Fabrication of La$_{1-x}$Sr$_x$MnO$_3$ thin films by chemical solution deposition for high-temperature resistive materials

Kentaro SHINODA,† Tomohiko NAKAJIMA and Tetsuo TSUCHIYA

Flexible Chemical Coating Group, Advanced Manufacturing Research Institute (AMRI), National Institute of Advance Industrial Science and Technology (AIST), 1–1–1 Higashi, Tsukuba, Ibaraki 305–8565, Japan

Epitaxial thin films of heavily doped perovskite manganite (La$_{1-x}$Sr$_x$MnO$_3$ or LSMO with $x \geq 0.5$) were successfully fabricated onto SrTiO$_3$(001) single crystal substrates by chemical solution deposition. The electrical resistivity and the Hall coefficient were measured from 200 to 673 K. The temperature coefficient of resistance reached a minimum at $0.6 \leq x \leq 0.7$. A high-temperature stability test showed that the LSMO thin films could be used up to 673 K. This study has shown that LSMO thin films are good candidates as high-temperature resistive materials that can be used in SiC power electronics.

Key-words : LSMO, MOD, SiC power electronics, Resistive materials

1. Introduction

The operating temperature of next-generation silicon carbide (SiC) power modules is expected to reach 250°C for higher efficiency and higher output power density mainly aimed at automobile applications. The increase in the operating temperature require peripheral components that can work at these high temperatures, including passive components such as resistors and capacitors, which are currently designed to work at the operating temperatures below 125°C (314). In particular, resistors need to withstand higher temperatures because of Joule self-heating. Figure 1 shows a thermographic image of a thick-film chip resistor to which the power of 1 W is applied. Resistors dissipate the applied power by converting it into heat, and the increase in temperature depends on a balance between heat generation and heat extraction. Depending on the heat balance, resistor temperature can increase by 50–150°C. In case of Fig. 1, the surface temperature of the resistor actually reached 160°C. Considering this self-heating of resistors, resistive materials must endure temperatures of at least 300°C, preferably 400°C for SiC power modules. The development of high-temperature resistive materials is thus important in order to realize high-temperature operation of SiC power modules.

The most common systems now in use for thick-film resistors are based on ruthenium compounds combined with glass. Although the use of glass has many advantages such as resistivity control and good adhesion to the substrate, softening of glass components in the resistive materials can cause a change of the resistivity at high temperatures. Another problem is that glass components used for resistors typically include lead, which is toxic and thus not desirable. Also, the low thermal conductivity of glass may not be desirable from the viewpoint of thermal management. The reduction of ruthenium usage is another demand. Ruthenium is relatively expensive and the price has not remained steady. Therefore, the development of alternative resistive mate-

† Corresponding author: K. Shinoda; E-mail: kentaro.shinoda@aist.go.jp
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Fig. 1. Thermography of a temperature rise of a resistor to which a power of 1 W is applied through the clips. The size of the resistor is 6.3 mm by 3.1 mm. The target line reads the maximum surface temperature of 160°C.
use of LSMO as a new lead-free and ruthenium-free resistive material for conventional thick film resistors.\textsuperscript{12,13} They showed that zero TCR of La$_{1-x}$Sr$_x$MnO$_3$ could be achieved at approximately 0.200 < $x$ < 0.225 and 0.45 < $x$ < 0.50 in the temperature range between 25 and 125°C. However, the temperature-dependence of resistivity above 125°C and below 25°C has not been reported yet. For use at high temperatures, the ideal composition may be different from the compositions used in previous studies.

In the present study, we investigated the electrical properties of LSMO, including TCR and stability, up to 400°C. The composition of La$_{1-x}$Sr$_x$MnO$_3$ with $x$ ≥ 0.5 in particular was examined. We utilized a metal–organic deposition (MOD) method to fabricate epitaxial LSMO thin films onto SrTiO$_3$ (STO) single-crystal substrates. MOD enables precise control of the metal composition.\textsuperscript{14,15} In the past, LSMO thin films have been fabricated by MOD,\textsuperscript{14-19} and it has been found that the use of STO(001) substrates enables the epitaxial growth of LSMO thin films.\textsuperscript{14,15,19} The target compositions used to fabricate La$_{1-x}$Sr$_x$MnO$_3$ in these studies were all $x$ < 0.4. This paper will also contribute to an understanding of the electrical properties of LSMO thin films, where $x$ ≥ 0.5, that are fabricated by chemical solution deposition.

2. Materials and Methods

LSMO thin films were fabricated onto single crystalline STO(001) substrates by MOD. The precursor solution used for fabricating the LSMO films contained premixed 2-ethylhexanoate solutions of La, Sr, and Mn diluted with xylene and toluene. Six solutions in which $x$ = 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 were prepared. These solutions were spin-coated onto the STO substrates at 4000 RPM (revolutions per minute) for 10 s. The coated films were dried at 100°C in air to remove the solvent, and then preheated at 500°C in air for 10 min to decompose the organic residues in the films. This procedure was repeated three times to increase the film thickness. The obtained amorphous films were fired at 800, 900, and 1000°C in air for 3 h. The final thickness was ~30 nm. The crystallinity of the films and the occurrence of epitaxial growth were measured by an X-ray diffraction method using Cu Kα radiation filtered by Ge(220) (SmartLab, Rigaku Corp., Tokyo, Japan). The distortion of LSMO from a cubic lattice was minimal, even though the crystal structure of LSMO depends on the amount of Sr substituted.\textsuperscript{14} Therefore, indices of LSMO were assigned as pseudo cubic. The temperature dependence of the electrical resistivity was measured by the van der Pauw method (ResiTest 8300, Toyo Corp., Tokyo, Japan). The Hall measurements were also conducted with the same system.

3. Results and discussion

We examined the effect of firing temperature on the crystallinity of La$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films first. All of the LSMO thin films fired at 800, 900, and 1000°C were epitaxial exhibiting only (00l) reflections in the XRD measurements. Figure 2 shows the XRD patterns near the STO(002) peaks of the La$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films on the single-crystal STO(001) substrates. The presence of a strong (002) reflection of LSMO near that of STO was confirmed. This epitaxial growth was consistent with our past demonstrations in other perovskite manganites on STO(001) substrates.\textsuperscript{20-23} When the firing temperature increased from 800 to 1000°C, the intensity of the (002) reflection increased and the full width at half maximum (FWHM) decreased, suggesting the improved crystallinity of LSMO thin films at high firing temperatures. No clear relationship between the position of the (002) peaks and the firing temperature was observed. This tendency is in contrast to the behavior of La$_{0.5}$Ca$_{0.5}$MnO$_3$ thin films on STO(001) substrates reported by Daoudi et al.\textsuperscript{20} They observed a shift of the (002) peak to a low angle when the firing temperature was increased from 800 to 1000°C. Dho et al. reported that an increase in oxygen pressure caused a shift of the (002) reflections to a lower angle in La$_{0.5}$Sr$_{0.5}$MnO$_3$ films grown by pulsed laser deposition on STO substrates.\textsuperscript{21} Therefore, Daoudi et al. considered that the shift of the (002) peaks to the low angle could be attributed to an increase in oxygen content with increased annealing temperature. In our case, the reduced dependence of the firing temperature on the lattice parameters would indicate that fabrication of LSMO films at this composition ($x$ = 0.5) is less dependent on the oxygen content that could be varied by the firing temperature. Mizusaki et al. reported that the electrical properties are less dependent on the oxygen pressure down to pressures of ~1 Pa at 600–1000°C for higher Sr content ($x$ > 0.4).\textsuperscript{25} Our results are consistent with their results, implying better stability of LSMO with $x$ = 0.5. The out-of-plane lattice parameter was calculated from the (002) reflections to be $c = 3.850$ Å. Spooren et al. reported unit cell data of a single crystal of La$_{0.5}$Sr$_{0.5}$MnO$_3$ fabricated by hydrothermal synthesis.\textsuperscript{26} The powder XRD results from the material were indexed using a primitive cubic unit cell with $a = 3.8467$ Å. They also measured high-resolution powder neutron data from the material, which is more sensitive to the positions of oxide ions than XRD, indicating that the material actually exists as a lower symmetry polymorph than as a primitive cubic structure. The powder neutron diffraction showed a distorted perovskite structure (tetragonal, I4/mcm, $a = 5.44778$ Å, $c = 7.7353$ Å). A reduced pseudo face-centered tetragonal unit of the material gives $a_0 = a/\sqrt{2} = 3.85216$ Å and $c_0 = c/2 = 3.8677$ Å. Thus, if the neutron data is adopted, it is expected that the LSMO thin films were slightly compressed in the out-of-plane direction; that is, the films were stretched in the in-plane direction by the STO substrate in which $a = 3.905$ Å. The magnitude of strain was of the same order as that of the distorted perovskite structure of the
LSMO single crystal. Therefore, the effect of biaxial strain on the electrical properties may not be significant with the composition used in this study.

Figure 3 shows the temperature dependence of the electrical resistivity \( \rho \) and the TCR \( C_R \) of LSMO thin films. With increasing firing temperature, the electrical resistivity decreased by an order of magnitude at 300 K and the peak temperature \( T_p \) indicated by the arrows increased from \( \sim 300 \) to 380 K. Here \( T_p \) is defined as either the temperature at which the electrical resistivity reaches a maximum when the peak of the electrical resistivity is observed clearly, or as an inflection point on the \( \rho-T \) curve. Although we have not measured the magnetic properties of LSMO, the existence of \( T_p \) was basically attributed to the ferromagnetic-to-paramagnetic transition at the Curie temperature \( T_C \). The value of \( T_C \) is reportedly \( \sim 360 \) K at \( x = 0.5 \) for single crystals,\(^{10,28}\) which was close to \( T_p \) at 1000°C. The TCR, which was calculated by \( C_R = (1/\rho) \times (d\rho/dT) \) from Fig. 3(a), is shown in Fig. 3(b). A maximum TCR of 1.4% at 320 K was obtained for the firing temperature of \( 1000°C \). Then, the TCR rapidly decreased but remained positive with increasing temperature, suggesting that La0.5Sr0.5MnO3 fired at 1000°C was a paramagnetic metal above \( T_C \). Meanwhile, the TCR of the other two firing conditions was negative, suggesting that at those temperatures the LSMO samples were the paramagnetic insulators (semiconductors). Previous papers reported that a La0.5Sr0.5MnO3 single crystal was paramagnetic above \( T_C \).\(^{10,29}\) Therefore, the quality of the LSMO fired at 1000°C was comparable to that of a single crystal. Figure 4 shows (a) the carrier concentration \( N_c \) and (b) the mobility \( \mu \) of La\( _{1-x} \)Sr\( _x \)MnO\( _3 \) thin films \((x = 0.5)\) fabricated by a chemical solution deposition method onto SrTiO\( _3(100) \) single crystal substrates. Three firing temperatures \( T_{\text{max}} = 800, 900, \) and \( 1000°C \) are shown.

![Figure 3](image1.png)

![Figure 4](image2.png)
which can be judged from the FWHM of the (002) peaks shown in Fig. 2. Therefore, the lower electrical resistivity at the higher firing temperature was mainly attributed to the higher mobility and larger grains. Therefore, we chose the firing temperature of 1000°C hereafter.

Figure 5(a) plots the XRD patterns of La$_{1-x}$Sr$_x$MnO$_3$ thin films fabricated at the firing temperature of 1000°C on STO(001) single crystal substrates, showing the effect of Sr substitution from 0.5 to 1.0 on the crystallinity of the La$_{1-x}$Sr$_x$MnO$_3$ thin films. (b) Out-of-plane lattice parameter c and intensity I calculated from peaks indicated by the arrows in (a). The pseudo cubic structure is assumed.

Figures 6(a) and 6(b) show the electrical resistivity and calculated TCR of LSMO, respectively, with $x = 0.5 - 0.9$. Here, two transitions were observed. One was a transition from metallic conduction to semiconducting conduction, which occurred between $x = 0.6$ and $x = 0.7$. This transition can be judged from the sign of TCR shown in Fig. 6(b). Although this transition seems to largely depend on the quality of LSMO, this transition suggests that a minimum TCR can be obtained at $x$ between 0.6 and 0.7 in MOD. Kagomiya et al. reported that the minimum TCR could be obtained around $0.200 < x < 0.225$ and $0.45 < x < 0.50$ at the temperature range between 25 and 125°C, which is clearly different from the results of our study. This study shows a third region in which zero TCR can be achieved. The other transition was the one associated with the ferromagnetic-paramagnetic transition, as indicated by the arrows as was observed in Fig. 3(a). This transition temperature decreased with increasing $x$ for $0.5 < x < 0.7$, but this transition was not observed for $x > 0.8$ at $T > 200$ K. The existence of the transition is not favorable for achieving low TCR for resistor applications. Lowering the ferromagnetic-paramagnetic transition below the lower limit of resistor usage will be required for realizing LSMO as resistive materials. Figures 7(a)–7(c) show the Hall coefficient $R_H$, carrier concentration $N_c$, and mobility $\mu$ of LSMO for $x = 0.5$, 0.6, and 0.7, respectively. The sign of $R_H$ was negative,
suggesting n-type conduction. Mizusaki et al. reported that LSMO for $x^{0.5}$ was no longer a p-type conductor but rather an n-type one.$^{26}$ Our results are consistent with their results. In the paramagnetic region, the larger the value of $x$, the higher the carrier concentration tends to increase with increasing $T$. Meanwhile, the mobility tends to decrease with increasing $x$. A detail analysis of the Hall measurement in the ferromagnetic region will require magnetic measurements.$^{31-34}$ which are beyond the scope of this study. At higher temperatures, the values of $\rho$, $N_c$, and $\mu$ tend to converge, that is, $2-3 \times 10^{-3}$ $\Omega$ cm, $5-7 \times 10^{-3}$ $cm^2/Vs$, and $3-5 \times 10^{-2}$ $cm^2/Vs$, respectively, despite different values of $x$. Due to scattering by phonon vibration, the mean free path of the charge carriers even in the metallic regime approaches interatomic distances once the resistivity exceeds $10^{-3}$ $\Omega$ cm based on free-electron ideas.$^{35,36}$ Above this value, electrons are localized and all transport processes must be considered within a hopping framework. This framework comes into existence in our case, and it has important implications in terms of finding new high-temperature resistive materials: If the electrical resistivity converges into a certain value at high temperature, then it is important to find a material with electrical resistivity on the order of $10^{-2} - 10^{-3}$ $\Omega$ cm at low temperature in order to obtain small TCR.

A long stability test was conducted for these thin films up to 400°C. Figure 8(a) shows the change of the sheet resistance $R_{sh}$ of La$_{1-x}$Sr$_x$MnO$_3$ thin films ($x = 0.5$) that are kept at temperatures of 150–400°C. (b) Deviation of sheet resistance ($R_{sh}/R_0$) from initial value with $t$. Fig. 7. (a) Hall coefficient $R_H$, (b) carrier concentration $N_c$, and (c) mobility $\mu$ of La$_{1-x}$Sr$_x$MnO$_3$ thin films ($x = 0.5-0.7$) fabricated by a chemical solution deposition method onto SrTiO$_3$(100) single crystal substrates. The firing temperature of the films is $T_{max} = 1000^\circ$C.
by MOD were shown to be stable up to \( T = 400^\circ\text{C} \).

4. Conclusions

We have investigated the electrical properties of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) thin films with \( x \geq 0.5 \) fabricated by chemical solution deposition. Epitaxial thin films of LSMO were successfully fabricated onto STO(001) single-crystal substrates. The TCR of the LSMO thin films reached a minimum at 0.6 \( \leq x \leq 0.7 \). The long-term stability test proved that LSMO thin films could be used at temperatures at least up to 400\(^\circ\text{C}\), which is sufficient for use as high-temperature resistors for SiC power electronics. Meanwhile, the TCR shows a relatively large value because of the existence of a ferromagnetic-paramagnetic transition. Reducing this transition temperature will be required for realization of LSMO-based high-temperature resistors. This study also shows that materials that have an electrical resistivity on the order of \( 10^{-2} - 10^{-3} \Omega\text{cm} \) at low temperatures will be good candidates for realizing low TCR for high-temperature resistive materials.

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