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Variable emissivity property of magnetron sputtering thermochromic film

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ABSTRACT

Thermochromic films are prepared on the substrate of yttria stabilized zirconia by radio frequency magnetron sputtering technique. Crystalline structure and surface morphology are characterized. Characterization result shows that the films are of perovskite structure exhibiting a dense and smooth surface morphology. Composition analysis is performed and the result indicated that the element composition of films can be adjusted to close its stoichiometric ratio by controlling the oxygen flow ratio. Temperature-dependent reflectivity and emissivity are studied. Reflectivity spectra show that the film undergoes a transition from a metallic state to a non-metallic state with increasing temperature. Emissivity of the films is large above the transition temperature and it decreases sharply below the temperature. The emissivity increment at 97–373 K can approach 0.39 by controlling sputtering pressure, working gas and film thickness.

1. Introduction

Manganese oxides $A_{1-x}B_xMnO_3$ (A = La, Sm, Pr, Nd; B is alkaline earth) are a typical thermochromic material which can change their thermal radiative properties with the variation of temperature. With this property, it is finding many applications in thermal furtivity and thermal control. For example, P. Laffez et al. [1–3] reported that Sm doped thermochromic material $Sm_{0.35}Ca_{0.65}MnO_3$ (SCMO) can be used as thermal furtivity coating because its emissivity decreases with increasing temperature. If a warm object coated SCMO appears on a cold background, it is difficult to be detected by the infrared camera in view of the weakened radiation sign from the object.

Another important application is the thermal control of miniature spacecraft, which has been reported in La doped thermochromic materials [4–8]. Contrary to the furtivity application, thermochromic materials for thermal control need a low emissivity at low temperature to maintain the heat, whereas at high temperature it is expected to have a high emissivity for dissipating the excess heat. If the material is fitted on the spacecraft surface, it can automatically control the emissive heat transfer from the spacecraft without assistance of any moving parts. Over the past years, many efforts on improving the applicability of the material have been carried out. Investigations from the Japan Aerospace Exploration Agency and Nippon Electric Company showed that the emissivity increment of two bulk materials $La_{0.825}Sr_{0.175}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ is 0.4 in a temperature range of 173–373 K [5–8]. Their results revealed that the material can be fabricated to a thin tile with a dimension of 40 × 40 × 0.2 mm^3 and a weight of 1.2 kg/m^2. We have also reported that the increment of normal emissivity is 0.5 at 173–373 K for the sample of Ca and Sr doping $La_{1-x}A_xMnO_3$ in our previous work [9]. The size of the sample is 40 mm × 40 mm with 400 μm thick and weight is 1.23 kg/m^2. J. Fang et al. [10] and J. Huang et al. [11] attempted to enhance the emissivity above T_p through introducing micro-structures or gratings on the material surface. In order to overcome the material drawback absorbing solar radiation, K. Shimazaki et al. [12,13] and D. Fan et al. [14,15] designed multi-layer optical structures on the material surface to reduce its solar absorptivity, and the reported solar absorptivity of the structured material can be reduced to 0.28. Moreover, the simulated experiment of space particles exposure revealed that the structured material possesses stabilized thermal radiative properties [5,16].

One can find these investigation efforts, which are mainly devoted to the performance of bulk material. Although the material can be fabricated into a ceramic tile with thickness in sub-millimeter dimensions to perform the temperature adjustment, it is still bulky or heavy in certain applications, especially in the spacecraft. In addition, it is also impossible to further reduce the thickness of bulk material in view of mechanical strength considerations. Meanwhile, the ceramic tile fabrication is inconvenient and low productive because of its low toughness. By comparison, thin film devices based on $La_{1-x}A_xMnO_3$ are more obvious to realize the weight reduction and there is no above-mentioned drawback. However, there exist only a few literatures to report the thermochromic film based on $La_{1-x}Sr_xMnO_3$. M. Soltani et al. [17] and D. Nikanpour et al. [18] prepared the $La_{1-x}Sr_xMnO_3$ (x = 0.175 and 0.3) thin films by reactive pulsed laser deposition method, but their emissivity variation remains modest. A. Boileau et al. [3]

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synthesized SCMO thin films using dc reactive magnetron co-sputtering and indicated that SCMO films show a thermochromic effect over a wide wavelength range at room temperature. M.R. Ammar et al. [19] investigated the thermochromic behavior of SCMO pigment-polymer coating for thermochromic applications. The result shows that the optical transmittance of the coating exhibited a large variation between 173 K and 343 K in the wavelength range of 8–14 μm. C. Wu et al. [20] prepared the $La_{0.8}Sr_{0.2}MnO_3$ thin film by magnetron sputtering, whose emissivity increases from 0.53 at 173 K to 0.72 at 310 K. Obviously, the emissivity variation of these thin films is much smaller than that of their bulk counterparts. Therefore, further investigation will be required to access the bulk material properties in emissivity as much as possible.

In the work, the aim is to prepare the $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films on the substrate of yttria stabilized zirconia (YSZ) by magnetron sputtering technique, and investigate the variable emissivity properties of the films. Furthermore, some key parameters that influence the performance of the LSMO film, such as working gas, sputtering pressure and film thickness, are also discussed. The encouraging results have been obtained, which can provide fundamental data for developing a light-weight thermal control device for application in spacecraft.

2. Procedure for experiment

LSMO films were prepared on YSZ substrate by the radio frequency (RF) magnetron sputtering system (JGP800, Shenyang Scientific Instrument Co., China). The LSMO target used during sputtering was synthesized by the conventional solid-state reaction method using La_2O_3, $SrCO_3$ and MnO_2 powders as starting materials [9]. LSMO films were grown on YSZ (100) single crystal substrate at different sputtering pressures and different working gas, which is a mixture of argon containing different volume oxygen. An RF power of 90 W was used and the substrate temperature was kept at room temperature during deposition. The distance of between LSMO target and YSZ substrate is 50 mm. Other parameters in the experiment were listed in Table 1. In order to improve the oxygen content, the LSMO films were annealed ex-situ at 1073 K in flowing oxygen for 1 h. The film structure was characterized by X-ray diffraction (XRD, D8 ADVANCE, Bruker Co., Germany) using a Cu Kα ($\lambda_{Cu} = 1.5406$ Å) radiation source at 40 kV and 30 mA. The scanning was performed from 20 to 80° with steps of 0.05°. Microstructure of the film was analyzed by field emission scanning electron microscopy (SEM, S-4800, Hitachi Co., Japan) using an accelerating voltage of 15 kV. Composition analysis was performed in the SEM at an acceleration voltage of 20 kV and magnification of 1290 times by the energy dispersive X-ray spectroscopy (EDS, Thermo Electron Co., USA) with Noran System Six evaluation software and silicon drift detector. The film's thickness was also determined by cross-sectional SEM images with accelerated voltage of 20 kV. Surface roughness of the film was measured by the atomic force microscope (AFM, CSPM4000, Being Ltd., Beijing in China). The lateral resolution of the AFM is 0.26 nm and the vertical one is 0.1 nm. Infrared emissivity ϵ(T) determining thermal radiative properties of film was derived from reflectivity spectra according to ECSS-Q-70-09 [21], as expressed by

$$\epsilon(T) = \frac{\int_{2.5}^{25} [1-\rho(\lambda,T)]E_{\lambda,b}(\lambda,T)d\,\lambda}{\int_{2.5}^{25} E_{\lambda,b}(\lambda,T)d\,\lambda} \quad (1)$$

where $E_{\lambda,b}(\lambda,T)$ is blackbody radiative intensity. Temperature-dependent reflectivity $\rho(\lambda,T)$ can be measured by an accessory of Transmission-Reflection Dewar (catalog no. DER-300, Harrick Scientific Products, Inc., America) mounting on the Fourier transform infrared spectrometer (FT-IR, VERTEX 80 v, Bruker Co., Germany). The measured wavelength and temperature ranges are 2.5–25 μm and 97–373 K, respectively. A gold film was employed as a reference mirror to determine the reflectivity.

Table 1
Deposition condition and characteristics of LSMO films.

Sample	P (Pa)	GFR (%)	t (min)	La:Sr:Mn atom ratio	ARS (nm)	FT (μm)	ϵ_l	ϵ_h	Δϵ
LSMO1	0.8	0	170	0.85:0.13:1	0.60	0.90	0.28	0.52	0.24
LSMO2	0.8	20	180	0.71:0.12:1	0.60	0.90	0.24	0.62	0.38
LSMO3	0.8	33	195	0.71:0.14:1	0.64	0.89	0.27	0.67	0.40
LSMO4	0.8	50	215	0.61:0.22:1	0.66	0.90	0.27	0.67	0.40
LSMO5	0.5	20	173	0.71:0.12:1	0.71	0.91	0.22	0.56	0.34
LSMO6	1.2	20	182	0.66:0.15:1	0.69	0.89	0.15	0.52	0.37
LSMO7	2.0	20	198	0.66:0.29:1	0.65	0.90	0.17	0.56	0.39
LSMO8	0.8	20	150	0.71:0.13:1	0.53	0.76	0.53	0.55	0.02
LSMO9	0.8	20	240	0.69:0.13:1	0.75	1.19	0.28	0.67	0.39
LSMO10	0.8	20	300	0.70:0.12:1	0.90	1.49	0.29	0.65	0.36

P: sputtering pressure, GFR: gas flow ratio of O_2 / (O_2 + Ar), *t*: sputtering time, ARS: average roughness, FT: film thickness.

3. Results and discussion

XRD detection was performed to determine if desired crystalline structures were obtained under the designed conditions, where LSMO films have been annealed and corresponding bulk target is the as-prepared specimen by solid state reaction. Fig. 1 shows the XRD patterns of four LSMO films and one bulk target. The bottom pattern is the $La_{0.7}Sr_{0.3}MnO_3$ JCPDS card (no. 51-0409). All diffraction peaks match well with that of bulk target and films. It is clear that our bulk target contains split peaks at 32.9°, 40.6°, 58.6°, 68.9°, and 78°, where corresponding films only exhibit a single peak. This perhaps is induced by the preferable orientation of particles in films. It is noted that bulk target and LSMO films are single perovskite phase with rhombohedral structure. In addition, YSZ peaks can be observed in LSMO3 and LSMO8 films as marked by symbol □, which is related to their minimum film thickness (See Table 1).

Fig. 2 shows the SEM microstructure of thermochromic film. No matter how they are seen from the surface morphology of Fig. 2(a) or the cross-sectional micrograph of Fig. 2(b), it is still dense, crack-free, and uniform.

Sputtering pressure and working gas are two important factors to influence the performance of LSMO film. Therefore, they are taken into account in this study as follows. The effect of sputtering pressure and working gas on the roughness and composition of LSMO films are

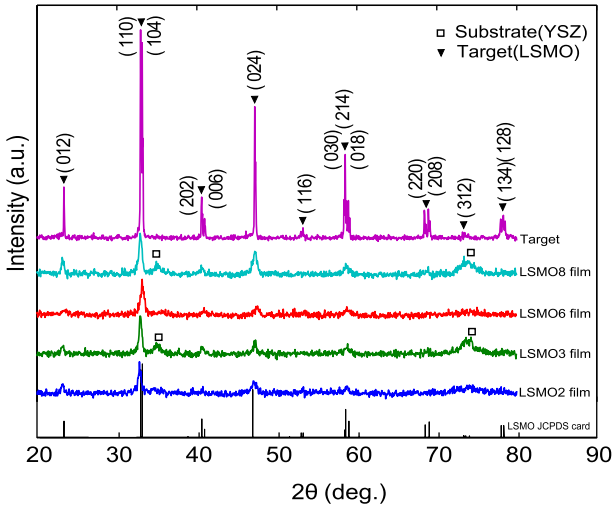

Fig. 1. XRD patterns of LSMO target and LSMO film.