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Microstructure and magnetoresistance of a $La_{0.67}Ca_{0.33}MnO_3$ film produced using the dip-coating method

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Abstract

The microstructure and magnetoresistance properties of polycrystalline bulk $La_{0.67}Ca_{0.33}MnO_3$ and a $La_{0.67}Ca_{0.33}MnO_3$ film produced on a $LaAlO_3$ (1 0 0) single-crystal substrate using the dip-coating method were investigated. X-ray powder diffraction indicated that both film and bulk samples have perovskite structure. Scanning electron microscope and X-ray results clearly indicated that a $La_{0.67}Ca_{0.33}MnO_3$ film was successfully produced using the dip-coating process. This film showed a metal–insulator transition at 269 K and a maximum magnetoresistance ratio (MR (%)) of 56% at 269 K and 6 T magnetic field.

Keywords: Manganites; Dip-coating; Thick film; Colossal magnetoresistance

1. Introduction

The perovskite manganites of general formula $RE_{1-x}AE_xMnO_3$ (RE: rare earth, AE: divalent alkaline earth metal) have attracted considerable attention due to the discovery of the colossal magnetoresistance (CMR) effect occurring in the vicinity of the metal–insulator (ferromagnetic–paramagnetic) transition temperature [1–6]. These materials have very rich magnetic, transport and structural properties and the strong correlation between these properties makes such materials more interesting. These materials show ferromagnetic and metallic character at a certain value of x (concentration of divalent cations). The metallic character, ferromagnetism and CMR effect in doped manganites can be qualitatively explained by the double-exchange (DE) model. In this model, electron hopping between the Mn^{3+} and Mn^{4+} ions produces a ferromagnetic coupling between the ions. In many experimental studies, it has been shown that the DE interaction and also the magnetic and transport properties of the doped manganites are very sensitive to the carrier concentration (Mn^{3+}/Mn^{4+}) and structural parameters (Mn–O bond length and the Mn–O–Mn bond angle).

The physical properties of mixed-valence perovskite manganites have mostly been investigated in the bulk [7–9], thin or thick film [10,12] and single-crystal forms [13]. The electronic and magnetic properties of the film forms are of more interest than those of the other forms due to their potential application for the development of spin electronics devices, such as magnetic recorders, magnetic-field sensors, read heads, nanostructured devices, etc. In order to use films of manganites actively in technology, however, it is of importance to grow high-quality films that are technologically viable. In the literature, there are many studies which investigate the physical properties of manganite films [10–20]. As for the preparation of CMR films, there are many methods available, such as pulse laser deposition (PLD), molecular beam epitaxy (MBE), magnetron sputtering, metalorganic chemical vapour deposition and sol–gel deposition.

Sol–gel deposition of films is a rapidly advancing technology. The sol–gel process is based on hydrolysis and condensation reactions of organometallic compounds in alcoholic solutions. In recent years, this technique has been extended to the fabrication of thin films or coatings on different substrates. This method exhibits a number of advantages: (1) increased chemical homogeneity in multicomponent systems; (2) large surface

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areas of gels or coated samples can be produced; (3) relatively high chemical purity can be maintained; (4) the cost of sol–gel film processing is low and the fabrication is easier compared to other conventional thin-film-forming processes such as evaporation, sputtering or chemical vapour deposition. Today sol–gel thin-film coatings are being intensively studied for different applications, such as protective and optical coatings, sensors, dielectric constant films, inorganic membranes, semiconducting coatings, superconducting films and ferroelectrics. Films can be produced on a piece of substrate by spin- or dip-coating in the sol–gel thin-film production process. The chemical composition of the solution and the deposition parameters, especially those from the heat-treatment, such as temperature, time and cooling-down conditions, will influence the properties of the film. Up to now films of manganites have been produced using the sol–gel spin-coating method and no study about the production of manganite films using the dip-coating method has been reported. In this article, a simple and very cheap film-preparation method is presented. The transport and magnetoresistance properties of $La_{0.67}Ca_{0.33}MnO_3$ films prepared by dip-coating have been investigated. The results are compared with those for bulk samples and other films prepared by different methods.

2. Experimental details

Reagent-grade $La(NO_3)_3$, $Ca(NO_3)_2$ and $Mn(NO_3)_2$ (Alfa Aesar, 99.9%) were used to prepare a colloidal solution in diethylene glycol (Fluka Chem Co.). The first step of the synthesis involves forming a precursor that has a high degree of chemical homogeneity and high reactivity. Nanoscale $La_{2/3}C_{1/3}MnO_3$ particles were prepared by mixing appropriate amounts of 2.27 mmol $La(NO_3)_3$ (99.9%), 1.13 mmol $Ca(NO_3)_2$ (99%), 3.40 mmol $Mn(NO_3)_2$ in the range 0.01–0.02 M and 50 ml diethylene glycol (99%), which was then heated to the desired reaction temperature in a water bath. In most cases the temperature was raised to 194 °C and held there for 2 h. When the mixed solution turned black, indicating the formation of a colloid, it was then removed to an ice bath to lower the reaction temperature quickly. In general, the reaction was fast and it usually took only minutes to complete the synthesis process.

Based on this process, a metal precursor was heated in a high boiling alcohol (bp > 200 °C). In the case of noble metals, the metal cations were reduced by the alcohol to form particles of the elemental metals. As a further advantage, the polyol medium efficiently complexed the surface of the particles. Consequently, the particle growth was limited. Furthermore, agglomeration of the particles was prevented in the colloidal solution. The mixture was heated to 150 °C for 2 h to obtain a viscous solution that was used for effective coating of the substrate. The $LaAlO_3$ (1 0 0) single-crystal substrate with an effective surface area of 10 cm^2 was first cleaned with water followed by acetone and then dip-coated with the sol using a homemade dip-coating apparatus at a withdrawal rate of 10 cm/min. After coating, the films were dried at room temperature for 1 h, calcined at a ramp rate of 1 °C/min in a programmable box furnace (Protherm), kept at 300 °C for 1 h and cooled down naturally. This procedure was repeated three times and after final coating, the sample was annealed at 1000 °C for 2 h. Finally, a thick (−1.5 μm) $La_{0.67}Ca_{0.33}MnO_3$ film was produced on the $LaAlO_3$ (1 0 0) single-crystal substrate. Bulk polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ samples were prepared by the conventional solid-state reaction using high-purity La_2O_3, $CaCO_3$ and MnO powders. The powders were mixed in stoichiometric ratio. Thoroughly mixed powders were ground and calcined in air at 800 °C for 10 h. After grinding, the mixed powders were pressed into a disk shape with a diameter of 13 mm and a thickness of about 2 mm. The $La_{0.67}Ca0_{.33}MnO_3$ disk sample was sintered at 1350 °C for 24 h in air.

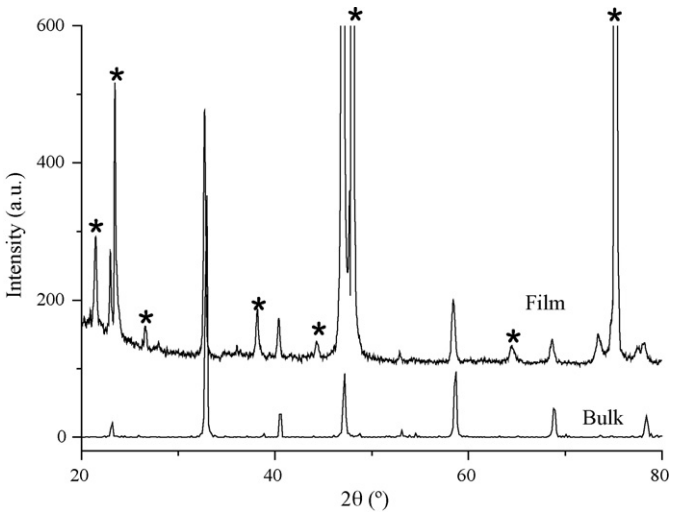

Fig. 1. X-ray diffraction patterns of the bulk $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ film produced on $LaAlO_3$ (1 0 0) single-crystal substrate; asterisk (*) indicates substrate peaks.

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 discussion

X-ray diagrams of the bulk $La_{0.67}Ca_{0.33}MnO_3$ and the $La_{0.67}Ca_{0.33}MnO_3$ film produced on a $LaAlO_3$ (1 0 0) single-crystal substrate are given in Fig. 1. The results indicate that both samples have perovskite structure and the X-ray results are in good agreement with previous studies. Fig. 2 shows typical SEM micrographs for the $La_{0.67}Ca_{0.33}MnO_3$ film. The SEM shows a polycrystalline nature with large number of grain boundaries and the grain size of these samples varies between 100 and 200 nm. Thus, it can be concluded that the thick $La_{0.67}Ca_{0.33}MnO_3$ film has a nanocrystalline structure. X-ray diagrams of the $La_{0.67}Ca_{0.33}MnO_3$ film showed a single phase. In order to understand the structure of the sample, we also performed a point EDX analysis (see Fig. 3) and found no impurity in the sample, which has the composition $La_{0.67}Ca_{0.33}MnO_3$.