J Electroceram (2006) 16:527–532
DOI 10.1007/s10832-006-9911-3

Substrate effect on the temperature coefficient of resistance of $La_{0.7}Ca_{0.3}MnO_3$ thin films prepared by metal organic deposition

K. Daoudi · T. Tsuchiya · I. Yamaguchi · T. Manabe · S. Mizuta · T. Kumagai

Abstract Epitaxial $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) thin films were successfully prepared by the metal-organic deposition process on various (001) single-crystal substrates: MgO, $LaAlO_3$ (LAO), $SrTiO_3$ (STO), and $(LaAlO_3)_{0.3}$-$(SrAlTaO_6)_{0.7}$ (LSAT). The crystallinity and the epitaxial growth of the LCMO films were characterized by X-ray diffraction ($\theta - 2\theta$ scans and pole-figure analysis). The temperature dependence of the resistance of the LCMO/LSAT, LCMO/STO and LCMO/LAO films exhibit typical characteristics with a transition from the paramagnetic-insulator state to the ferromagnetic-metallic state at a temperature peak (T_p) ranging from 258 to 270 K. However, the LCMO/MgO films exhibited a semiconducting behavior without any transition. Based on the $R(T)$ measurement, we calculated the temperature coefficient of resistance (TCR) for a bolometric application and we obtained 22%/K, 10.2%/K and 27.5%/K for the film grown on the LSAT, STO and LAO substrates, respectively. This difference in the TCR properties is related to the strain induced by the lattice mismatch between LCMO and the different substrates.

Keywords Thin films · Epitaxial growth · MOD · LCMO · TCR

1 Introduction

Perovskite manganese oxide materials of the type $Ln_{1-x}A_x$ MnO_3 (with Ln the rare earth—La, Pr or Nd; A the divalent alkali earth metal—Ca, Ba or Sr) have recently attracted much attention both from a fundamental point of view and also for their application in devices. These perovskite manganite compounds exhibit colossal magnetoresistance (CMR) effects and are characterized by a peak in the temperature (T_p) dependent resistivity close to the Curie temperature (T_c) at which a phase transition occurs from the low temperature ferromagnetic metallic state to the high temperature paramagnetic semiconducting state [1–3]. The CMR could be related to the double exchange mechanism, which depends on the Mn−O−Mn bond distance and angle [4]. Recent theoretical and experimental studies have shown that the double exchange model does not totally explain the magnitude of the magnetoresistance [5–7]. The physical properties of the manganite thin film are sensitive to structure, oxygen content, and disorder, therefore, the T_c and resistivity of the film are somewhat different from those of the bulk material. Consequently, the growth method, the deposition parameters, and also the substrate induced strain will influence these properties. Understanding the strain is of particular interest since it can be used to advantage in tuning film properties, as has already been demonstrated in cuprates [8]. Since the resistance change occurs over a relatively narrow temperature range, it is accompanied by a large temperature coefficient of resistance (TCR) in the phase transition region, making these materials excellent candidates for infrared detectors utilizing resistance bolometers. Goyal and coworkers [9] studied the TCR and T_p properties of different perovskite materials, such as $La_{0.7}Ba_{0.3}MnO_3$ (LMBO), $La_{0.7}Sr_{0.3}MnO_3$ (LSMO), $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) and $Nd_{0.7}Sr_{0.3}MnO_3$ (NSMO) on $LaAlO_3$ (LAO) substrates. As a result, LCMO and NSMO were found to be the most promising materials for bolometric applications in terms of their TCR values. However, the effect of the lattice mismatch between LAO and the different systems (NSMO, LCMO, LBMO and LSMO) and its

K. Daoudi (✉) · T. Tsuchiya · I. Yamaguchi · T. Manabe · S. Mizuta · T. Kumagai
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, 305-8565 Tsukuba, Japan
e-mail: k-daudexi@aist.go.jp

effect on their electrical properties have not yet been discussed. Therefore, in order to understand the effect of the lattice mismatch on the TCR properties, we investigated the epitaxial growth of LCMO thin films by metal-organic deposition (MOD) on LAO and $SrTiO_3$ (STO) substrates [10, 11]. The LCMO/LAO system exhibited a TCR value of 27.5%/K compared to the 10 %/K measured for the LCMO/STO system. This difference in the TCR values was attributed to the effect of strain induced by the lattice mismatch between LCMO and the used substrate. The lattice mismatches of the LCMO/STO and LCMO/LAO systems are approximately $+1.12\%$ and -1.81%, respectively. Using transmission electron microscopy (TEM) and high resolution TEM (HRTEM) studies, we demonstrated that the local structure of the LCMO film depends on the substrate material type [11]. In this study, we prepared LCMO thin films on $(LaAlO_3)_{0.3}$-$(SrAlTaO_6)_{0.7}$ (LSAT) and MgO substrates having different lattice-mismatches with LCMO values of $+0.2\%$ and $+8.14\%$, respectively. The choice of LSAT and MgO is based on their extreme values of lattice mismatch with LCMO in order to better understand the effect of the substrate and to compare their structural and electrical properties with the films prepared on the STO and LAO substrates. The LCMO thin films were prepared using the MOD, which is a simple and low cost process.

2 Experimental

Details of the preparation procedure of the $La_{0.7}Ca_{0.3}MnO_3$ thin films by MOD have already been described in previous papers [10–12], and we only now recall the main features. The starting solution was prepared by mixing the constituent metal-naphthenate solution (Nihon Kagaku Sangyo) and diluting with toluene to obtain the required concentration and viscosity. The molar ratios of La, Ca and Mn in the coating solution were 0.7, 0.3 and 1.0, respectively. This solution was spin-coated onto LSAT, STO, LAO and MgO (001) substrates at 4000 rpm for 10 seconds. To eliminate the toluene, the metal (La, Ca or Mn) naphthenate film was then dried in air at 100°C for 10 min. Before the final annealing, a preheating step at 500°C for 30 min is necessary to decompose the organic part. This preheating step is also required to prevent the formation of fissures on the film surface during the final annealing at high temperature. To obtain a satisfactory film thickness for bolometric applications, the above procedure (coating, drying, and preheating) was repeated four times to produce a corresponding number of superimposed layers in the LCMO product film. The final annealing was carried out using a conventional furnace at 1000–1500°C for 60 min in air.

The crystallinity and epitaxy of the obtained films were examined by X-ray diffraction (XRD; MAC Science, MXP3A) $\theta - 2\theta$ scan analysis, and pole-figure analysis using the Schulz reflection method. The surface morphology and roughness of the samples were studied by atomic force microscopy (AFM: Nanopics 2100) in the damping mode. The resistance–temperature $R/R_{300} - T$ (R_{300}: resistance value at 300 K) curves were measured by the usual dc four-probe method and by cooling the samples from 320 K to liquid nitrogen temperature (77 K).

3 Results and discussion

3.1 Crystallinity and surface morphology

In our previous studies of LCMO thin films prepared by MOD on LAO and STO substrates, we have demonstrated using XRD (*θ-2θ* scans and pole-figure analysis) that all the films are well epitaxially grown [10–12]. Figure 1 shows the $\theta - 2\theta$ scanning profiles of the four-layer LCMO films grown on (a) STO, (b) LAO and (c) MgO substrates using MOD with a thermal annealing at 1000°C for 60 min in air. On the MgO substrate (Fig. 1(c)), we note that the LCMO film is (002) oriented. However, the film crystallinity appears low according to the low intensity of the (002) peak of the film grown on MgO in comparison with those grown on the STO or LAO substrates. This low crystallinity would be related to the high lattice mismatch between LCMO and the MgO substrate which is approximately 8.14%. Also, one can note that the (002) LCMO peak on the MgO substrate is shifted to the low angles compared with those of the films grown on the STO or LAO substrates. The (002) peak position of the LCMO film grown on the MgO substrate coincide with that of the pure $LaMnO_3$ material. This would be considered to be due to the change in the film composition by

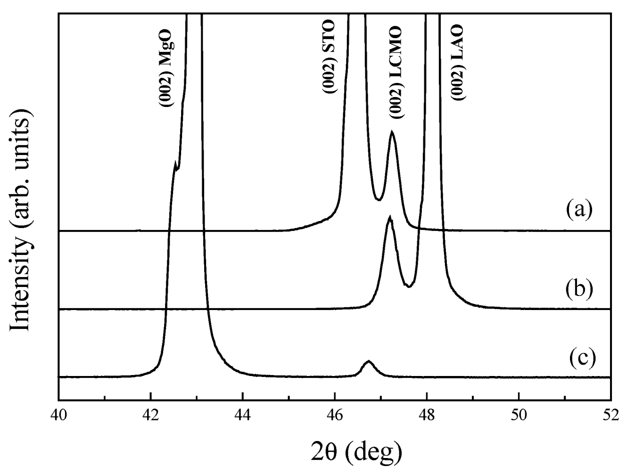

Fig. 1 XRD $\theta - 2\theta$ scan profiles for the LCMO films prepared by MOD process at 1000°C for 60 min in air on (a) STO, (b) LAO, and (c) MgO substrates

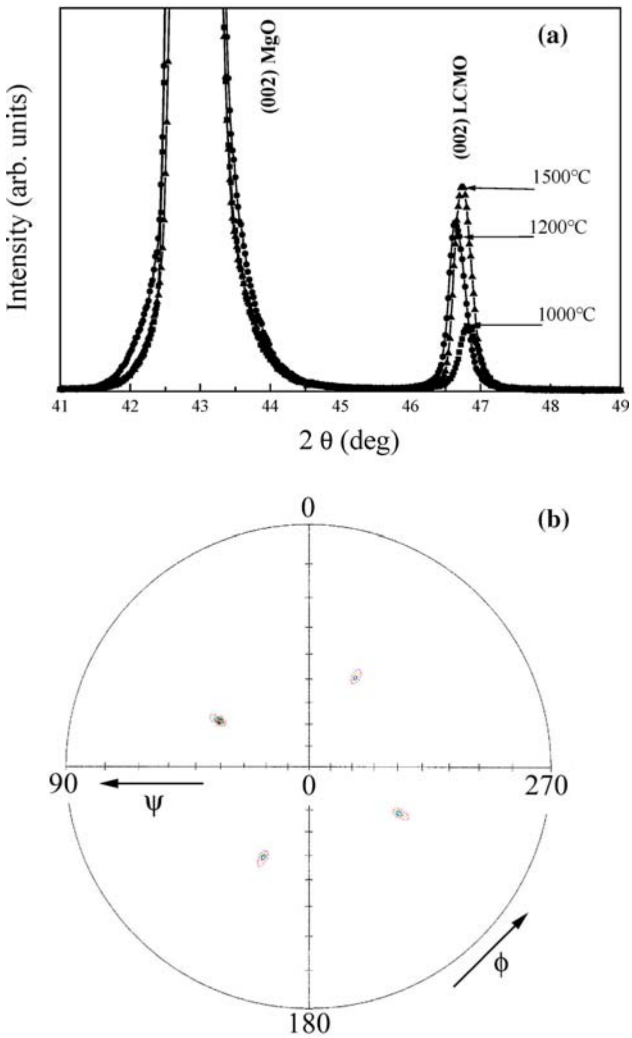

Fig. 2 (a) XRD $\theta - 2\theta$ scan profiles for the LCMO films grown on MgO substrates with thermal annealing at 1000°C, 1200°C and 1500°C. (b) XRD pole-figure of LCMO (220) reflection for the film annealed at 1000°C

a chemical reaction between the LCMO solution and MgO substrate during the thermal annealing. In order to increase the film crystallinity, we prepared LCMO films on MgO by MOD using thermal annealing at 1200°C and 1500°C for 60 min in air. Consequently, the (002) peak intensity increased indicating an improvement in the film crystallinity as shown in Fig. 2(a). Since the XRD θ-2θ cannot provide information on the in-plane alignment, we performed an XRD pole-figure analysis to investigate the in-plane alignment of the LCMO films. Figure 2(b) shows the XRD pole-figure of the LCMO 220 reflection for the film grown on MgO at a thermal annealing of 1200°C. As shown in Fig. 2(b), four distinct spots were recognized for the film, and each spot was located at the same ϕ angle as that for the 110 reflection of the substrate. In conclusion, the LCMO films were well epitaxially grown on the MgO substrates in spite of the large lattice mismatch.

The lattice mismatch between the LCMO film and LSAT substrate is very low (+0.2%), therefore, using the XRD analysis, it is difficult to distinguish between the (00l) peaks of the film and those of the substrate. Indeed, the (00l) reflections of the LSAT substrate overlap the peaks of the film reflections. High resolution TEM and electron diffraction observations suggest the epitaxial growth of the LCMO films on the LSAT substrate. This microscopic study is actually in progress and will be reported in future papers.

The substrate dependence surface morphology was studied using atomic force microscopy (AFM). Figure 3 shows three-dimensional AFM images of the four-layer LCMO films on the LSAT, STO, LAO and MgO substrates. It can be seen that the film grown on the LSAT, STO and LAO substrates have a smooth surface compared to the film grown on the MgO substrate. The root mean square roughness (rms) of the films grown on LSAT, SATO and LAO (Fig. 3(a), (b) and (c)) are in the range of (2.5–3.5 nm); however, for the film grown on MgO (Fig. 3(d)) the rsm is approximately of 4.8 nm. The relatively high roughness of the LCMO films grown on the MgO substrate using the MOD process has already been reported by other authors [13]. The high lattice mismatch between LCMO and MgO is supposed to be responsible of the high film roughness.

3.2 Electrical properties

Figure 4 shows the temperature dependence of the resistance R/R_{300} (T) and TCR(T) of the LCMO thin films obtained by the MOD process with thermal annealing at 1000°C on the LSAT substrate. The LCMO film is composed by four layers giving rise to a film thickness of approximately 80 nm. It can be seen that the LCMO film shows the typical characteristic of the CMR material with a transition from the paramagnetic-insulator to the ferromagnetic-metallic state at the T_p temperature (Fig. 4(a)). The transition temperature T_p is approximately 263 K and is in agreement with that of the LCMO films obtained by other techniques [9], though slightly higher than that of the bulk material (260 K) [14]. The temperature coefficient of resistance, TCR, was calculated from the R(T) data as TCR = $(1/R)(dR/dT)100\%$. The TCR behavior as a function of temperature is shown in Fig. 4(b). As can be seen, the TCR(T) has the same behavior as the R(T) with a transition from the paramagnetic-insulator to the ferromagnetic-metallic state at the temperature denoted T_m of approximately 248 K. For the proposed application as an IR detector, the devices must be cooled to the T_m temperature, which shows the maximum TCR value. The maximum TCR value of the LCMO/LSAT system is approximately 22%/K at 248 K. The sharpness of the R(T) curve and the high TCR value indicate that the prepared LCMO thin films on the LSAT substrates have a good epitaxial structure.

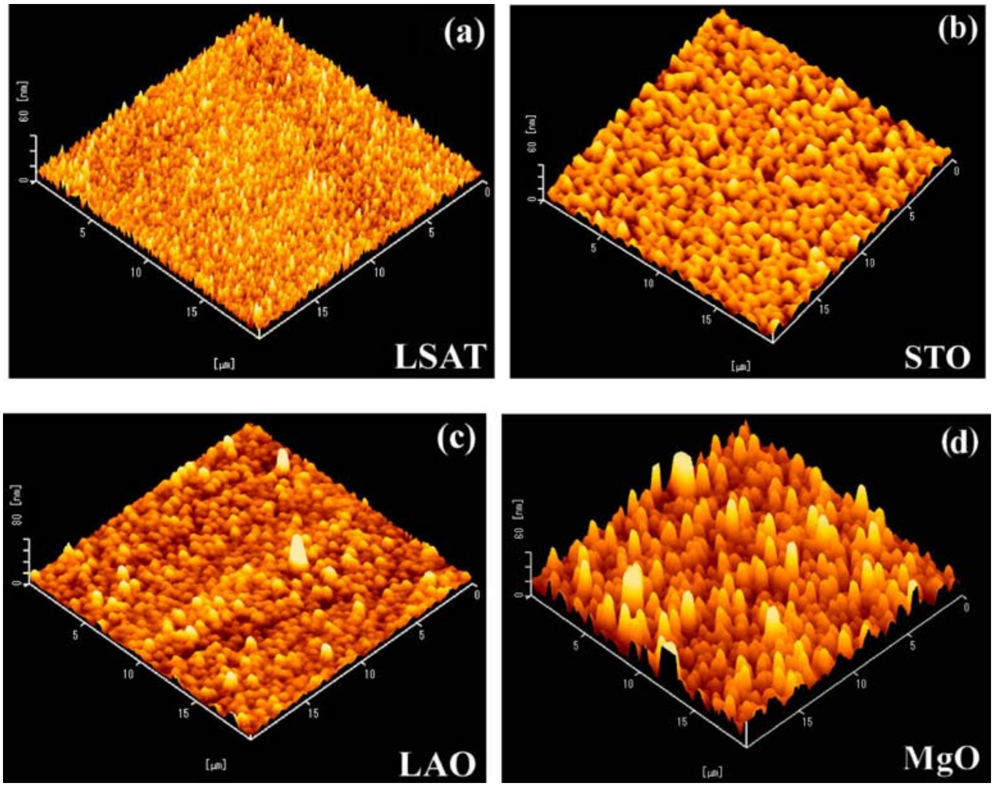

Fig. 3 Three-dimensional AFM images of LCMO thin films obtained by MOD by thermal annealing at 1000°C for 60 min in air on (a) LSAT, (b) STO, (c) LAO, and (d) MgO substrates

The R(T) characteristics of the LCMO films deposited on the MgO substrates at different annealing temperatures (1000, 1200 and 1500°C) are shown in Fig. 4. In contrast to the films grown on LSAT substrates, the films grown on MgO do not show the metal-insulator (MI) transition (Fig. 5). The film resistance exponentially increases as the temperature decreases indicating a semiconducting behavior. By increasing the film crystallinity, i.e., by increasing the annealing temperature, the film resistance decreases, but the R(T) is still that of semiconducting material. This behavior is similar to that

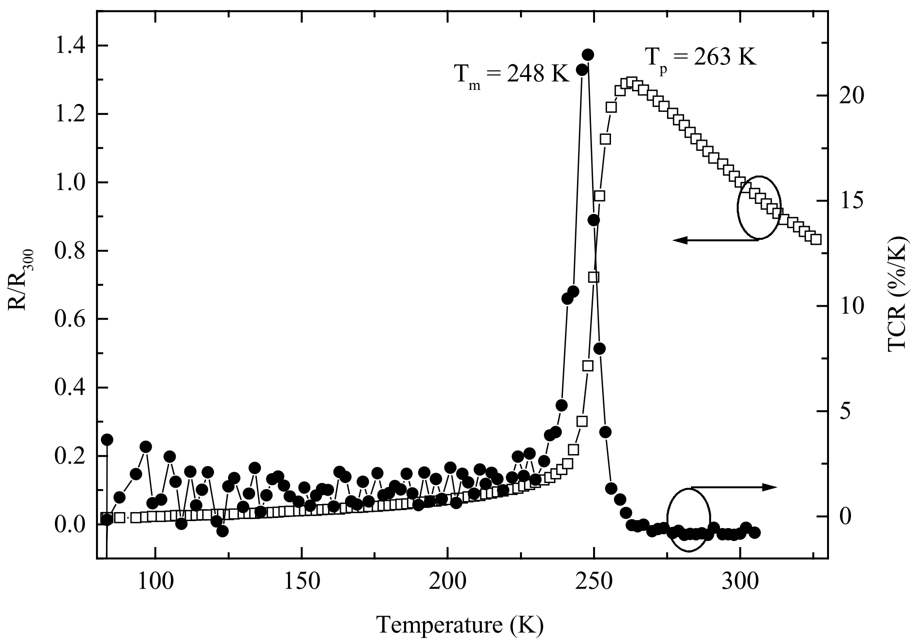

Fig. 4 (a) Temperature dependence of resistance (R/R_{300}), and (b) TCR of LCMO thin film obtained by MOD at 1000°C in air for 60 min on LSAT substrate

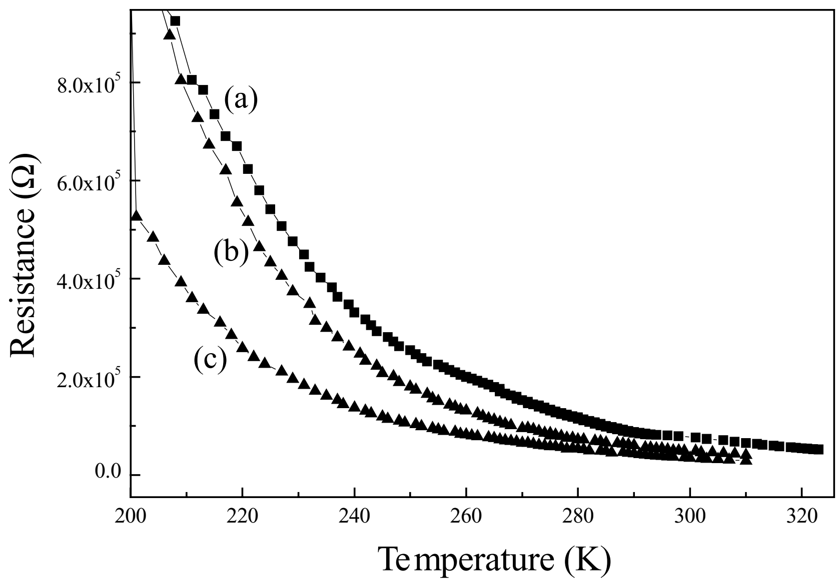

Fig. 5 Temperature dependence of resistance of LCMO thin films prepared by MOD at (a) 1000°C, (b) 1200°C, and (c) 1500°C on MgO substrates

of the pure $LaMnO_3$ (LMO) materials. The high reactivity of the MgO material with the metal-organic film during the thermal annealing at high temperature (1000–1500°C) can maybe accompanied by the diffusion of Ca into the substrate. Therefore, the Ca deficiency of the film might be responsible for this semiconducting behavior. On the other hand, the LCMO thin films prepared by pulsed laser deposition on MgO substrates show the typical R(T) characteristics of a metal-insulator transition [15, 16]. Hence, the semiconducting behavior of our films on the MgO substrates is probably due to the MOD process requiring a high annealing temperature. Thus, the doping Ca atoms might be diffused into the MgO substrate during the thermal annealing. From the R(T) data of the LCMO/MgO films (Fig. 4), we calculated the TCR(T), and the obtained values of the TCR are less than 2%/K (not shown here).[15pc]

To point out the effect of the substrate on the R(T) of LCMO, we summarized in Fig. 6 the $R/R_{300}(T)$ of the LCMO thin films prepared on different lattice-matched LSAT, STO, LAO and MgO substrates. It can be seen that the LCMO films grown on the LSAT and LAO substrates have similar R(T) characteristics with a sharp transition at the T_p of approximately 263 K and 258 K, respectively. However, the film grown on the STO substrate exhibits a broad transition at a higher T_p of approximately 270 K compared to the films grown on the LSAT and LAO substrates. Figure 7 shows the temperature dependence of the TCR of the four-layer LCMO films prepared on the LSAT, STO and LAO substrates. In

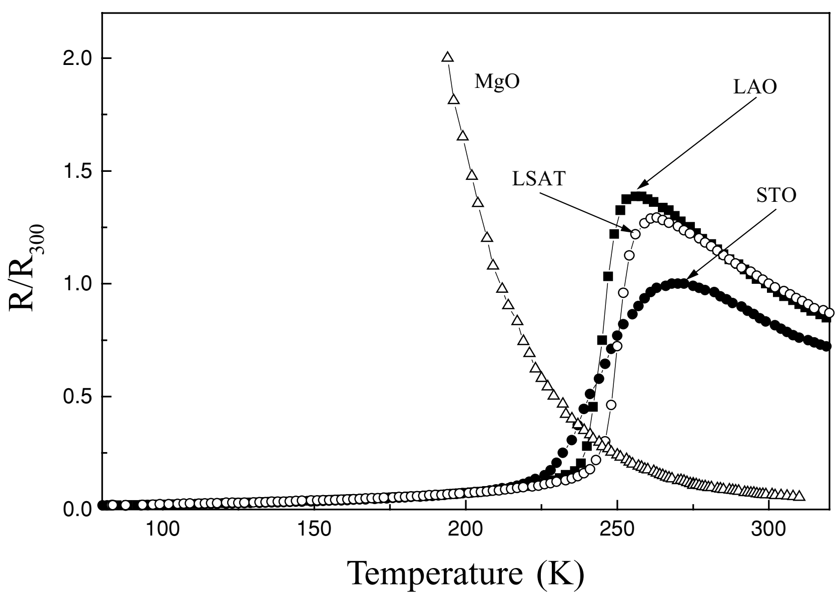

Fig. 6 Temperature dependence of resistance (R/R_{300}) of LCMO thin films on different substrates (LSAT, STO, LAO and MgO)

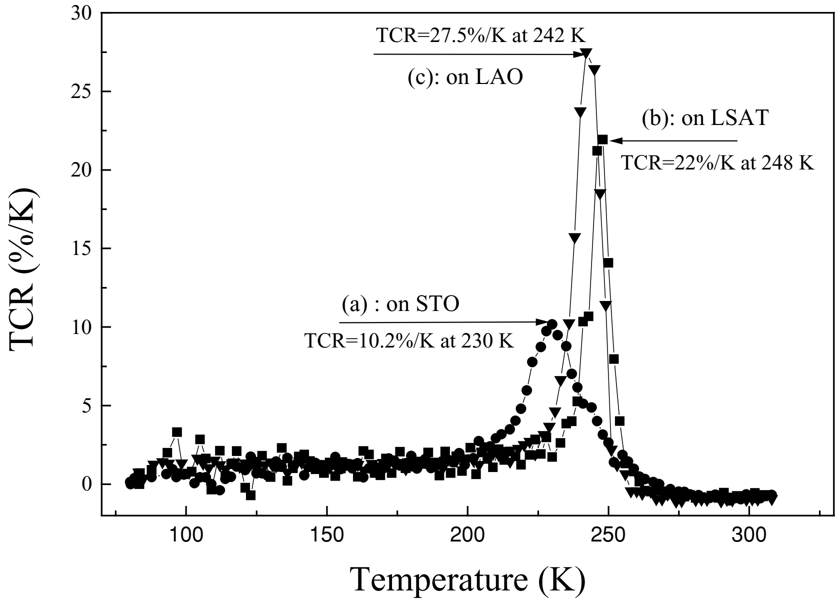

Fig. 7 Temperature dependence of the TCR of LCMO thin films on different substrates (LSAT, STO and LAO)

Fig. 7, the maximum TCR values and the corresponding T_m temperatures for the different samples are shown. As can be seen (Fig. 7), the films grown on the LSAT and LAO substrates exhibit the highest TCR values of approximately 22%/K at 248 K and 27.5%/K at 242 K, respectively. For the film grown on the STO substrate, the maximum TCR value is approximately 10.2%/K at 230 K. Among the substrates used in this study, the LSAT and LAO substrates are most suitable substrates for the epitaxial growth of the LCMO films having high TCR values. The obtained TCR values are significantly higher than that of other bolometric materials such as vanadium oxide, which has a TCR value of less than 5%/K [17].

4 Conclusion

Using a simple and low cost MOD process, the LCMO thin films were epitaxially grown on various lattice-mismatched substrates (LSAT, STO, LAO and MgO). AFM observations show evidence for a smooth surface for the films prepared on different substrates except for the film grown on the MgO substrate. The effect of the substrate on the electrical properties of the LCMO films is discussed. LCMO thin films grown on the LSAT, STO and LAO substrates show typical R(T) characteristics with a transition at T_p (258–270 K). However, the films grown on the MgO substrates exhibited semiconducting behavior. For further application as infrared detectors, we calculated the maximum TCR values for the different films. As a result, the films grown on the LSAT and LAO substrates were found to exhibit the highest TCR values (22–27.5%/K). Therefore, for future integration in silicon based devices, LAO or LSAT would be good buffer layers for growing epitaxial LCMO films with high TCR values.

Acknowledgments This study was supported by the Industrial Technology Research Grant Program in 2005 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

1. R. von Hemlolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.*, **71**, 2331 (1993).
2. K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, *Appl. Phys. Lett.*, **63**, 1990 (1993).
3. S. Jin, T.H. Tiefel, M. MCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen, *Science*, **264**, 413 (1994).
4. C. Zener, *Phys. Rev*., **82**, 403 (1951).
5. G.M. Zhao, K. Conder, H. Keller, and K.A. Muller, *Nature* (*London*), **381**, 676 (1995).
6. A.J. Millis, P.B. Littlewood, and B.I. Shraiman, *Phys. Rev. Lett.*, **74**, 5144 (1995).
7. E. Muller-Hartmann and E. Dagotto, *Phys. Rev. B*., **54**, R6819 (1996).
8. J.P. Locquet, J. Perret, J. Fomperyine, E. Machler, J.W. Seo, and G.V. Tendeloo, *Nature*, **34**, 453 (1998).
9. A. Goyal, M. Rajeswari, R. Shreekala, S.E. Lofland, S.M. Bhagat, T. Boettcher, C. Kwon, R. Ramesh, and T. Venkatesan, *Appl. Phys. Lett*., **71**, 2535 (1997).
10. K. Daoudi, T. Tsuchiya, S. Mizuta, I. Yamaguchi, T. Manabe, and T. Kumagai, *Jpn. J. Appl. Phys. Part*, **2**(43), L1054 (2004).
11. K. Daoudi, T. Tsuchiya, I. Yamaguchi, T. Manabe, S. Mizuta, and T. Kumagai, *J. Appl. Phys*., **97**, 013507 (2005).
12. K. Daoudi, T. Tsuchiya, S. Mizuta, I. Yamaguchi, T. Manabe, and T. Kumagai, *Jpn. J. Appl. Phys*., **44**, 5129 (2005).
13. T. Manabe, I. Yamaguchi, W. Kondo, S. Mizuta, and T. Kumagai, *J. Mater. Res*., **12**, 541 (1997).
14. P. Schiffer, A. Ramirez, W. Bao, and S.W. Cheong, *Phys. Rev. Lett*., **75**, 3336 (1995).
15. B. Vengalis, A. Maneikis, F. Anisimovas, R. Butkute, L. Dapkus, and A. Kindurys, *J. Magn. Magn. Mater*., **211**, 35 (2000).
16. J.Y. Gu, K.H. Kim, T.W. Noh, and K.S. Suh, *J. Appl. Phys*., **78**, 6151 (1995).
17. B. Meyer, R. Cannata, A. Stout, A. Gin, P. Taylor, E. Woodbury, J. Deffner, and F. Ennerson, in *Proc. SPIE* 2746, (1996) p. 13.