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LaBaMnO films produced by dip-coating on a quartz substrate

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Abstract

The electrical transport and magnetoresistance properties of the polycrystalline $La_{0.67}Ba_{0.33}MnO_3$ film produced on a quartz substrate were investigated first time. X-ray powder diffraction indicated that film sample has perovskite structure. Scanning electron microscope indicated that $La_{0.67}Ba_{0.33}MnO_3$ film thickness is approximately 20 μm and the average grain size of this sample varies between 8 and 10 μm. $La_{0.67}Ba_{0.33}MnO_3$ film showed a phase transition from paramagnetic to ferromagnetic at (T_C) 130 K and a metal-insulator transition at (T_{MI}) 137 K at 2 mT magnetic field. The upturn of the resistance observed at low temperatures (<49 K) was attributed to the Coulomb blockade and the strong structural disorder due to the large lattice mismatch and strain relaxation. A large magnetoresistance ratio (MR(%)) of 230% was observed at 125 K and 6 T magnetic fields.

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Keywords: Manganite films; Colossal magnetoresistance; Strain effect; Coulomb blockade

1. Introduction

The phenomenon of colossal magnetoresistance (CMR) in perovskite manganites of the type $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba) has recently attracted considerable attention because of their value in fundamental physics and their potential applications [1–10]. The physical properties of these perovskite manganites are mostly investigated in the form of the bulk [7], single crystal [8] and thin or thick film [9]. The electronic and magnetic properties of film forms are of special interest than the other forms due to the large MR effect and potential technological usefulness such as sensor and magnetic recording applications and also development of spin electronic devices [10]. It has been discovered that these systems have a rich variety of electronic and magnetic phases from insulating antiferromagnetism to metallic ferromagnetism [11,12]. The appearance of the ferromagnetic and metallic state in the mixed-valence perovskite systems is attributed to the double exchange (DE) model between the Mn^{3+} and Mn^{4+} ions [13]. It has been shown that the strength of DE interactions is very sensitive to variation of the Mn–O bond length, the Mn–O–Mn bond angle. The substitution of cations with different ionic sizes at A-site results in the structural distortion in the Mn–O bond length and the Mn–O–Mn bond angle which affects the magnetic and transport property.

Among the various La-based perovskite manganites, $La_{1-x}Ba_xMnO_3$, especially the $La_{0.67}Ba_{0.33}MnO_3$ film form, are of great interest because of their Curie temperature which can reach up to 360 K [14]. It is known from many reports that when the average size of the A-site ions increases, T_C increases. Due to the rather large ionic radius of Ba^{2+} (=1.47 Å) compared with Ca^{2+} (=1.18 Å) and Sr^{2+} (=1.31 Å), an increase in the average La site radius by partial substitution of Ba at La site is expected to lead to improvement in magnetotransport properties rather than Ca^{2+} and Sr^{2+}. Therefore, the properties of the $La_{1-x}Ba_xMnO_3$ can be different from other ones, and investigation of these compounds can bring new interesting results. The other important effect on the magnetotransport properties of the film systems is the structure of used substrate. It is generally known that substrate-induced strain plays an important role on Curie temperature (T_C), metal-insulator transition temperature (T_{IM}) and resistivity [15–17] for the film systems. In this study, $La_{0.67}Ba_{0.33}MnO_3$ film was first time

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prepared on a quartz substrate by dip-coating method. The magnetoresistance and the transport properties were discussed.

2. Experimental

The polycrystalline film of $La_{0.67}Ba_{0.33}$ MnO_3 manganite was prepared by sol–gel dip-coating method. First, stoichiometric amounts of $Ba(OCH(CH_3)_2)_2$ (% 99.5), $La(NO_3)_3{\cdot}6H_2O$ (%99.9) and $Mn(NO_3)_2{\cdot}XH_2O$ (% 99.9) were dissolved in glacial acetic acid in different beakers. Then these different homogenous solutions were mixed in the same beaker. We have added triethanolamine drop by drop to get the homogeneous solution. And then accommodating amounts of ethanol, methanol and ethanolamine were added for coordinate agents to produce absolute homogeneous transparent solution. The pH of this solution has been measured to be 4.77. After stirring the solution for 42 h, it was subjected to slow evaporation at 300 K until the formation of a highly viscous residual. Then the gel was coated on quartz by dip-coating with heat treatment at 873 K. In the film fabricating process, quartz substrate withdrawn from the solution with a velocity of 15 cm/min and then the sample was moved vertically in furnace which has size of 120 cm along to moving direction and a temperature gradient from a room temperature up to crystal formation temperature. Finally, the LaBaMnO film was annealed in air atmosphere at 1073 K for 3 h.

The X-ray diffractograms were recorded with a Rigaku power diffractometer at room temperature using Cu Kα radiation. A LEO EVO 40 VP SEM system attached to a Röntec 3000 detector was used and microstructural analysis was carried out on an energy-dispersive X-ray (EDX) system. The temperature and magnetic-field dependence of the resistance were measured using a Q-3398 (Cryogenic) system by the conventional four-probe method in the temperature interval from 5 to 300 K.

3. Results and discussions

Fig. 1 shows the X-ray diffraction pattern of the $La_{0.67}Ba_{0.33}MnO_3$ film produced on a quartz substrate by dip-coating. As shown in Fig. 1, only the diffraction lines for cubic perovskite were obtained. The hallow curve at low 2θ values rises due to sample holder. Fig. 2 shows typical SEM micrographs for the $La_{0.67}Ba_{0.33}MnO_3$ film. The SEM pictures show a polycrystalline nature with a film thickness of approximately 20 μm and the average grain size varies between 8 and 10 μm. The shapes of grown grains are very different than previously reported grain shapes for manganite type samples. The SEM pictures show a homogeneous structure with a leaf type grain structure.

The temperature dependence of magnetization for the $La_{0.67}Ba_{0.33}MnO_3$ film sample, shown in Fig. 3, was measured using a vibrating sample magnetometer system in a wide range of temperatures (from 5 to 300 K) at various applied magnetic fields. The Curie temperature (T_C) of film sample was determined to be 130 K, which is much lower than that of the bulk sample (360 K for bulk sample [14]). Fig. 4 shows the temperature dependence of resistance for the $La_{0.67}Ba_{0.33}MnO_3$ film at 2 mT and 5 T magnetic fields. It was observed that the resistance plot shows a peak corresponding to the metal-insulator transition temperature (T_{MI}) and the applied magnetic field suppressed the resistance peaks significantly. The T_{MI} was observed to be 137 K at 2 mT magnetic fields. Several publications have reported that there are many factors could cause a considerable decrease in T_C and T_{MI} of manganite films compared with bulk samples [15–17]. One of the important factors for the thin films is the substrate induced lattice strain rises from the lattice mismatch between substrate and films. For a quartz substrate it is well known that the lattice mismatch and consequently lattice strain is very high. But, it has been reported that the strength of the strain decreases with increasing film thickness [20]. In this study, $La_{0.67}Ba_{0.33}MnO_3$ film was prepared on a quartz substrate. The film thickness was measured to be approximately 20 μm. For such a thick film, the lattice strain can be expected to be almost completely relaxed. It is known that this relaxation process could also produce various

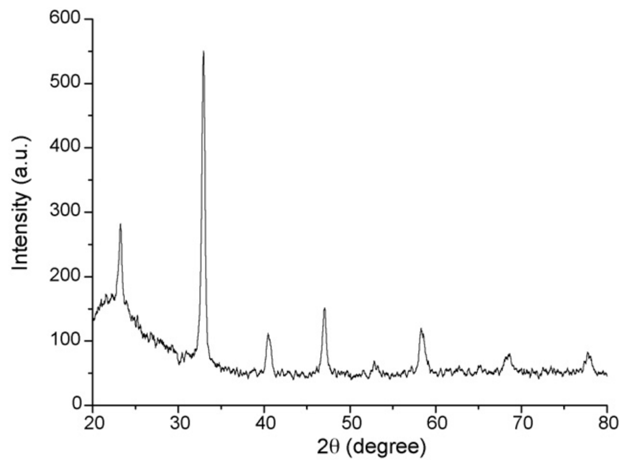

Fig. 1. X-ray diffraction patterns of the $La_{0.67}Ba_{0.33}MnO_3$ film produced on quartz substrate.

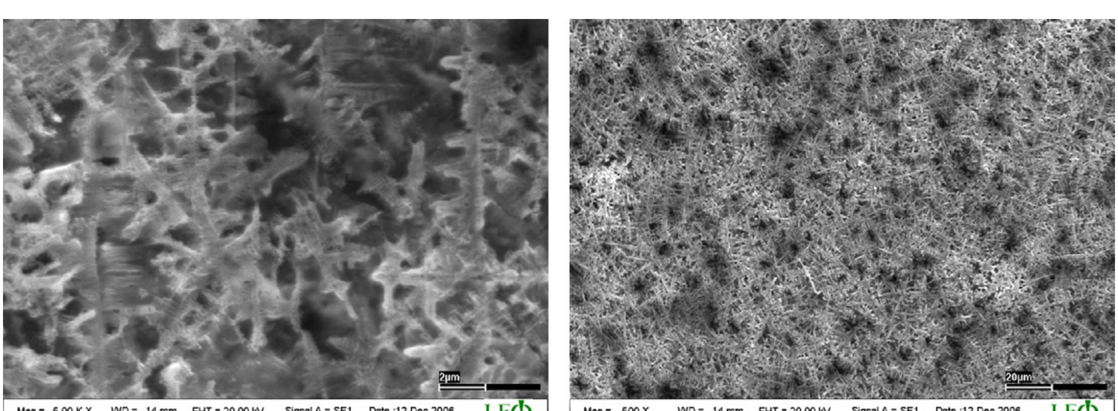

Fig. 2. SEM photographs of the $La_{0.67}Ba_{0.33}MnO_3$ film sample.