Temperature-dependent emissivity property in La_{0.7}Sr_{0.3}MnO₃ films

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Abstract

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.

Keywords: Thermochromic film, variable emissivity, thermal control

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, 2, 3]. Since their emissivity is small at temperature below the phase transition and large at higher temperature,

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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 $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (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 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, 9, 10, 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’ space-

craft 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 Y. Xuan[15, 16, 17, 18] from the standpoint of surface structures attempt to improve the tunable emissivity properties of thermochromic material. J. Huang *et al.*[15] calculated the spectral emissivity distribution of $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$ 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 $\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3$ 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. Y. Shimakawa *et al.*[19] investigated the dependence of the emissivity property on the thickness of thermochromic films $(\text{La,Sr})\text{MnO}_3$, 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]. M. Soltani *et al.*[21] and D. Nikanpour *et al.*[22] prepared the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.175$ and 0.3) thin films by reactive pulsed laser deposition method, but their emissivity variation remains modest. C. Wu *et al.*[23] prepared the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ thin film by magnetron sputter-

ing, 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, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (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.

96 2. Procedure for Experiment

97 LSMO films were prepared on ACQ substrates by magnetron sputtering
 98 technique. The LSMO target used during sputtering was synthesized by the
 99 conventional solid-state reaction method using La_2O_3 , SrCO_3 and MnO_2 pow-
 100 ders as starting materials[5]. The LSMO films were grown in a mixed gas of
 101 argon with 20 vol% of oxygen and at different sputtering pressure P_{gas} . The
 102 substrate was kept at room temperature in view of instrument limit. After
 103 deposition, the as-grown films on ACQ substrate were annealed ex-situ at 873
 104 K in flowing oxygen atmosphere for 2 h. In case of the films on Si, YSZ, and
 105 quartz substrates were sputtered in an oxygen flow ratio 20 vol% and a sput-
 106 tering pressure 0.8 Pa and were annealed ex-situ at 1073 K for 1 h. Deposition
 107 conditions in experiment were listed in Table 1. The film structure was char-
 108 acterized by X-ray diffraction (XRD, D8, Bruker Co., Germany) with the Cu
 109 $\text{K}\alpha$ ($\lambda=0.15406$ nm) radiation source at room temperature. Surface microstruc-
 110 ture of the film was analyzed by field emission scanning electron microscopy
 111 (SEM, S-4800, Hitachi Co., Japan). Composition analysis was performed by
 112 the energy dispersive X-ray spectroscopy (EDS, Thermo Electron Co., USA).
 113 The thicknesses of several films were obtained from the cross-sectional SEM im-
 114 ages, and the deposition rate Γ was estimated. Thus, the film thickness can be
 115 easily controlled by the sputtering time. LSMO film was characterized by X-ray
 116 photoelectron spectroscopy(XPS, PHI Quantera II, Ulvac-Phi Co., JPN). Sur-
 117 face roughness of the film was measured by the atomic force microscope (AFM,
 118 CSPM4000, Being Ltd., Beijing in China). The lateral resolution of the AFM is
 119 0.26 nm and the vertical one is 0.1 nm. Infrared emissivity ϵ determining ther-
 120 mal radiative properties of film was derived from reflectivity spectra according
 121 to ECSS-Q-70-09[26], as expressed by

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

122 where $E_{\lambda,b}(\lambda, T)$ is blackbody radiative intensity. Temperature-dependent re-
 123 flectivity $\rho(\lambda, T)$ was measured by an accessory of Transmission-Reflection De-

124 war (Catalog No. DER-300, Harrick Scientific Products, Inc., America) mount-
 125 ing on the FT-IR spectrometer (VERTEX 80v, Bruker Co., Germany). The
 126 measured wavelength and temperature ranges are 2.5–25 μm and 97–373 K,
 127 respectively. A gold film was employed as a reference mirror to determine the
 128 reflectivity. It is inappropriate to the emissivity calculation at 97 K using equa-
 129 tion (1) because the wavelength of maximum radiation energy $\lambda_m=29.87 \mu\text{m}$ ex-
 130 ceeds the measured wavelength regions of 2.5–25 μm on the basis of the Wien’s
 131 displacement law ($\lambda_m T=2.8976 \times 10^{-3} \text{ m}\cdot\text{K}$). In present work, therefore, the
 132 emissivity calculation is only considered in the temperature ranges of 123–373
 133 K.

134 **3. Results and discussion**

135 The sputtering pressure difference in LSMO film growth creates a non uni-
 136 form deposition rate as shown in Talbe1. An interesting behavior is observed
 137 that the deposition rate increases firstly, and then decreases with the increase
 138 of sputtering pressure. It is understandable that a higher sputtering pressure
 139 tends to increase the frequency of Ar ions sputtering LSMO target, which in
 140 turn increase the deposition rate of film, while the deposition rate decreases in
 141 an overlarge pressure environment because it increases the collision between the
 142 mixed gas and the sputtered atoms, and then reduces the amounts of sputtered
 143 atoms arriving to substrate. The XRD patterns of several samples are shown in
 144 Fig. 1. The thickness of all the films is similar (900 nm). It can be seen that the
 145 annealed films show a perovskite character, which is in accord with the LSMO
 146 target. The non-annealed film in the inset of Fig. 1 exhibits an amorphous
 147 bread peak at $2\theta=29^\circ$, which is a typical quartz glass state. The fact means
 148 that the LSMO film is difficult to crystallize with deposition at room tempera-
 149 ture. A high temperature treatment therefore is necessary to obtain the desired
 150 provskite structure through post annealing or in-situ heating substrate reported
 151 elsewhere[27]. For the films deposited on ACQ substrate, its diffraction peaks
 152 shift toward to lower angle direction (See the inset of Fig. 1) with the increase

153 of sputtering pressure indicating that the lattice constant becomes larger, which
 154 is favor of enhancement of metal-insulator transition[28]. Compared to LSMO
 155 target, thin film has a relative larger diffraction angle owing to the easier strain
 156 relaxation in film[29]. In addition, Al diffraction peak at $2\theta=38^\circ$ can be de-
 157 tected in the annealed LSMO film as marked by symbol ∇ , which is related to
 158 the use of Al layer.

159 SEM microstructure of LSMO film on ACQ substrate with different film
 160 thickness are shown in Fig. 2. The film with thickness about $0.9\ \mu\text{m}$ is dense and
 161 crack-free, while the film with thickness about $1.52\ \mu\text{m}$ exhibits a multi-crack
 162 character. The fact indicates that LSMO film deposition is difficult to obtain a
 163 thick film without defect by magnetron sputtering. In view of the instrument
 164 limit, the thick film with $1.52\ \mu\text{m}$ thick is achieved through multiple pass sput-
 165 ter deposition. In other word, the thick film is composed of many single-pass
 166 films. If the film is too thick, the crack becomes more obvious due to existing
 167 strain. In addition, the crack formation is further exacerbated during the an-
 168 nealing process as a result of expanding with heat and contracting with cold.
 169 Consequently, the thick film will be not considered in present. A typical EDS
 170 spectrum of LSMO film on ACQ is presented in Fig. 2(c). Au element is from
 171 the Au layer used to enhance the image quality. Beside the detected Al element
 172 from Al layer and Si element from quartz substrate, the ratio of La:Sr:Mn:O
 173 is 0.66:0.41:1:2.6, which seems to be comparable with the stoichiometry ratios.
 174 However, the Sr concentration may be lower than the EDS results. As can be
 175 seen from the EDS spectra of LSMO film on ACQ in Fig. 2(c), it is difficult to
 176 discern the Sr and Si peak around 1.74 KeV due to their similar characteristic
 177 peak in EDS pattern. Thus, this means that the evaluated Sr concentration
 178 from EDS analysis may not be accurate enough. The similar result has been
 179 reported by other authors[30].

180 Fig. 3 shows the XPS patterns for LSMO film. From this global scan spectra
 181 it is clear that La, Sr, Mn, O, and C elements are present in the film. An
 182 enthetic S element is also observed due to the surface contaminant during test
 183 because our sample is impossible to contain the S element under the strict

sputtering process. The S source may be from the SO_2 absorption experiment of other groups, which is performed simultaneously during our sample test. It was reported that the typical analysis depth is less than 10 nm for XPS, and it can arrive to 5 μm for EDS[31], the information of Al layer and substrate are not observed in the XPS global scan pattern in our LSMO film. The carbon (C1s) region is from the atmospheric carbon contaminant and the other atmospheric hydrocarbons.

It can be noted that the $\text{La}3d$ region in Fig. 3(b) shows a double-peak feature at 832 eV and 849 eV, which correspond to $\text{La}3d_{5/2}$ and $\text{La}3d_{3/2}$ core levels, respectively. The splitting energy both the core levels is equal to 17 eV. Meanwhile, an hump can be also observed for each of $\text{La}3d_{5/2}$ and $\text{La}3d_{3/2}$. The separation energy, for example, is 4 eV for the hump of $\text{La}3d_{5/2}$. Also, a split peak at 132 eV can be found in the $\text{Sr}3d$ pattern (See Fig. 3(c)) due to the $\text{Sr}3d_{5/2}$ and $\text{Sr}3d_{3/2}$ core levels. The $\text{Mn}2p$ region in Fig. 3(d) shows two broad peaks at 640 and 651 eV, due to the $\text{Mn}2p_{1/2}$ and $\text{Mn}2p_{3/2}$ core levels, respectively. The measured photoelectron spectra of $\text{O}1s$ in Fig. 3(e) shows the $\text{O}1s$ peak at 528 eV and another shoulder peak at 530 eV, indicating two types of oxygen present on the sample surface. The former is assigned to O^{2-} ion of the metal oxide[32], while the broad shoulder peak is probably due to a superposition of two peaks between the absorbed hydroxide on sample surface and the SrO [21]. According to the statistics of atom % shown in the embedded table of Fig. 3, the ratios of La/Mn , and Sr/Mn in LSMO film surface can be obtained, which is 0.5 and 1.38, respectively. The ratio of La/Mn is close to that of EDS result, while it is larger than that of EDS result for the Sr/Mn . The high ratio of Sr/Mn is similar with previous observations on the film fabricated by reactive pulsed laser deposition[21]. In fact, it is difficult to ensure the concentration of La, Sr, Mn, and O elements from XPS analysis in LSMO film in agreement with that from EDS analysis.

AFM images of LSMO film with different film thickness are displayed in Fig. 4. It is noted that the surface morphology of the films change with thickness due to the change in the growth mode, which in turn causes a variation in surface

roughness. The root mean square roughness is estimated to be 6.29 nm and 45.6 nm for the film with thickness 0.9 μm and 1.52 μm respectively, revealing a relative smooth LSMO film surface.

Fig. 5 shows the measured reflectivity of LSMO film in the temperature range of 97–373 K. It is noted that the reflectivity of film decreases with increasing temperature. A sharp infrared peak at the wavelength of 17 μm under different test temperature can be observed, which dues to the transverse optical phonons. In theory, there are three strong transverse optical phonon peaks in perovskite sample[33, 34, 35]. The other two phonon peaks occur at 30 μm and 60 μm , corresponding to Mn-O-Mn bending mode, and La-site external mode, respectively. In view of the limited spectral range of spectrometer, we only observed the optical phonon peak corresponding to Mn-O stretching vibration in our samples. The phonon peak toward the low temperature 97 K is still sharp comparing with that of LSMO bulk material, which has been reported in the previous works[5, 35]. The fact suggests that LSMO film is “more non-metallic” than its bulk counterpart at low temperature zones. For the LSMO bulk material, the lower temperature is, the smoother peak at 17 μm becomes. The phenomenon has been explained by an dielectric screening effect[33, 36]. Namely, the electron activity in bulk material is heighten under a lower temperature. Therefore, it is considered that the contribution of optical phonon in LSMO film is still dominant under the lower temperature, which leads to LSMO film exhibiting more nonmetallic features. The sharp peaks under low temperature zones seem to be common in manganite film as reported by these authors[19, 20]. With the increase of temperature, there are still notable broad peaks appearing in the wavelength range of 5–10 μm in present films. The fact reveals that the film samples become more prone to insulator at high temperature. Similar features have been observed by pervious authors in both single crystalline[35, 37] and thin film manganites[19, 21, 38, 39, 28]. For the single crystalline samples $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.1, 0.175, \text{ and } 0.3$), it has been observed that the insulator phase sample for $x = 0.1$ also shows a broad peak at the same wavelength range, while the peak disappears for the sample $x = 0.175$

and 0.3[35]. Likewise, the single crystal sample $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ also exhibits a broad peak above 200 K at the same region, which is suggested to come from the optical transitions between electronic levels[37]. Hartinger *et al.*[38] reported that the broad peaks are related to the large polarons excitation in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ thin film. Other possibilities may be exist such as oxygen deficiency, inhomogeneity, and disorder. Since the oxygen content increases with the rise of sputtering pressure resulting in the reduction of oxygen deficiency in film, the broad peak exhibits an obvious diminution at high sputtering pressure, epically 2.0 Pa.

In order detect the transmission properties of LSMO film, the integrating sphere method using the integrating sphere accessory (A-562-G, Bruker Optik GmbH) and general transmissivity method are used. The accessory is possible to transmission assessment, although there is a high signal loss as shown in instruction manual. The integrating sphere transmissivity includes the light transmission and scatter of the measured sample, which is collected inside the integrating sphere and detected by detector. It can be found from the Fig. 6 the integrating sphere transmissivity shows a high signal loss especially beyond the wavelength of 15 μm . The transmissivity of three samples (S1, S2, and S3) from the same growth condition (1.4 Pa sputtering pressure) shows almost coincident results as shown in Fig. 6. It can be seen that the samples are opaque except for the low transmissivity less than 0.35 around the wavelength of 3.6 μm . According to the blackbody radiation spectra at 300 K as shown in Fig. 6, which is determined by Planck's spectral distribution of emissive power, the proportion of emissive energy is small below 5 μm wavelength. The emissivity calculation in present work therefore ignores the transmissivity of the samples.

Infrared emissivity of LSMO film on ACQ substrate is obtained by integrating its reflectivity spectra[11]. The results are shown in Fig. 7. It can be observed that the LSMO films show different emissivity variation with the change of sputtering pressure. The emissivity of these films increases with increasing temperature and undergoes a sharp variation except the film grown at 2.0 Pa. Film grown at 0.5 Pa sputtering pressure has a high emissivity in the

277 whole temperature range. This is caused by the low pressure sputtering process
 278 that contains less oxygen due to the small amount of oxygen atoms in the depo-
 279 sition environment. Moreover, the low bombardment frequency resulting from
 280 the low pressure is conducive to form defect in the films. The formed defect such
 281 as oxygen defect is detrimental to break the hoping bridge of double-exchange
 282 presented by Zener[40], which reduces the conduction activity of electron. With
 283 the increase of pressure up to 2.0 Pa, the variation of oxygen concentration
 284 leads to hole doping through an augment of the $\text{Mn}^{4+}/\text{Mn}^{3+}$. In addition, the
 285 oxygen incorporation within columns or grains of the film structure can also
 286 be suggested to strengthen the metal-insulator transition toward to a higher
 287 temperature. Therefore, these contributions lead to a decrease of the emissivity
 288 of film in addition to an increase of metal-insulator transition temperature re-
 289 ported by Sahu[41]. Temperature-dependent emissivity of film deposited at 2.0
 290 Pa is smaller than that of the other film samples and no drastic change can be
 291 observed in the entire temperature range as the film is in the metallic state in
 292 the temperature region like its bulk counterpart reported in reference[1]. Large
 293 emissivity at higher temperature is necessary to enhance the ability of heat dis-
 294 sipation in spacecraft application and small emissivity at lower temperature is
 295 still important to prevent the heat loss from the inside of spacecraft. Thereby,
 296 the emissivity variation properties of the film deposited at 1.4 Pa is attractive
 297 in spacecraft application.

298 Spacecraft thermal control materials are described by their heat rejection
 299 capacity. If the thermochromic film is deposited onto the spacecraft skin with-
 300 out suffering solar radiation, its heat rejection capacity $\dot{Q}$ can be represented by
 301 $\dot{Q}/A = \dot{q} = \epsilon\sigma(T_s^4 - T_b^4)$. Here, σ is the Stefan-Boltzmann constant($5.67 \times 10^{-8} \text{W/m}^2 \cdot$
 302 K^4), A is the thermal control surface area, $\dot{q}$ is the heat rejection density, T_s is
 303 the thermal control surface temperature, T_b is the space background temper-
 304 ature(4 K), ϵ is the emissivity of the thermal control material. This is only a
 305 simplified model to account for a thermal control application for thermochromic
 306 film. Here, we calculated the heat rejection density $\dot{q}$ of three thermal control
 307 materials (Aluminium, OSR, and LSMO film deposited at 1.4 Pa, respectively.)

308 to evaluate their application performance. The calculated results are show in
 309 Fig. 8. If the temperature fluctuation of spacecraft surface is required in the
 310 range of 250–300 K, one expects a large enough heat rejection density above
 311 300 K and a small enough heat rejection density or a suitable heating below
 312 250 K. It can be found that OSR film ($\epsilon = 0.8$) and Al film ($\epsilon = 0.04$) are
 313 the expected thermal control materials above 300 K and below 250 K, respec-
 314 tively. Unfortunately, the usage of OSR requires an auxiliary heater when the
 315 temperature is low to 250 K and the usage of Al film needs an auxiliary cooler
 316 above 300 K. This means an additional power consumption and moving parts
 317 are required. However, the usage of LSMO film can reduce or avoid heater re-
 318 quirement because of its lower heat loss than that of OSR film below 250 K and
 319 comparable heat rejection capacity above 300 K. By comparison, the thermal
 320 control performance of LSMO film is obvious.

321 Comparisons are given for the emissivity of LSMO film deposited at differ-
 322 ent substrate in Fig. 9. Considering the effect of substrate on the emissivity of
 323 LSMO film, it can be found that the largest emissivity is obtained for the film on
 324 quartz substrate. Its emissivity value is larger than that of literature results in
 325 the entire temperature range[28], probably because of the influence of substrate.
 326 The adherence strength of the film on the quartz is low. The inset in Fig. 9
 327 shows a broke film sample deposited on quartz after standing for several days in
 328 air. Therefore, the contribution of substrate can be reflected in the emissivity
 329 curve. The metal-insulator transition in manganite films is extremely related
 330 to the growth condition and substrate characteristics which influence the mi-
 331 crostructures of the manganite films, and then their optical, thermal, electrical,
 332 and magnetic properties[21, 42, 43]. The transition temperature point estimated
 333 from the emissivity-temperature curves is different in our films which apparently
 334 accounts for this. The emissivity of the film on ACQ substrate is relative larger
 335 than that of the film on YSZ and Si substrate. Difference in the emissivity
 336 value may be due to the interface problems and change in the strain behaviors
 337 of the film and substrate. The presence of inhomogeneity, mostly existing at the
 338 interface, also significantly influences the thermal radiative properties. There

may be exist other possibilities such as oxygen nonstoichiometry in films. These factors are important to device design and application.

4. Conclusion

Thermochromic films are prepared on different substrates by magnetron sputtering technique. Ex-situ annealing in oxygen atmosphere improves the film crystallization and oxygen balance. Surface morphology indicated that crack-free thick films is difficult to be deposited by sputtering. XRD analysis showed that the films exhibit the characteristics of perovskite structure. Reflectivity spectra show that the oxygen deficiency is related to the sputtering pressure. Sputtering pressure effect on thermochromic film properties is investigated. Emissivity of the film is large at high temperature and it decreases sharply upon cooling. Difference in emissivity is not only dependent on the sputtering pressure but also strain behavior of film and substrate. Film deposited on ACQ substrate with 1.4 Pa sputtering pressure shows good thermochromic properties, which is comparable with existing OSR film in spacecraft thermal control.

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Figure captions page

Fig. 1: XRD patterns of (a) LSMO film onto ACQ substrate without annealing, (b) LSMOACQ08, (c) LSMOACQ14, (d) LSMOACQ20, and (e) LSMO target.

Fig. 2: Surface micrographs of LSMO film on ACQ substrate with film thickness (a) $0.9\ \mu m$ and (b) $1.52\ \mu m$, and (c) EDS pattern.

Fig. 3: XPS spectra of (a) LSMO film on ACQ substrate, (b) La3d, (c) Sr3d, (d) Mn2p, and (e) O1s.

Fig. 4: AFM images of LSMO film on ACQ substrate with film thickness (a) $0.9\ \mu m$ and (b) $1.52\ \mu m$.

Fig. 5: Reflectivity of LSMO film at different working pressure for (a) 0.5 Pa, (b) 0.8 Pa, (c) 1.4 Pa, and (d) 2.0 Pa.

Fig. 6: Room temperature transmissivity of LSMO film at 1.4 Pa sputtering pressure. Transmissivity consistency is verified by measuring three samples (S1, S2, and S3) from the same growth condition.

Fig. 7: Emissivity of LSMO film at different sputtering pressure.

Fig. 8: Emissivity effect on the heat rejection capacity due to the temperature fluctuation.

Fig. 9: Emissivity of LSMO film with different substrate. The inset is a broken film sample deposited on quartz and the peeled portions are marked by arrows.

Table 1: Deposition conditions of preparing LSMO films.

Table 1

Film sample	Substrate	P_{gas} (Pa)	Γ (nm/min)
LSMOACQ05	ACQ	0.5	5.6
LSMOACQ08	ACQ	0.8	5.8
LSMOACQ14	ACQ	1.4	5.9
LSMOACQ20	ACQ	2.0	5.2
LSMOSi08	Si	0.8	4.9
LSMOYSZ08	YSZ	0.8	5.0

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Image Name: 1112--1-2sio2(2)
 Accelerating Voltage: 20.0 kV
 Magnification: 1000

Full scale counts: 986

1112--1-2sio2(2)_pt1

Weight %

	O	Al	Si	Mn	Sr	La	Au
1112--1-2sio2(2)_pt1	18.45	14.14	8.91	13.99	9.44	23.11	11.94

Atom %

	O	Al	Si	Mn	Sr	La	Au
1112--1-2sio2(2)_pt1	44.63	20.28	12.28	9.85	4.17	6.44	2.35