Structure and electromagnetic properties in thin films of $Pr_{0.65}Ca_{0.35}MnO_3$

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Abstract

We report the thin-film growth of $Pr_{0.65}Ca_{0.35}MnO_3$ by using RF sputter deposition on $SrTiO_3$ (010). Electrical resistivity clearly shows the trace of the charge-ordered state at 247 K. Dc magnetization and electron-spin resonance show the onset of the spontaneous magnetization around 120 K, which is attributed to the existence of the clusters arising from the spin-cant antiferromagnetism.

Key words: RF magnetron sputtering; Thin films; Manganite; Electron spin resonance

1. Introduction

The peorvskite manganese oxide has attracted much attention by virtue of their unusual electric and magnetic properties (for example, colossal magnetoresistance). For the $Pr_{1-x}Ca_xMnO_3$ system, the space group *Pbnm*, magnetic field-induced or photo-induced collapse of the charge-ordered (CO) state with the Mn^{3+} and Mn^{4+} alternation, which is the transition from antiferromagnetic charge-ordered state to ferromagnetic charge-delocalized, was found together with the structural evidence at low temperature [1,2].

These materials are expected to be utilized as the magnetic-optical hybrid devices, with which one can control the electric property by magnetic field or photo injection. The fabrication of the thin films provides the advantages to the industrial application. In the present communication, we report the growth of the thin-filmed $Pr_{0.65}Ca_{0.35}MnO_3$ (PCMO) with RF magnetron sputtering, influence of the substrate temperature and the annealing on structure, the electric and the magnetic properties.

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2. Experimental results and discussion

PCMO thin films were grown on the (010) surface of $SrTiO_3$ (STO), $LaAlO_3$ (LAO) and MgO by RF magnetron sputtering from a stoichiometric target in Ar/O_2 (1:1) mixture gas atmosphere at 40 mTorr total pressure. The deposition was performed at different substrate temperatures between 650 °C and 850 °C with 100 W RF power for 2 h or 4 h. After the deposition, the thin films were annealed in O_2 gas atmosphere at 1000 °C for 10 h. The thin films deposited for 2 h were typically 4000 Å thick. According to the X-ray diffraction, the well-defined orientation of the c-axis was confirmed on STO and LAO substrates after the annealing procedure. The structural order of the thin films was improved with increasing substrate temperature.

Presently, the PCMO film deposited on STO substrate at 850 °C for 4 h is focussed due to its relative high quality. Electrical resistance was measured by a standard dc four-probe technique. The dc magnetization and the electron-spin resonance (ESR) were detected by a SQUID susceptometer (Quantum Design, 7T-MPMS) and ESR spectrometer (JEOL-JES-RE1X), respectively. We attribute the ESR signal to

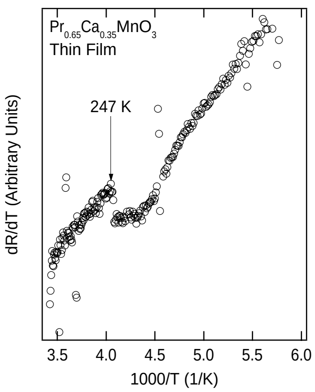

Fig. 1. Temperature dependence of the differential resistance ($\mathrm{d}R/\mathrm{d}T$) of $Pr_{0.65}Ca_{0.35}MnO_3$ thin film.

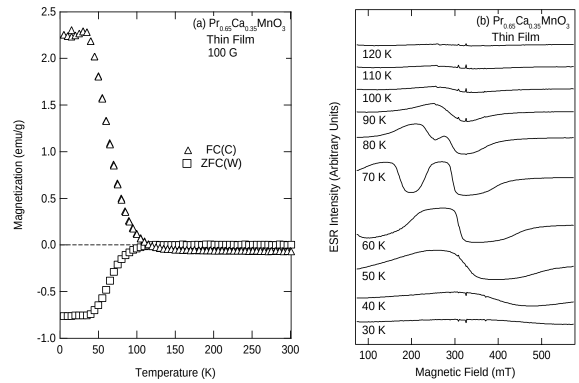

Fig. 2. (a) DC magnetization as a function of temperature in $Pr_{0.65}Ca_{0.35}MnO_3$ thin film. Measurements were done under the magnetic field 0.01 T ($H_0 \perp$ c-axis). FC(C) and ZFC denote the magnetizations in the cooling run after field cooling run and the warming run after zero field cooling, respectively. (b) ESR spectra measured at 9 GHz for $Pr_{0.65}Ca_{0.35}MnO_3$ thin film under $H \perp$ c-axis geometry. The sharp resonance peaks around 320 mT come from the reference material Mn^{2+}/MgO as a marker.

the electron spins on Mn^{3+} and/or Mn^{4+}.

The temperature dependence of the differential resistance ($\mathrm{d}R/\mathrm{d}T$) of the PCMO thin film is shown in Fig. 1. The $\mathrm{d}R/\mathrm{d}T$ shows a prominent peak anomaly at 247 K. We suppose that it gives a sign of the appearance of the CO state as has been reported in the PCMO powder sample at 215 K (T_{CO}) [2]. It is worth to note that there is no trace of such anomaly in the case of the thin films prepared by sputtering for 2 h and by Sol-Gel method [3]. The increase of T_{CO} in the present film may originate from the different composition from nominal and/or the oxygen deficiency [1].

Fig. 2(a) shows the dc magnetization as a function of temperature in PCMO thin film. The magnetization taken in both FC(C) and ZFC grows remarkably below 120 K with decreasing temperature. In FC(C), a positive spontaneous magnetization appears below 120 K. On the contrary, in ZFC it shows a magnetic pole inversion. The present results indicate that the thin film specimen is composed of an ensemble of small clusters and/or magnetic domains.

The ESR signal appears around 120 K, which is associated with the spontaneous dc magnetization. As shown in Fig. 2(b), the ESR spectrum for PCMO thin film splits into at least two lines below 80 K. The center magnetic field of the lower-field resonance line shifts to lower magnetic field with decreasing temperature. Besides, higher-field resonance line shifts to higher field below 50 K, which corresponds to the decrease of the dc magnetization in FC(C) in Fig. 2(a). These results are attributed to the existence of the different size clusters arising from the spin-cant antiferromagnetism. Possibly, there exists a mixing two separated phases, i.e., the CO clusters and the photo-induced ferrometalic ones [4].

In conclusion, we showed the electric and magnetic properties of the RF sputter-deposited $Pr_{0.65}Ca_{0.35}MnO_3$. The film grows with the c-axis orientation on the substrate. The resistivity anomaly assigned as the onset of the charge-ordered phase was observed. Both dc magnetization and the ESR under H $\perp$ c-axis configuration showed the spontaneous magnetization interpreted as a spin-cant magnetic transition. The observed phase transition temperatures are different from those of the powder with the same nominal composition. This may be coming from the growth process of the thin film, i.e., oxygen deficiency. The present results give a basis for study on the possible near-infrared photo induced effect as has been observed in the powder sample [2].

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References

[1] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, Y. Yokura, Phys. Rev. B **53** (1996) R1689.

[2] O. Yanagisawa, M. Izumi, W-Z. Hu, K-H. Huang, K. Nakanishi, H. Nojima, Physica B **271** (1999) 235.

[3] O. Yanagisawa, M. Izumi, K-H. Huang, W-Z. Hu, Y. Shen, K. Nakanishi, Y. Takahashi, H. Nojima, J. Magn. Magn. Mater. **211** (2000) 133.

[4] S. Mori, C. H. Chen, S-W. Cheong, Phys. Rev. Lett. **81** (1998) 3972.