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Magnetic oxide thin solid films deposited at room temperature under ambient pressure using an electro-spray method

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ABSTRACT

The deposition and characterization of magnetic metal-oxide, $Eu_{1-x}Sr_xCoO_3$ ($x = 0.2, 0.5$) thin films using an electrostatic spray method are presented. The nano-sized particles were electro-sprayed from a colloidal suspension onto $Pt/TiO_2/SiO_2/Si$ substrates at room temperature under ambient pressure. X-ray diffraction patterns showed a perovskite tetragonal structure with an *I*4/*mmm* space group. Optical and scanning electron microscopy of the thin films revealed their crack-free and uniform nature. The temperature-dependent magnetization showed a ferromagnetic-paramagnetic transition above 350 K. Magnetic moments hysteresis loops demonstrate that the thin films exhibited a hard ferromagnetic state at 10 K and a soft ferromagnetic one at room temperature. The Hall measurement revealed metallic behavior at room temperature, confirming the transition from a metallic state to an insulating one at $T > 300$ K. The correlation is explained based on the double exchange interaction and spin state transitions at both low and high temperatures.

1. Introduction

Magnetic transition metal oxides including of Fe, Co and Mn possess interesting physical properties like superconductivity, thermoelectricity, ferromagnetism, and giant magneto-resistance [1–3]. The magnetic and electronic properties of magnetic transition metal oxides strongly depend on the electron-electron interactions of the transition metal atoms [3]. The doping level of *A*-site perovskite $Sr_{1-x}R_xCoO_3$ (R: rare earth element) plays an important role in determining the transport and magnetic properties of the magnetic transition metal oxide, which can make it a potential candidate for industrial applications [4–7]. Some magnetic oxide thin films exhibit high permeability and ferromagnetic resonance (FMR) in the GHz frequency range which is suitable for electromagnetic applications [8–10].

The $Sr_{1-x}R_xCoO_3$ material family in thin film form is known to exhibit a ferromagnetic state at room temperature [11,12]. $Eu_{1-x}Sr_xCoO_3$ is a member of the $Sr_{1-x}R_xCoO_3$ material family that required to be investigated for a ferromagnetic ram device application. Also, new facile synthetic approaches for magnetic oxide thin film fabrication are of great interest to the device industry.

The electrostatic spray method (ESD) incurs lower production cost than others thin film deposition methods, such as RF-sputtering, pulsed laser deposition, molecular beam epitaxy, sol-gel and spin-coating processing [13,14]. Rare earth cobaltates oxides need to be grown carefully in order to produce high quality films with strong adhesive properties using the ESD process. The ESD method can spray solutions of organic or inorganic compounds, bio-macromolecules and synthetic polymers. Selection of the proper conditions including applied voltage, flow rate, and substrate temperature allows the deposition of functional layers with particular physical properties [15].

In this paper, we demonstrate the successful growth of magnetic metal oxide thin films of $Eu_{1-x}Sr_xCoO_3$ ($x = 0.2, 0.5$) using ESD at room temperature under ambient pressure. X-ray diffraction, the optical electron microscopy (OEM) and field emission scanning electron microscopy (FE-SEM) were used to examine the films structure and surface features, respectively. The zero-field-cooled (ZFC) and field-cooled (FC) modes magnetization of the films were investigated as the function of temperature. Magnetic moment (*M*–*H*) hysteresis loops of $Eu_{1-x}Sr_xCoO_3$ ($x = 0.2$, 0.5) thin films have been investigated at both of low (10 K) and high (300 K) temperatures. The electrical properties at room

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temperature were also measured using a Hall measurement system.

2. Experimental detail

Nano-powders of $Eu_{1-x}Sr_xCoO_3$ (x = 0.2, 0.5) were prepared by a conventional solid-state reaction method. Highly pure powders of all chemicals, Eu_2O_3 (99.99%), $SrCO_3$ (99.99%), and Co_3O_4 (99.99%) (MTI, USA), were mixed in various molar ratios. The mixtures were well-grinded, pelletized, and fired in air at 1000 °C for 12 h, at 1100 °C for 12 h and finally sintered at 1300 °C for 10 h, and this process was repeated twice. The 2nd phase formation as well as the lattice constants were verified for the $Eu_{1-x}Sr_xCoO_3$ (x = 0.2, 0.5) powders using powder X-ray diffraction (XRD) with Cu Kα radiation (Philips Co.) as described elsewhere [16,17].

The suspensions were prepared by stirring the nano-powder in ethanol in a glass vessel for 24 h, centrifugal separator had been used to collect the fine and homogenous size of particles. The suspension was loaded into a syringe and mounted in the precision fluid metering pump (KDS100, min 0.21 μL/h). The liquid was supplied via a polyethylene pipe with a 0.8 mm inner diameter during 4–6 h. The flow rate of the suspensions was set to 1.1–1.3 mL/h. The distance between the nozzle tip and the heater was fixed 35–40 mm. The substrate ($Pt/TiO_2/SiO_2/Si$) was kept to 80 °C. A grounded ring-shaped extractor electrode with an inner diameter of 0.1 mm was mounted to the level of the needle tip to improve meniscus and droplet formation in the electric field and create a wider spray plume distribution over the substrate. The dual concentric nozzle was connected to a high voltage AC/DC generator (30 kV, PM04015, TREK) switched to positive polarity, while grounding the plate and extractor electrode. Finally, the samples were kept for 2 h at the same temperature to evaporate any remaining liquid. The schematic of electrospray system is presented in Fig. 1.

Tentative compositions of the electro-sprayed $Eu_{1-x}Sr_xCoO_3$ (x = 0.2, 0.5) thin films were confirmed by EDX (energy dispersive X-ray spectroscopy); film crystal structures were investigated by x-ray diffraction (XRD, Cu Kα radiation 1.542 Å). The optical microscopy (OEM; Nikon, Japan) and field-emission scanning electron microscopy (FE-SEM, JSM 840, JEOL) were used to characterize the surface morphology and thickness of the deposited films. ZFC and FC mode magnetization of the films were investigated as a function of temperature. M–H hysteresis loops of $Eu_{1-x}Sr_xCoO_3$ (x = 0.2, 0.5) thin films have been investigated at both of low (10 K) and high (300 K) temperatures using a SQUID magnetometer (Quantum Design, MPMS). The electrical properties were measured using a Hall system at room temperature.

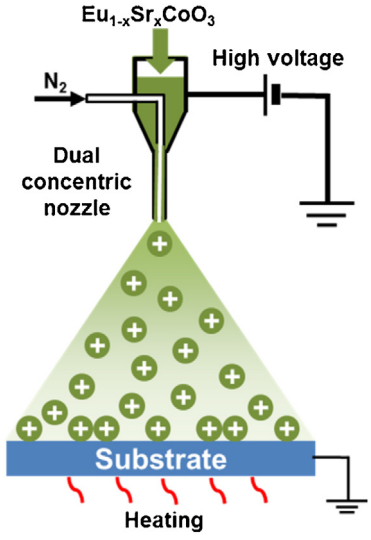

Fig. 1. Schematic of electrostatic spray system for thin film deposition from a suspension.

3. Results and discussion

Fig. 2(a) depicts the XRD patterns for $Eu_{1-x}Sr_xCoO_3$ (x = 0.2, 0.5) thin films on the $Pt/TiO_2/SiO_2/Si$ substrates. The XRD patterns clearly confirm that the deposited films have a single phase tetragonal perovskite structure and all XRD reflections correspond to the crystalline plane of $SrCoO_3$ without any residual peaks [16,19]. The structure is demonstrated by the presence of the principle perovskite peaks (402), (400) and (440), characteristic of the $I4/mmm$ crystal structure, as well as one peak from the platinum substrate. The lattice parameters a and c, fitted using a powder cell software were found to be 3.892 and 3.882 Å for x = 0.2 and 3.904 and 3.894 Å for x = 0.5, respectively, consistent with the literature (JCPDS 83-1880) [18,20]. The increased lattice parameters between the $Eu_{0.8}Sr_{0.2}CoO_3$ and $Eu_{0.5}Sr_{0.5}CoO_3$ samples are attributed to the increased Sr content; the ionic radius of Sr is larger than that of Eu ions. These results agree well with previous reports for polycrystalline samples [18]. The full width at half maximum (FWHM) of the (440) XRD peak is estimated using so-called Scherrer's equation [17]. For the $Eu_{0.8}Sr_{0.2}CoO_3$ film, the FWHM was found 0.8911° at 2θ = 68.166° with the crystal grain size 196.2 nm, while $Eu_{0.5}Sr_{0.5}CoO_3$ film showed the FWHM of 1.1628° at 2θ = 68.247° with the crystal size 150.4 nm. The analysis of the XRD pattern shows the decrease of the crystal size of the films with the Sr-content (x = 0.2–0.5) due to the broadening of the peak, which is related to the increase of the random arrangement of the crystals. Fig. 2(b) presented the XRD pattern of $EuCoO_3$ system in ceramic form, which shows orthorhombic structure. Here it is clear that the difference between the structures of the compound $EuCoO_3$ and $(Eu,Sr)CoO_3$ thin films systems are different.

Fig. 3(a) and (b) presents the FE-SEM images of the $Eu_{0.8}Sr_{0.2}CoO_3$ and $Eu_{0.5}Sr_{0.5}CoO_3$ thin films deposited on the $Pt/TiO_2/SiO_2/Si$-substrates. It shows that the thin films are homogeneous and made up of evenly sized grains due to the annealing affect after deposition. The FE-SEM images, as well as the cross-sectional SEM images (not shown hear) revealed that the average grain size of $Eu_{1-x}Sr_xCoO_3$ thin films ranged from 100 to 150 nm and from 80 to 120 nm for x = 0.2 and 0.5 respectively, which is consistent with XRD analysis. In addition, the thicknesses measured approximately 210 and 138 nm for the two films.

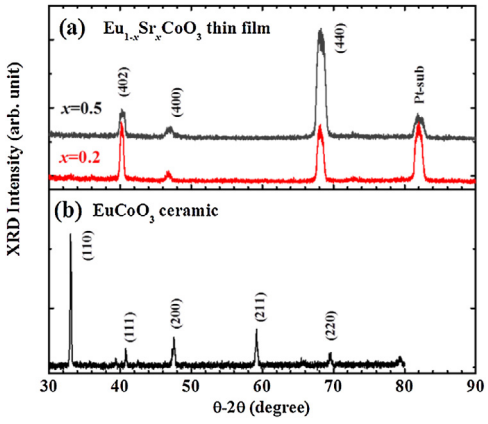

Fig. 2. XRD patterns of (a) $Eu_{0.8}Sr_{0.2}CoO_3$ and $Eu_{0.5}Sr_{0.5}CoO_3$ thin films grown on $Pt/TiO_2/SiO_2/Si$ substrates using an ESD method (a) $EuCoO_3$ ceramic.

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