La–Ca–Mn–O Thin Film based Thermistor for Measuring Low Temperature of 77–230 K

Jae-Hoon SONG, Kyoung-Kook KIM, Hyung-Jin JUNG, Duck-Kyun CHOI1 and Won-Kook CHOI*
Thin Film Technology Research Center, Korea Institute of Science and Technology, Cheongryang P.O. Box 131, Seoul 136-791, Korea
1Department of Inorganic Materials Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-Ku, Seoul 133-791, Korea

(Received January 17, 2000; accepted for publication May 24, 2000)

Perovskite manganite La–Ca–Mn–O (LCMO) thin films were deposited on LaAlO3 (001) single crystal substrate by radio-frequency magnetron sputtering at room temperature. After annealing at 800–1000°C in O2 atmosphere for 1 h, sheet resistance (R) of the LCMO thin films was measured by van der Pauw method in the range of 77–300 K. The characteristic resistance-temperature curves of all the annealed films showed typical insulator to metal transition behavior of colossal magnetoresistance (CMR) materials on cooling. The sheet resistance of LCMO films changes with temperature, conforming to a function of expβ(T) in the temperature range from 77 K to 230 K, which is applicable to an oxide thin film thermistor.

KEYWORDS: Perovskite manganite La–Ca–Mn–O, colossal magnetoresistance, sheet resistance, thin film thermistor

1. Introduction

Several solid-state resistance-thermometers (RTs), thermistor, have been developed for measurement of cryogenic temperature. RTs are available with either negative or positive temperature coefficient of resistance (TCR). The former is typified by a variety of semiconductor sensing elements, the latter by pure metal elements of wire-wound or film construction.1

The standard platinum RT (PRT) is known to be highly accurate and pre-eminent among RTs. Dilute alloy type RTs like Rh-Fe (RIRT) and Pt–Co appeared to extend the useful range provided by PRT. As for semiconductor RTs, Ge RT has been used for high-precision sensor.2,3 An amorphous semiconductor-metal alloy of Ge and Cu was developed as a thin-film sensor showing high sensitivity in the range of helium. The carbon RT (CRT) is probably most popular and massive in use. In cases of ceramic RTs, RuO2 thick film of lithium. The carbon RT (CRT) is probably most popular and

2. Experimental

LCMO thin films were grown on LaAlO3 (001) single crystal substrate by RF planar magnetron sputtering using 2-in La0.67Ca0.33MnO3 target which was sintered from oxide powders prepared by sol–gel processing. The films were deposited at room temperature as large as 7 mm × 7 mm with about 150 nm thickness. A mixture of Ar : O2 = 4 : 1 was used for plasma gas and the RF power range adopted was 100 W. As-deposited LCMO films were annealed in O2 atmosphere for 1 h and then crystalline and surface microstructure were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. In order to find temperature dependence of resistance, the sheet resistance of the LCMO films was measured by a conventional van der Pauw method in the temperature range of 77–300 K.

3. Results and Discussion

3.1 Crystallinity and surface microstructure

Figure 1 shows the XRD spectra for each of the LCMO thin films annealed at 800–1000°C and at RF power of 100 W. In the XRD patterns, the peaks related found at 2θ = 24°, 29.5°, and 47.5° are believed LCMO (100), (110) and (200) peaks, respectively, by comparison with the lattice parameters of the previously reported LCMO films11,12 and in particular it was difficult to discern the reflections from LCMO (100) existing just beside those of LAO (001) substrate. As shown in Fig. 1(a), the film deposited at 10 mTorr shows only the reflections of LCMO (100) and (200), and so regarded as being grown with highly oriented direction parallel to the substrate. Since the XRD peaks of LCMO (110) and (111) appeared in the film deposited at 50 mTorr, it is believed polycrystalline structure. Those peaks disappeared once again in the film deposited at 100 mTorr, but the crystalline quality might be poorer than that deposited at 10 mTorr due to the broadening of LCMO (100) and (200) diffraction linewidth.

In case of 900°C and 1000°C annealing, the only peaks of LCMO (100) and (200) could be detected in the films deposited at both 10 mTorr and 50 mTorr, and the latter has narrower FWHM of the peak than the former. As shown

*Corresponding author: E-mail: wkchoi@kist.re.kr

Part 1, No. 8, August 2000
©2000 The Japan Society of Applied Physics

4993
in Fig. 1(c), especially the films deposited at 50 mTorr look like being grown with highly preferred orientation along with (200) direction. Compared to the films annealed at 800°C, the crystalline quality was similarly not improved in the film deposited at 100 mTorr, either. From the above XRD results, no peaks shift in the position was observed as the annealing temperature increased from 800 to 1000°C. This means that the crystallinity of all the films was almost equivalent to that of bulk sample when annealing temperature was higher than 800°C.

Figure 2 shows the changes of surface microstructure of annealed LCMO films deposited at the conditions of 50 mTorr
seems that the grain growth was not fully progressed during 1 h annealing at 800°C. But after 900°C annealing at 1 h, grains were observed well formed and uniformly distributed. The grain size was measured about as much as 300 Å on the average. This result is agreeable with the report that complete grain growth in the as-deposited La–Sr–Mn–O films by RF sputtering could not be observed on annealing at 800°C, but was found only after 900°C annealing. On the further annealing at 1000°C, coalescence of the islands seems to be happened from the increase of the size of both the islands and pores in Fig. 2(c).

3.2 Sheet resistance vs. temperature

Figure 3 represents the sheet resistance change of the annealed LCMO films taken by van der Pauw method without magnetic field applied in the temperature ranges of 77–300 K. All the films showed typical characteristic curves of CMR materials in which the transition from insulator to metal should be existed on cooling. In cases of La_{0.67}Ca_{0.33}MnO_{3}, the transition temperature \(T_c\) was known to be around \(T_c = 250\) K and at which temperature resistance coefficient was altered from negative to positive above and below \(T_c\), respectively. As mentioned in the section of Introduction, the relationship between resistivity and temperature in the range of \(T < 0.5T_c\), the resistivity was followed by \(T^2.5\) or \(T^4.5\) etc considering the scattering theory based upon electron-electron, electron-magnon, electron-phonon interactions. However, there was no acceptable theory to explain well the change of resistivity.

Let assume the sheet resistance of the LCMO film is proportional to resistivity. In order to ensure the meaningful data available for an empirical fitting, the valid range of temperature was properly defined as follows. The inflection temperature \(T_t\), the highest temperature, above which the rate of the increment turns from positive to negative can be obtained by differentiating and satisfying the condition of \(dR/dT = 0\) at \(T = T_t\). The change of \(dR/dT\) vs. temperature are shown in inset of Fig. 3 and the \(T_t\)’s are listed in Table I. \(T_t\) shows the lowest value of 212.8 K (800–100) and the highest one of 263.9 K (900–50) and mostly lies in the range of 240–260 K. It is so natural that \(T_t\) is increased as \(T_c\) increased. At first sight, the sheet resistance seems to exponentially increase as a function of temperature. Therefore without con-

\[R = A \exp(\beta T)\]

Table I. Empirically fitted function of \(R-T\), error (%) in the temperature range of 77–\(T_t\) (K), and the temperature range having the accuracy of an error less than 0.5%.

<table>
<thead>
<tr>
<th>Samples (800-10^2)</th>
<th>10.085</th>
<th>0.638</th>
<th>245.9</th>
<th>94.0</th>
<th>78–200 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>800–50</td>
<td>0.0013</td>
<td>0.046</td>
<td>242.0</td>
<td>92.3</td>
<td>91–179 K</td>
</tr>
<tr>
<td>800–100</td>
<td>0.1738</td>
<td>0.048</td>
<td>212.8</td>
<td>99.4</td>
<td>90–173 K</td>
</tr>
<tr>
<td>900–50</td>
<td>0.0103</td>
<td>0.047</td>
<td>263.9</td>
<td>95.2</td>
<td>77–232 K</td>
</tr>
<tr>
<td>900–100</td>
<td>26.8993</td>
<td>0.023</td>
<td>249.9</td>
<td>98.5</td>
<td>77–210 K</td>
</tr>
<tr>
<td>1000–10</td>
<td>0.0047</td>
<td>0.046</td>
<td>261.8</td>
<td>95.1</td>
<td>81–204 K</td>
</tr>
<tr>
<td>1000–50</td>
<td>0.013</td>
<td>0.043</td>
<td>261.7</td>
<td>90.3</td>
<td>77–214 K</td>
</tr>
</tbody>
</table>

(a) \(T_t\): Inflection temperature taken from \(dR/dT = 0\) at \(T = T_t\)
(b) 800–10 indicates the sample deposited and annealed at 10 mTorr and 800°C, respectively.

Fig. 2. Scanning electron microscopy images for the LCMO films deposited at 50 mTorr and annealed at (a) 800°C, (b) 900°C, and (c) 1000°C in O\(_2\) for 1 h.
Considering any special functions based upon theoretical calculation, the sheet resistance \( R \) was fitted by exponential function of \( R = A \exp(\beta T) \) in the range of 77 K–\( T_\text{f} \) (K). Fitted values of \( A \), \( \beta \) and also the accuracy \( \sigma \) (%) between fitted value and experimental data within 77 K–\( T_\text{f} \) (K) are listed in Table I, respectively. It is very interesting that the \( \beta \)'s lie in the very similar values of 0.043–0.048 except two samples of 0.638 (800–50) and 0.023 (900–100). Even though the acquired \( \beta \) seems to hold some general value, however, its physical meaning can hardly be interpreted up to now and should be further deeply investigated what it is related to. On the other hand, more accurate \( \beta \) can be derived and determined experimentally by accurate measurements using a lots of LCMO thin films. Consequently the film sheet resistance is proportional to the function \( \exp(\beta T) \), where \( T \) is temperature of 77K–\( T_\text{f} \) (K). As can be seen in Table I, obtained empirical curves was quite well fitted to the sheet resistance data with higher accuracy than 90% up to \( T_\text{f} \) (K). From these results, it can be easily predicted that the logarithm of \( R \), called \( R' \), would be linearly proportional to temperature. Such linearity between resistance and temperature will be very appropriate for fabricating a new concept of thin oxide film-based thermistor.

\( R' \) data for the LCMO samples were plotted as a function of temperature in Fig. 4. As mentioned above, most curves of \( R' \) show a similar slope except two samples of 800–50 and 900–

Fig. 3. Changes of sheet resistance \( R \) of the LCMO thin films annealed at (a) 800°C, (b) 900°C, and (c) 1000°C. \( R \) was measured by van der Pauw method in the temperature of 77–300 K. Inset represents each corresponding change of \( dR/dT \) vs. temperature.
For the application of the LCMO/LAO as a thermistor, temperature ranges showing a good linearity are required to be determined, and which will be a key factor to estimate the quality of characteristic $R - T$ as a temperature-sensor of the LCMO thin films. In this experiment, temperature ranges are decided by linear fit satisfying the accuracy having errors less than than 0.5%. As shown in Table I, the 800–50 shows very constant TCR in relatively small range of 90–173 K, but the 900–50 sample exhibits further wide temperature ranges of 77–232 K, respectively.

### 4. Conclusions

From perovskite manganite LCMO thin film grown on LAO (001) by RF magnetron sputtering, the sheet resistance $R$ is empirically found to be proportional to $\exp(\beta T)$ in the positive TCR temperature range below $T_c$. Most annealed LCMO thin films at 800–1000°C show good linear $R - T$ characteristic curves in the low temperature range of 90–170 K, and especially the 900–50 sample exhibit the best linearity in the temperature as wide as 77–232 K within the accuracy of 99.5%. Using such a superior peculiar property of having constant TCR below $T_c$ in perovskite manganite, a new thin oxide film thermistor for precisely measuring the low temperature can be successfully fabricated and moreover by simply different doping and changing stoichiometry of perovskite manganites (La,Pr,Sm,Nd)$_{1-x}$(Sr,Pb,Ba)$_x$MnO$_3$, the low temperature range in which resistance varies linearly with temperature can be carefully controlled.