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Temperature-dependent emissivity property in $La_{0.7}Sr_{0.3}MnO_3$ films

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Thermochromic films have been deposited by magnetron sputtering technique on different substrates. The crystallinity and surface morphology of the films have been characterized. Characterization result shows that the films are of perovskite structure. Composition analysis is performed and the result indicated that the element composition of the film can be close to its stoichiometric ratio. Temperature-dependent reflectivity and emissivity are studied. Reflectivity spectra show a downward trend with increasing temperature. Emissivity of the film is large at high temperature and it decreases sharply upon cooling. The emissivity increment at 123–373 K can approach 0.43 at 1.4 Pa sputtering pressure environment, which is attractive for thermal control application in spacecraft.

1. Introduction

Thermochromic materials based on manganese oxides are very suitable for radiator application in space. They are characterised by tunable thermal radiative properties with the variation of their own temperature, as a result of a metal-insulator (MI) phase transition [1–3]. Since their emissivity is small at temperature below the phase transition temperature and large at higher temperature, emissivity adjustment can be achieved automatically by temperature control. If a radiator composed of thermochromic material is fitted on a spacecraft surface, the emissive heat transfer from spacecraft can be automatically controlled without additional power consumption and moving parts [4,5]. Thermochromic materials, therefore, attracted great attention in space thermal control application since the 1990s. Thermal radiative properties of the doped manganites $La_{1-x}A_xMnO_3$ (A is alkaline earth) have been deeply investigated since 1999 by Tachikawa et al. [6], who reported for the first time that a large emissivity variation for the thermochromic materials was observed in the Ca- or Sr-doped $LaMnO_3$ samples. Moreover, the emissivity of the material shows a drastically increase upon heating to a critical temperature called MI transition temperature T_{MI}.

Investigators have performed a series of explorations concerning the development of variable emissivity device based on the thermochromic materials in order to realize an attractive industrial application. These explorations involve the method of device fabrication, the evaluation of device thermal radiative properties (i.e., emissivity and solar absorptivity), and the stability of device in space environment. A ceramic tile device with sub-millimeter thickness was fabricated by machining and polishing the high-temperature sintered samples, which is the most employed fabrication method in present [2,5,7]. The investigation result of thermal radiative properties shows that a large emissivity variation ($\Delta\epsilon = 0.4$) for the device is comparable to that of the convectional thermal control louver, although it is imperfect to possess a high solar absorptivity about 0.8. In order to overcome the drawback of absorbing solar radiation and simultaneously hold the

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large emissivity variation, a spectral selective structure was designed on the device surface, and the solar absorptivity of the structured device was reduced to 0.28 [8–11]. The simulated experiment of space particles exposure revealed that the structured device possesses stable thermal radiative properties [3,12]. The applicability of the device have been demonstrated on the 'Hayabusa' spacecraft launched in 2003 by Japan Aerospace Exploration Agency [13]. It is reported that the device in 'Hayabusa' spacecraft reduces the energy consumption of the on-board heater, and decreases the weight and the cost of the thermal control system [14]. The groups of Xuan [15–18] from the standpoint of surface structures attempt to improve the tunable emissivity properties of thermochromic material. Huang et al. [15] calculated the spectral emissivity distribution of $La_{0.825}Sr_{0.175}MnO_3$ with one-dimensional grating structured surfaces using the finite difference time domain method. The results showed that the thermochromic performance of the material was improved by the structured surface, which have been demonstrated experimentally by means of photolithographic technique to construct a similar structured surface [16]. Then, by combining $La_{0.825}Sr_{0.175}MnO_3$ with Al and SiO_2 gratings, they theoretically enhanced the emissivity increment of the structure based on the near-field effect of thermal radiation [17,18].

In these previous works, a series of investigation efforts showed that thermochromic materials for space applications are very attractive due to their suitable thermal radiative properties and high radiation durability. However, the fabrication and application of the ceramic tile device is inconvenient and low productive because of its low toughness. In addition, it is also difficult to further lose weight by machining and polishing way in view of the weakened mechanical strength. By comparison, thin film devices based on thermochromic material may be more advantageous from the viewpoint of producibility. At present, several studies on the tunable emissivity properties of thermochromic film have been undertaken. Shimakawa et al. [19] investigated the dependence of the emissivity property on the thickness of thermochromic films (La,Sr)MnO_3, which were synthesized by a sol-gel method. Their results revealed that thermochromic film with the thickness of 1500 nm can be used for variable emissivity radiators. Thermal radiative properties of plasma sprayed thermochromic coating were reported that the coating with thickness 190 μm can be developed as variable emissivity coating [20]. Soltani et al. [21] and Nikanpour et al. [22] 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. Wu et al. [23] 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 still 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.

Thermochromic films that are fabricated on flexible substrates, such as PI substrate, will significantly broaden the applications and greatly reduce the material cost. However, it is extremely difficult to fabricate the films on flexible substrate because the thermal, chemical properties of the substrates are not compatible with the processes of high temperature used for preparing thermochromic film. For example, a melting temperature of PI material is less than 300 °C, which is far below the recrystallization temperatures 700 °C for thermochromic films. Recently, it was reported that a transfer printing method has been developed for flexible Si or GaAs film cells preparation without changing the cell material deposition conditions [24]. The process includes the film deposition onto rigid substrate with high temperature resistance, the film peeling-off from rigidness substrate, and the transfer printing of film. During the process, the film peeling-off from rigidness substrate relies on the phenomenon of water-assisted subcritical debonding at interface between metallic layer and rigidness substrate, which separates the metallic layer together with thin film cells from the original substrate [25]. As such, we expect that the method can be used to the peeling-off of thermochromic films. In present work, $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films were deposited on the Al coated quartz (ACQ) substrates at different sputtering pressure by a magnetron sputtering technique, and followed by annealing in oxygen atmosphere. The Al layer is used to as the metallic layer of transfer printing method. The structural, surface morphology, and thermochromic properties of the films have been investigated. The films grown on quartz, Si, and YSZ substrates were also presented to make a comparison.

2. Procedure for experiment

LSMO films were prepared on ACQ substrates by magnetron sputtering technique. 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 [5]. The LSMO films were grown in a mixed gas of argon with 20 vol% of oxygen and at different sputtering pressure P_{gas}. The substrate was kept at room temperature in view of instrument limit. After deposition, the as-grown films on ACQ substrate were annealed ex-situ at 873 K in flowing oxygen atmosphere for 2 h. In case of the films on Si, YSZ, and quartz substrates were sputtered in an oxygen flow ratio 20 vol% and a sputtering pressure 0.8 Pa and were annealed ex-situ at 1073 K for 1 h. Deposition conditions in experiment were listed in Table 1. The film structure was characterized by X-ray diffraction (XRD, D8, Bruker Co., Germany) with the Cu Kα ($\lambda=0.15406$ nm) radiation source at room temperature. Surface microstructure of the film was analyzed by field emission scanning electron microscopy (SEM, S-4800, Hitachi Co., Japan). Composition analysis was performed by the energy dispersive X-ray spectroscopy (EDS, Thermo Electron Co., USA). The thicknesses of several films were obtained from the cross-sectional SEM images, and the deposition rate Γ was estimated. Thus, the film thickness can be easily controlled by the sputtering time. LSMO film was characterized by X-ray photoelectron spectroscopy (XPS, PHI Quantera II, Ulvac-Phi Co., JPN). Surface roughness of the film was measured by the atomic force