Sol-Gel Synthesis and Transport Properties of La$_{23}$Sr$_{13}$Mn$_{0.99}^{57}$Fe$_{0.01}$O$_3$ Granular Thin Films

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We have used acetic acid, ethanol and distilled water as a solvent to synthesize La$_{23}$Sr$_{13}$Mn$_{0.99}^{57}$Fe$_{0.01}$O$_3$ (LSMFO) precursor. Crack-free LSMFO granular polycrystalline thin films have been deposited on thermally oxidized silicon substrates by spin coating. The dependence of crystallization, surface morphology, magnetic and transport properties on annealing temperature was investigated. With increasing annealing temperature, the metal-semiconductor (insulator) transition temperature and the magnetic moment decrease while the resistivity increases. The lattice constants remain almost unchanged. For LSMFO thin films, spin-dependent interfacial tunneling and/or scattering magnetoresistance were observed. Our results indicate that the annealing temperature is very important in determining the intrinsic and extrinsic magnetotransport properties.

1. Introduction

The doped manganese perovskite Ln$_1$:A:MnO$_3$ (where Ln is a rare-earth ion and A is a divalent ion) has stimulated interest because of its huge negative magnetoresistance [1, 2]. Double exchange [3] interaction and Jahn-Teller distortions have been used to explain qualitatively the transport phenomena observed in these perovskite oxides. The magnetic and transport properties of these samples are determined by several factors, such as the percentage of divalent ions, the ionic radii of the metal ions, the method used in the preparation of the samples, etc. [4-6]. In a similar way, the replacement of Mn ions by other transition metal ions in perovskites of composition Ln$_1$:A:Mn$_{1-x}$Fe$_x$O$_3$ (TR=transition metal), which show ferromagnetism and colossal magnetoresistance (CMR) at $y=0$, gives rise also to changes in the Mn$^{3+}$/Mn$^{4+}$ proportion. This alters the magnetic coupling between these ions, which is reflected in a gradual weakening of the ferromagnetism as the doping level of the TR ion increases, with important modifications in the magnetic and transport properties [7]. Up to date, some authors have investigated the Fe doping effects on the structural, transport and magnetic properties of La$_{1-x}$Ca$_x$Mn$_{1-x}$Fe$_x$O$_3$ [8, 9], La$_{1-x}$Pb$_x$Mn$_{1-x}$Fe$_x$O$_3$ [10] and La$_{1-x}$Sr$_x$Mn$_{1-x}$Fe$_x$O$_3$ [11, 12] bulk samples and found that the dopant Fe causes no structure change, but suppresses ferromagnetism and modifies magnetoresistance. As we know, there are some differences between bulk samples and thin films, such as crystal growth, microstructure etc. However, the thin film properties of Fe doped manganite has not been reported in a systematic study.

We thus report structural, magnetic, and transport properties of La$_{23}$Sr$_{13}$Mn$_{0.99}^{57}$Fe$_{0.01}$O$_3$ (LSMFO) thin films, which have been prepared by a novel water-based sol-gel process. This method should be attractive since precise composition control, low-temperature synthesis, and high homogeneity are easily achieved. We have focused our effort on the preparation of thin films with a small amount of Mn replaced by Fe ions.

2. Experiments

La$_{23}$Sr$_{13}$Mn$_{0.99}^{57}$Fe$_{0.01}$O$_3$ thin films were prepared by spin-coating on Si(100) substrates with thermally oxidized to 2000 Å of SiO$_2$ a precursor prepared by water-based sol-gel processing. To fabricate the LSMFO precursor, we dissolved La(CH$_3$COOH)$_3$ · $x$H$_2$O, Sr(CH$_3$COO)$_2$, Mn(CH$_3$COOH)$_2$, 4H$_2$O and Fe metal (dissolved in HNO$_3$) in a mixed solvent (acetic acid : ethanol : distilled water = 1 : 1 : 0.5) with an appropriate molar ratio. All reactions were carried out under dry nitrogen in a glove box. Lanthanum and strontium acetates were placed in a 3-neck flask, fitted with a reflux condenser, and boiled at 110 °C for 1 hr. After cooling to room temperature, an appropriate amount of manganese acetate and dissolved iron metal was added, and the solution was refluxed for 3 h at 80 °C and then cooled. The dissolved reactant species were partially hydrolyzed with an added mixture of distilled H$_2$O and anhydrous ethanol. The molar ratio of H$_2$O to the calculated LSMFO content was 2 : 1. Then, the precursor was aged at room temperature for 1 day and then vacuum dried at 150 °C for 3 h.

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