Ar and O₂ is fixed at 6 : 1.

In the results of AES analysis, the depth profile displays the peaks of Al, O₂, N₂, Ti, and Cr elements. The profile coating consists of Al₂O₃ antireflection layer, AlTiNO and AlCrNO cermet multi-layer, and Al reflector layer extending from the surface to the substrate sequentially. The result of AES profile indicates that total thickness of multi-layer cermet films is approximately 240

Fig. 3. SEM micrographs of multi-layer absorber films with different dc power. (a) DC power of 200 W and (b) DC power of 300 W.

Fig. 4. AES depth profile of multi-layer cermet film (sputtering rate: 12 nm/min).

Table 3. Sputtering conditions of multi-layer cermet films as shown in Fig. 4.

Dep. Conditions	AlCrNO layer	AlTiNO layer
	Ar:(N ₂ +O ₂)	Ar:(N ₂ +O ₂)
HMVF	20 : 1	1.5 : 1
LMVF	10 : 1	1.2 : 1
DC power [W]	200	300
T-S distance [cm]	10	10

Fig. 5. Absorptance of multi-layer cermet films at different gas mixture of Ar and (O_2+N_2).

Table 4. Deposition conditions and optical properties of cermet samples as shown in Fig. 5.

Sample	AlCrNO		AlTiNO		α
	HMVF	LMVF	HMVF	LMVF	
1	20 : 1	10 : 1	1.5 : 1	1.2 : 1	0.955
2	12.5 : 1	6.25 : 1	1.2 : 1	1 : 1	0.948
3	8 : 1	4 : 1	1.2 : 1	1 : 1	0.947
4	2.5 : 1	1.25 : 1	1 : 1	0.86 : 1	0.935

Fig. 6. Reflectance of multi-layer cermet films at different gas mixture of Ar and (O_2+N_2).

nm. The concentration of Ti and Cr elements increases gradually, while the concentration of Al and oxygen elements decreases from the surface to the substrate. This trend essentially agrees well with the deposition conditions, as indicated in Table 3. From the surface to the substrate, the gas mixture rate of multi-layer increased sequentially. Consequently, the multi-layer was changed from LMVF to HMVF in AlTiNO and AlCrNO layer. Note that, oxygen is present as an element in all the layers. This can be ascribed to the high sensitivity of AES instrument. Furthermore, the oxygen contamination usually originates from the residual oxygen in a chamber.

Figure 5 shows the absorptance spectra of a multi-layer cermet films, with various gas mixture rates of Ar and (O_2+N_2). Table 4 summarizes the sputtering conditions of AlTiNO and AlCrNO cermet films, which are illustrated in Fig. 5. Moreover, the ab-

sorptance of each sample was calculated using standard AM1.5 solar spectrum. All the absorptance curves of multi-layer cermet films approach values above 93%; however, slightly different traces are reported in the wavelength range of 0.3–2.5 μm . When the gas mixture rates were increased, the absorptance also showed a corresponding increase; the curve of this relationship has been elucidated and summarized in Fig. 5 and Table 4, respectively. On the other hand, Fig. 6 exhibits the reflectance spectra of multi-layer cermet films at different gas mixture rates. The reflectance curve exhibited a decreasing trend as the gas mixture rates were increased. The optimized value of optical properties is achieved in sample 1, having an absorptance of 95.5% and reflectance of 1.89%.

4. CONCLUSIONS

In this paper, we have described how to prepare a solar selective absorber. Five layers of the antireflection layer and multi-layer, AlTiNO/AlCrNO cermet films, were subsequently deposited using a dc reactive magnetron sputtering system. The exact structure of As-deposited multi-layer films is Al_2O_3 /AlTiNO (LMVF and HMVF)/AlCrNO (LMVF and HMVF)/Al/substrate. In the four absorbing cermet layers of AlTiNO/AlCrNO, the metal volume fraction was prepared using the controlling method of Ar and (N_2+O_2) gas mixture rate. As the gas mixture rate increases, the grain size of solar absorber films shows to grow up; the curve is illustrated in an SEM micrograph. Moreover, the grain size becomes larger as the dc power is increased. As the gas mixture rates were increasing, the absorptance also increased and the reflectance became low. The optimized value in sample 1 is achieved, with an absorptance of 95.5% and a reflectance of 1.89%.

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REFERENCES

- [1] H. C. Barshilia, N. Selvakumar, and K. S. Rajam, *Appl. Phys. Lett.*, **89**, 1 (2006). [DOI: <http://dx.doi.org/10.1063/1.2387897>]
- [2] D. H. Oh, S. U. Han, H. H. Kim, G. E. Jang, and Y. J. Lee, *J. Korean Inst. Electr. Electron. Mater. Eng.*, **12**, 820 (2014).
- [3] C. E. Kennedy, *NREL Technical Report No. NREL/LP-520-31267* (2002).
- [4] S. Esposito, A. Antoniaia, M. L. Addonizio, and S. Aprea, *Thin Solid Films*, **517**, 6000 (2009). [DOI: <http://dx.doi.org/10.1016/j.tsf.2009.03.191>]
- [5] R. C. Juang, Y. C. Yeh, B. H. Chang, W. C. Chen, and T. W. Chung, *Thin Solid Films*, **518**, 5501 (2010). [DOI: <http://dx.doi.org/10.1016/j.tsf.2010.04.025>]
- [6] H. C. Barshilia, *Sol. Energy Mater. & Sol. Cells*, **130**, 322 (2014). [DOI: <http://dx.doi.org/10.1016/j.solmat.2014.07.037>]
- [7] J. Chen, C. Guo, J. Chen, J. He, Y. Ren, and L. Hu, *Material. Lett.*, **133**, 71 (2014). [DOI: <http://dx.doi.org/10.1016/j.matlet.2014.06.159>]
- [8] H. Murata and T. Ohba, *Mater. Trans.*, **12**, 2907 (2008). [DOI: <http://dx.doi.org/10.2320/matertrans.MRP2008206>]
- [9] H. C. Barshilia, *Sol. Energy Mater. & Sol. Cells*, **130**, 322 (2014). [DOI: <http://dx.doi.org/10.1016/j.solmat.2014.07.037>]

- [10] Q. C. Zhang, *Sol. Energy Mater. & Sol. Cells*, **62**, 63 (2000). [DOI: [http://dx.doi.org/10.1016/S0927-0248\(99\)00136-1](http://dx.doi.org/10.1016/S0927-0248(99)00136-1)]
- [11] M. Du, X. Liu, L. Hao, X. Wang, J. Mi, L. Jiang, and Q. Yu, *Sol. Energy Mater. & Sol. Cells*, **111**, 49 (2013). [DOI: <http://dx.doi.org/10.1016/j.solmat.2012.12.010>]
- [12] H. C. Barshilia, N. Selvakumar, B. Deepthi, and K. S. Rajam, *Surf. Coat. Technol.*, **201**, 2193 (2006). [DOI: <http://dx.doi.org/10.1016/j.surfcoat.2006.03.037>]
- [13] Q. C. Zhang, M. S. Hadavi, K. D. Lee, and Y. G. Shen, *J. Phys. D: Appl. Phys.*, **36**, 723 (2003). [DOI: <http://dx.doi.org/10.1088/0022-3727/36/6/315>]
- [14] K. D. Lee, *J. Kor. Sol. Energy Soc.*, **33**, 31 (2013). [DOI: <http://dx.doi.org/10.7836/kses.2013.33.4.031>]
- [15] T. I. Ohm, W. T. Yeo, and D. C. Kim, *J. Kor. Sol. Energy Soc.*, **33**, 27 (2013). [DOI: <http://dx.doi.org/10.7836/kses.2013.33.3.027>]
- [16] A. R. Shashikala, A. K. Sharma, and D. R. Bhandari, *Sol. Energy Mater. & Sol. Cells*, **91**, 629 (2007). [DOI: <http://dx.doi.org/10.1016/j.solmat.2006.12.001>]
- [17] E. Barrera-Calva, A. Avila, J. Mena, V. H. Lara, M. Ruiz, and J. Mendez-Vivar, *Sol. Energy Mater. & Sol. Cells*, **76**, 387 (2003). [DOI: [http://dx.doi.org/10.1016/S0927-0248\(02\)00290-8](http://dx.doi.org/10.1016/S0927-0248(02)00290-8)]