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Substrate temperature dependence of La_{0.7}Ca_{0.3} MnO₃ epitaxial films grown by pulsed laser deposition

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We report on the growth of high quality $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) epitaxial layers by pulsed laser deposition. The effect of substrate temperature on structural, magnetic and transport properties of LCMO has been investigated. Single-crystal epitaxial layers have been successfully grown on (100) LaAlO₃ at relatively low substrate temperatures between 600 °C and 750 °C. It is confirmed that 700 °C is the most suitable substrate temperature. We investigated the effect of substrate temperature on the properties of LCMO epitaxial films.

Key words: CMR; LCMO; Epitaxial films; Substrate temperature dependence; Currie temperature (T_c); Magneto resistance (MR%).

Introduction

The colossal magnetoresistance (CMR) in R_{0.7}A_{0.3}MnO₃ (R = trivalent rare-earth ion, A = divalent alkaline ion) witha perovskite structure has aroused great interest in these materials. The CMR effect in these materials makes them good candidates for magnetic random access memories and read-head applications [1-3]. Among various techniques to prepare a thin film, pulsed laser deposition (PLD) is a powerful and versatile method for synthesis of good quality thin oxide films with a uniform composition [4, 5]. Since most applications require thin films with good magnetic and electrical properties, it is of great importance to prepare high quality epitaxial films. Recently, growing attention has been paid to enhance the magnetic property [6-9]. However, previous reports have not systematically investigated the effect of substrate temperature on the La_{0.7}Ca_{0.3}MnO₃ (LCMO) layers.

In this study, we report on the growth of high quality LCMO epitaxial layers by PLD. The effect of substrate temperature on the properties of the LCMO has been investigated.

Experimental

LCMO films were deposited on (100) LaAlO₃ substrates by PLD using a KrF pulsed eximer laser ($\lambda = 248$ nm) at a laser fluency of 2-3 J/cm² with a laser frequency of 10 Hz. The target was prepared by the usual solid state reaction method with a mixture of precursor La₂O₃, Mn₂O₃, and CaCO₃. The distance of the target to the substrate

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was maintained at 45 mm in all experiments. The target and the substrate holder were kept at a certain rotation speed to obtain homogeneous thin films. The thickness of all thin films was about 200 nm which was controlled by an estimated deposition rate by a surface profile meter. During the deposition, the substrate temperature was held at a number of temperatures from 600 °C to 750 °C at intervals of 50 °C. The heating was performed with an average heating ratio of 20 K · minute⁻¹ and cooling was applied after the deposition in a vacuum chamber. During the deposition process, the oxygen partial pressure in the chamber was maintained at 39.9 Pa.

The thickness of the thin films was checked by a JSM 5610 scanning electron microscope (SEM). The structural properties of the La_{0.7}Ca_{0.3}MnO₃ films were analyzed by high resolution X-ray diffraction (HRXRD, Cu K_{α 1}, $\lambda = 0.15406$ nm) and the scans were performed with 0.02° θ step size in the 2 θ range of 20-80°. The surface morphology of the films was examined with a Veeco D3100 atomic force microscope (AFM), in the tapping mode on 10 μ m² surface areas. M-T curves, resistivity ($\Omega \cdot$ m) and magneto resistance(MR%) were measured with a Quantum Design Physical Properties Measurement System (PPMS) over a temperature range of 20-320 K.

Results and Discussion

We checked the thickness of LCMO films grown on LaAlO₃ substrate by SEM. The thickness of films was fixed at 200 nm by controlling the deposition time, which was based on the calculated deposition rate. Figure 1 shows a typical XRD pattern of LCMO film grown on LaAlO₃ substrate. According to the XRD patterns, the existence of only (100), (200) and (300) pseudo cubic reflections of the film and substrate reveals that the film has grown

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Fig. 1. XRD pattern of a LCMO film prepared on a LAO (100) substrate.



Fig. 2. FWHM of LCMO films prepared on the LAO (100) substrates.

epaxially. This is the same as that reported by S. Canulescu et al [11].

In order to determine the optimum substrate temperature, HRXRD were carried out. Figure 2 shows the relationships between the FWHM values of the LCMO epitaxial layers and the substrate temperature. FWHM of out-ofplane (ω -scan) shows that the FWHM of films decrease from 600 °C to 700 °C, on the other hand, when the temperature exceeds 700 °C, the FWHM greatly increases. This can be explained that below 700 °C, an increase in temperature is beneficial to promote uniform orientation of the nucleation and to enhance the migration and diffusion of the atoms for growth. When the temperature is 750 °C, however, the number of thermally introduced defects in the epilayers increases substantially, and this is disadvantageous to growth. Therefore, it is confirmed that 700 °C is the most suitable substrate temperature.

Figure 3 shows that the surface morphology measurements which were done in the tapping mode of the AFM. The scans have been performed across an area of $10 \times 10 \ \mu m^2$ in order to get detail information about the topography. We note that as the substrate temperature increased from 600 °C to 700 °C, at intervals of 50 °C the surface



Fig. 3. AFM scans of the LCMO films prepared on the LAO (100) substrates at different temperatures: a) 600 °C, b) 650 °C, c) 700 °C, d) 750 °C.



FIg. 4. RMS of the LCMO films prepared on the LAO (100) substrates at different temperatures.

root mean square (RMS) roughness of the films decreased. On the other hand, when the substrate temperature was 750 °C, the RMS values were higher (Fig. 4). This indicates that 700 °C is the turning temperature point. For the depositions at 700 °C and 750 °C, the numerical values of the RMS are 3.13 and 6.15 nm, respectively. The substrate temperature has an influence on the film topography [11]. The reason why the RMS increases can be explained that an insufficiency of atom migration causes a few mountains to grow on the film surface below 700 °C, while on the other hand, the grain size in films begins to grow quickly at 750 °C.

Figure 5 shows the temperature dependencies of the magnetic transition from a paramagnetic phase into a ferromagnetic, Curie temperatures (T_c), phase under a magnetic field (2 T) by a quantum interference device (SQUID) system. The curie temperatures of 249 K for a substrate temperature of 600 °C, 257 K of 600 °C,



Fig. 5. M-T curves of the LCMO films prepared on the LAO (100) substrates at different temperatures.

Table	1.	Currie	Tempertur	(T_c)	of the	LCMO	films

Substrate(°C)	$T_{c}(K)$
600 °C	249 K
650 °C	257 K
700 °C	262 K
750 °C	246 K

262 K of 700 °C and 246 K of 750 °C were obtained (Table 1). These results show that T_c is increasing until 700 °C but a drop occurs suddenly at 750 °C. It can clearly be seen that T_c has an opposite tendency to the FWHM.

The magneto resistance (MR%) of the LCMO thin films at different temperatures was measured in a temperature range from 100 K to 300 K in the presence of 3, 7 Tesla magnetic fields and the corresponding data is plotted in Fig. 6. MR is defined by $MR = (R(\theta) - R(H))/R(\theta)$ where R(H) is the value in the applied field and $R(\theta)$ is the value in none external applied field. It is observed that at $H_{dc} = 3$, 7T, the maximum MR value is around T_c [12]. Figure 6 shows the temperature dependent magneto resistance (MR%) of the LCMO thin films at 700 °C with different magnetic field ($H_{dc} = 3$, 7T). The observed values of the MR are 66.9% at 200 K for the film with $H_{dc} = 3T$ and a little increase to 84.8% at 210 K for the film at with $H_{dc} = 7T$. It can be clearly seen that the maximum resistance was observed near T_c and it is also clear that



Fig. 6. Temperature dependent magneto resistance (MR%) of LCMO thin at 700 °C with different magnetic field (H = 3, 7T).

the maximum MR value of the film has a 10K shift at room temperature with higher magnetic field.

Conclusions

LCMO thin films were prepared by PLD on (100) LaAlO₃ substrates from 600 °C to 750 °C. We confirmed that 700 °C is the most suitable substrate temperature. All the films was crystalline and epitaxial. XRD and AFM analyses show that when the substrate temperature is 700 °C, we obtained high quality epitaxial thin films compared

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References

- R. von Helmolt, L. Haupt, K. Bärner and U. Sondermann, Solid State Communications 80 (1991) 865-867.
- 2. S. Jin, T.H. Tiefel, M. McCromark, R.A. Fastnatch, R. Ramesh and L.H. Chen, Science 264 (1994) 413.
- H.L. Ju, C. Know, L. Qi, R.L. Greene and T. Venkatesan, Appl. Phys. Lett. 65[16] (1994) 2108-2110.
- V. Nelea, C. Ristoscu, C. Chiritescu, C. Ghica, I.N. Mihailescu and A. Cornet, Appl. Surf. Sci. 168 [1-4] (2000) 127.

- I.N. Mihailescu, P. Torricelli, A. Bigi, I. Mayer, M. Iliescu, J. Werckmann, G. Socol, F. Miroiu, F. Cuisinier, R. Elkaim and G. Hildebrand, Appl. Surf. Sci. 248 (2005) 344-348.
- L. Balcells, A.E. Carrillo, B. Martinesz and J. Fontcuberta, Appl. Phys. Lett. 74[26] (1999) 4014-4016.
- D.K. Petrov, L. Krusin-Eibaum, J.Z. Sun, C. Feild and P.R. Duncombe, Appl. Phys. Lett. 75[7] (1999) 995-997.
- 8. S. Gupta, R. Ranjit, C. Mitra, P. Raychaudhuri and R. Pinto, Appl. Phys. Lett. 74[3] (2001) 362-364.
- J.M. Liu, G.L. Yuan, H. Sang, Z.C. Wu, X.Y. Chen, Z.G. Liu, W.Y. Du, Q. Huang and C.K. Ong, Appl. Phys. Lett. 78[8] (2001) 1110-1112.
- S. Canulescu, Th. Lipper, A. Wokaun, R. Robert, D. Logvinovich, A. Weidenkaff, M. Do"beli and M. Schneider, Progress in Solid State Chemistry 35 (2007) 241-248.
- S. Canulescua, Th. Lippert, H. Grimmer, A. Wokaun, R. Robert b, D. Logvinovich, A. Weidenkaff and M. Doebeli, Appl. Surf. Sci. 252 (2006) 4599-4603.
- Osami Yanagisawa, Mitsuru Izumi, Kai-Hua Huang, Wei-Zhi Hu, Yi Shen, KenjiNakanishi, Yoshihiro Takahashi and Hideo Nojima, Journal of Magnetism and Magnetic Materials 211 (2000) 254-258.