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Nanocomposite films with magnetic field sensing properties

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ABSTRACT

$La_{0.67}Sr_{0.33}MnO_3$ (LSMO) and LSMO:ZnO nanocomposite thin films were fabricated on SiO_2/Si and (0001) Al_2O_3 substrates through solution deposition routes. The LSMO grain size reduced in the composite films as compared to that in pure LSMO film resulting in a larger volume fraction of grain boundaries. Further, compositional or magnetic disorder at the grain boundary region resulted in a reduction of the ferromagnetic-paramagnetic and metal–insulator transition temperatures in LSMO:ZnO films. The magnetoresistance (MR) behavior in the composite films was revealed to be dominated by extrinsic effects with large values of MR at low temperatures and low applied fields. A maximum low-field MR value of −23.9% was observed at 0.5 T and 10 K with the field applied parallel to the current for LSMO:ZnO film on Al_2O_3, with a maximum field sensitivity of 632%/T.

1. Introduction

Hole-doped perovskite rare-earth manganites have been intensely studied since colossal magnetoresistance (CMR), which is a large change in resistivity with applied magnetic field, was revealed in single crystals and thin films of $La_{1-x}Sr_xMnO_3$ (LSMO) and $La_{1-x}Ca_xMnO_3$ (LCMO) [1–3]. CMR is an intrinsic effect that is generally observed at high magnetic fields (≥ 1 T) and it maximizes near the ferromagnetic-paramagnetic transition temperature (T_C) of the material. Such intrinsic behavior is related to the fluctuating ferromagnetic (FM) clusters controlling spin-dependent transport behavior. An extrinsic MR effect has also been observed in bulk ceramics and polycrystalline LSMO or LCMO films in wide range of temperatures below T_C with significant MR values even at low applied magnetic fields (≤ 0.5 T) [4–6]. This low-field magnetoresistance (LFMR) effect is of great interest for applications in bolometric detectors, magnetic read heads, and magnetic field sensors or position sensors [7–9]. In bulk ceramics, LFMR values has been enhanced by introducing oxygen deficiencies, grain boundaries, structural or chemical disorder, or through the addition of a secondary (generally insulating or semiconducting) phase in LSMO and LCMO [4,10–13]. The interfacial effects in biphasic ceramic composites with CeO_2 [10], $SrTiO_3$ [11], ZnO [13,14], etc. could lead to modified spin-dependent transport in the grain boundary (GB) region. There have also been several studies of LFMR in composite thin films. For example, LSMO:ZnO and LSMO:Al_2O_3 composite films have been fabricated by pulsed laser deposition (PLD) [15–17], LSMO:MgO by metal-organic aerosol deposition technique [18], and mixed solution route [19]. However, work on the MR properties of biphasic composite films is limited with most studies reporting enhanced values of LFMR at high applied fields [20,21], which is not practical for magnetic field sensing applications. Thus, there is a need to study manganite:insulator biphasic composite films that can be grown by a cost-effective route (that does not require high vacuum systems) and show large values of LFMR at low applied magnetic fields.

In the present work, $La_{0.67}Sr_{0.33}MnO_3$:ZnO composite films were fabricated on (0001) Al_2O_3 and SiO_2/Si substrates through facile and low-cost solution routes. The composite films exhibited extrinsic MR effects due to enhanced spin-polarized scattering and tunneling at the grain boundaries with a maximum LFMR value of −23.9% at 0.5 T and 10 K for a composite film on Al_2O_3. A magnetic field sensitivity of ~632%/T was achieved when the magnetic field was applied parallel to the current, as compared to MR of −8.4% and field sensitivity of 42%/T for pure LSMO film on Al_2O_3 substrate.

2. Experimental

2.1. Nanocomposite sample preparation

First, ~400 nm long ZnO nanorods were prepared on (0001) oriented Al_2O_3 substrate and SiO_2/Si substrates by hydrothermal process [22]. An alcoholic Zn precursor was spin coated onto the substrates and annealed at 600 °C to form the ZnO seed layer. The substrate with the seed layer were immersed in the Zn precursor solution and placed in a water bath with the temperature set to

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90 °C. Once the desired height of nanorods was achieved, the samples were rinsed with DI water and dried.

In order to fabricate $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) films, a 0.2 M precursor solution was prepared by dissolving high-purity nitrate precursors of La, Sr, and Mn in an ethylene glycol based solvent with La:Sr:Mn molar ratio of 0.67:0.33:1. The precursor solution was spin coated at 6000 rpm/20 s onto (0001) Al_2O_3 substrate as well as on vertically aligned ZnO nanorods coated substrates to fabricate LSMO and LSMO:ZnO films, respectively. After each coating, the films were heated at 600 °C for 5 min and after desired thickness was reached, the films were annealed at 850 °C for 2 h in oxygen.

2.2. Sample characterization

X-ray diffraction (XRD) measurements were performed to understand the structure of the films using a Bruker D-5005 powder diffractometer. Scanning electron microscopy (SEM) was utilized to analyze the growth of ZnO nanorods and the LSMO:ZnO films using a JEOL 6335F Field Emission SEM. Temperature dependent resistivity values $\{\rho(T)\}$ of the samples were measured from 10 K to 350 K and magnetic field dependent resistivity values $\{\rho(H)\}$ were measured from −3 T to +3 T (−30,000 Oe to +30,000 Oe) at several temperatures using a four-probe technique using an Evercool Physical Property Measurement System (PPMS, from Quantum Design). The $\rho(H)$ data was measured with magnetic field applied perpendicular to the current and the substrate ($H \perp I$) and for the in-plane measurements, resistivity was measurements with magnetic field applied parallel to the current and substrate ($H//I$). The temperature dependence (from 10 K to 400 K with 100 Oe applied field) and magnetic field dependence (from −2 T to 2 T at 10 K) of the magnetic moment was measured using vibrating sample magnetometer attached to the PPMS.

3. Results and discussion

3.1. Structure and microstructure

The XRD peaks of the perovskite LSMO phase are observed in the θ–2θ scans of all films as shown in Fig. 1. The LSMO phase in the LSMO:ZnO film on SiO_2/Si is found to be polycrystalline with randomly oriented crystallites. However, increased relative

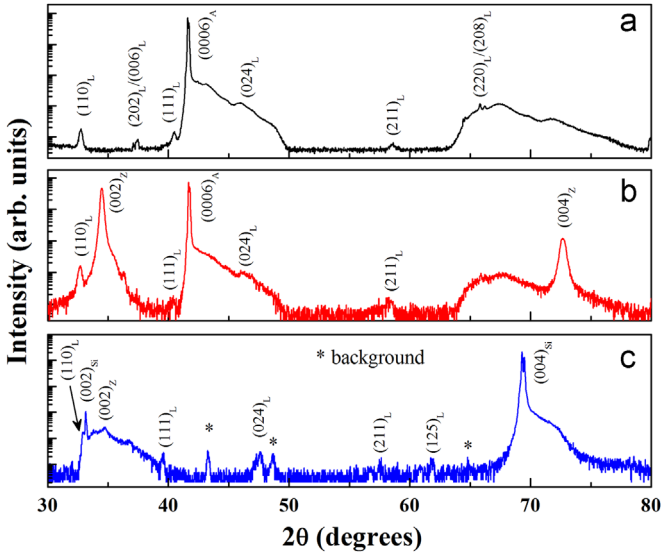

Fig. 1. The XRD θ–2θ scans of (a) LSMO film on Al_2O_3, (b) LSMO:ZnO film on Al_2O_3, and (c) LSMO:ZnO film on SiO_2/Si substrates.

intensity of the (110) peak in the films on Al_2O_3 substrate ($I_{(111)}/I_{(110)}=0.845$ for the present LSMO film on Al_2O_3 as compared to 0.118 in JCPDS #01-075-9827 for bulk LSMO) suggests preferred orientation. The pseudocubic lattice parameter of LSMO phase in pure LSMO film was 3.857 Å and in LSMO:ZnO composite films on Al_2O_3 and SiO_2/Si substrates, these were 3.871 Å and 3.837 Å, respectively. These values are smaller but close to the lattice parameter for bulk LSMO (3.873 Å) [23], indicating that the LSMO phase in composite films is relaxed. Further, these values suggest the lack of oxygen vacancies that tend to increase the lattice parameters [24]. The average crystallite size (D) of the LSMO phase was calculated from the XRD data using Scherrer's equation, $D=0.9\lambda/\beta\cos\theta$, where λ is the wavelength of the X-ray source and β is the full width at half maximum. The value of D was calculated to be 29.3 nm for the present LSMO film, which reduced to 20.5 nm and 26.5 nm for LSMO:ZnO composite films on Al_2O_3 and SiO_2/Si, respectively.

From SEM images (not shown here), the as-grown ZnO nanorods are determined to be ~400 nm in length, with 30-50 nm spacing between the nanorods. Cross-sectional SEM images of the LSMO:ZnO composite films (presented in Fig. 2(a) and (b)) shows that the LSMO phase fills up the area between ZnO nanorods resulting in a 3-1 type (LSMO phase connected in three and ZnO phase in one direction) nanocomposite films on both Al_2O_3 and SiO_2/Si substrates. The spacing between nanorods is therefore expected to limit the grain growth of LSMO phase in the composites as compared to pure LSMO. The top-view SEM image of LSMO:ZnO on Al_2O_3 (Fig. 2(c)) reveals an average LSMO grain size of ~20 nm that is reduced as compared to the pure LSMO film (not shown) that is consistent the decrease in crystallite size D. It should be noted that the reduced LSMO grain size means large grain boundary region in the composite films in addition to the presence of LSMO:ZnO interfaces.

3.2. Magnetic behavior

The temperature dependent zero-field cooled (ZFC) and field-cooled (FC) magnetization data (normalized to the moment at 10 K) for pure LSMO film as well as for the LSMO:ZnO composites on Al_2O_3 and SiO_2/Si is plotted in Fig. 3. The ferromagnetic-paramagnetic transition temperature, T_C, of the pure LSMO film on Al_2O_3 is ~360 K as determined from a peak in the temperature coefficient of magnetization (TCM) for the FC data, defined as $TCM=(1/M)(dM/dT)$ [25,26]. The value of T_C in the present LSMO film is similar to values found for single crystals [27]. Further, the peak in TCM data of pure LSMO is sharp, which is consistent with a first-order FM transition. However, T_C shifts to lower temperatures in both LSMO:ZnO composite films (~315 K and ~258 K for the composite films on Al_2O_3 and SiO_2/Si, respectively). The corresponding peak in TCM (not shown here) is also broadened in the composites as compared to pure LSMO, suggesting weakened ferromagnetism and magnetic disorder. This broad transition behavior could be due to the larger volume fraction of GBs in the composite films as compared to the pure LSMO film due to the reduced grain size. The ferromagnetism in the GB region are thought to be weaker than in a LSMO grain due to disorder inherent in this region and dilution of the FM double exchange interaction [5,26,28]. It could also suggest the presence of compositional disorder at the GBs resulting in the broadening of TCM. In LCMO:ZnO ceramic composites, a small amount of Zn has been shown to substitute for Mn at LSMO/ZnO interface [29]. Thus, compositional disorder in the present composite films (composition at the GB region is different from that inside the grain) may result in the GBs still ordered paramagnetically as compared to the FM ordering in the core of the grain that would result in a broadened transition. This may also lead to enhanced values of