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Ferroic metal-oxide films grown by polymer assisted deposition

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Abstract

Polymer assisted deposition is a versatile technique to grow simple and complex metal-oxide thin films. In this paper we report the structural and electrical properties of ferroic materials, namely $La_{0.67}M_{0.33}MnO_3$ (M=Sr and Ca) and $Ba_{1-x}Sr_xTiO_3$ (x=0.3, 0.5, and 0.7) prepared using this process. The films were prepared on single crystalline $LaAlO_3$ substrates. The films were highly c-axis oriented and epitaxial in nature. The ferromagnetic $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ films show intrinsic transport properties with maximum magnetoresistance values (at applied field of 5 T) of −50% and −88%, respectively. The highest dielectric constant (~1010) and tunability (~69%) of $Ba_{1-x}Sr_xTiO_3$ film occurs at x=0.3 for films, which is at the phase boundary of tetragonal and cubic.
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Keywords: Polymer assisted deposition; BST; Colossal magnetoresistance; Ferroelectric; Tunability

1. Introduction

Solution deposition techniques are generally viewed as being less capital-intensive. In addition, large area deposition is possible as compared to other dry-techniques like pulsed laser deposition (PLD) and RF sputtering. These features make the solution techniques attractive for the deposition of a variety of functional oxide films. However, control of the stoichiometry and uniformity of the film highly depends on the reactivity of the chemicals used in the preparation of solutions. Among solution techniques, sol–gel, chemical solution deposition (CSD), and metal-organic depositions are the most popular and widely-used techniques for the preparation of various metal-oxide films such as ferroelectric, ferromagnetic, and multiferroic materials [1–3]. However, the solution preparation using these methods typically is carried out in organic solvents. The use of organic solvents is not desirable in many materials systems. Continual efforts have been expended in the development of chemical solution deposition processes which are organic solvent-free. Recently, polymer assisted deposition (PAD) has been demonstrated as a novel technique to deposit metal-oxide thin films [4,5]. In the PAD process, an aqueous solution of metal-precursors is mixed with a soluble polymer. This polymer actively binds, encapsulates the metal ions, and uniformly distributes them within the solution. By varying the ligands and using appropriately functionalized polymers, different binding sites can be created for metals. The controlled strength of solution and molecular weight of the polymer help in achieving the desired viscosity of the solution and hence the thickness of the film can be controlled. It should be pointed out that the sol–gel technique has also been very successful in the preparation of high quality epitaxial functional oxide films [2,6] However, the alkoxides used in the process are very water sensitive and may precipitate out from the solution during preparation. Such reactions are slowed down by the addition of chelating agents during processing. In contrast, the use of non-reactive precursors and pre-binding the metals with the polymer in the PAD process give more reproducible results. Thin films of many simple and complex metal-oxides, such as TiO_2, Eu_2O_3, and $SrTiO_3$ have been grown using PAD [4,5].

The aim of this paper is to demonstrate the successful use of this technique to deposit epitaxial ferroic films, namely: ferroelectric $Ba_{1-x}Sr_xTiO_3$ (BST) and ferromagnetic lanthanum manganites, $LaMMnO_3$ (where M=Sr and Ca). Thin films of perovskite structured BST have been extensively investigated for potential applications in dynamic random access memory and

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electrically tunable microwave device [7–9]. The strong response of the dielectric constant of BST to applied dc electric fields makes it attractive for tunable microwave devices such as phase shifters, frequency agile filters, etc. For microwave dielectric applications, epitaxial films are required, as high-angle grain boundaries in the polycrystalline films increase the dielectric losses and consequently limit the device performance. Hole-doped lanthanum manganites, $LaMMnO_3$ (M=Sr and Ca), on the other hand, display the unusual property of being paramagnetic insulators at high temperatures and ferromagnetic metals at low temperatures. These manganites are widely studied as colossal magnetoresistance (CMR) materials, which show large reductions in their resistivity values with the application of a magnetic field [10,11]. This CMR effect in hole-doped manganites has attracted significant interest in the past decade due to their potential applications in magnetic random access memory, disk-drive read heads, and magnetic field sensors [12,13].

In the present investigation, the PAD process was used to prepare ferroic films such as $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), $La_{0.67}Ca_{0.33}MnO_3$ (LCMO), and $Ba_{1-x}Sr_xTiO_3$ with $x=0.3$, 0.5, and 0.7 on single crystalline $LaAlO_3$ (LAO) substrates. These films were evaluated in term of their structural, transport, and dielectric properties.

2. Experimental

To prepare $La_{0.67}Sr_{0.33}Mn$ and $La_{0.67}Ca_{0.33}Mn$ solutions using the PAD process, first, solutions of lanthanum, strontium, manganese and calcium were prepared separately. A representative example is as follows: high purity (>99.99%) $La(NO_3)_3 \bullet 6H_2O$ (5.73 mmol) was dissolved in 40 mL H_2O. Ethylenediamine-tetraacetic acid (5.82 mmol) was added, followed by polymer polyethyleneimine (4.32 g). The solutions were placed in an Amicon filtration unit containing a YM3 filter (designed to pass materials having a molecular weight <3 000 g/mol) and washed twice with water. The remaining solutions were prepared using $Sr(NO_3)_2$, $MnCl_2 \bullet H_2O$, and $Ca(OH)_2$ as the starting salts. The solutions were combined in the required stoichiometric ratios to prepare solutions for $La_{0.67}Sr_{0.33}Mn$ and $La_{0.67}Ca_{0.33}Mn$. Precursors for the $Ba_{1-x}Sr_xTi$ solutions were prepared using $Ba(NO_3)_2$, $Sr(NO_3)_2$, and $TiCl_4$ as the starting materials. A detailed preparation method for the preparation of the BST solutions can be found elsewhere [5]. Metal analysis was conducted on a Varian Liberty 220 inductively coupled plasma-atomic emission spectrometer. These solutions were mixed in the appropriate stoichiometric ratios and spun coat onto (001) LAO substrates. A multilayer coating approach was used to deposit films of LSMO and LCMO. After each coating, the films were pyrolized at 600 °C. After ten coatings; the films were heated to (rate=10 °C/min) 950 °C and annealed for 2 h in oxygen as optimized in our previous study [14]. For deposition of the BST film, the substrate was coated with the BST solution at room temperature. A slow heating rate (1 °C/min) was used to ramp the temperature to 500 °C to pyrolyze the polymer. Final annealing was performed at 1000 °C for 1 h to induce crystallization. The homogeneous distribution of metals ions in the solution lead to the formation of uniform metal-oxide films upon thermal decomposition of the polymer matrix.

X-ray diffraction (XRD) patterns of all the films were measured on a Siemens D5000 diffractometer. Transmission electron microscopy (TEM) was performed with a JEOL 3000F microscope. Resistivities (ρ) of LSMO and LCMO films were measured from 5–400 K at different applied magnetic fields ($\mu_0 H=0$–5 T) using a standard four probe technique and Physical Property Measurement System (Quantum Design) by applying magnetic field perpendicular to the substrate. Also, magnetic field dependences of ρ were measured at different temperatures. To measure dielectric properties of the BST films, coplanar capacitors were fabricated on the BST film. Electric field dependent capacitance measurements of BST films were performed at 1 MHz and room temperature using a HP4194A impedance analyzer. The dielectric constants of the BST films were extracted using the coplanar striplines model [15].

3. Results and discussion

3.1. Structural characterization of films

3.1.1. $La_{0.67}Sr_{0.33}Mno_3$ and $La_{0.67}Ca_{0.33}Mno_3$ films

XRD θ–2θ scans for LSMO and LCMO films show only (00l) peaks, indicating that films were c-axis oriented (Fig. 1). The (002) peaks of the LSMO and LCMO peaks are shown in the inset of Fig. 1. Lattice parameters were found to be 0.3884 nm for LSMO and 0.3869 nm for LCMO films. These values are similar to those obtained for pellets (bulk) of the same compositions by Snyder et al. [16]. The full widths at half maximum (FWHM) of rocking curves from the (002) reflections of LCMO and LSMO films are in the range of 0.4–0.5°, suggesting good cystallinity of these films. The epitaxial nature of the LSMO and LCMO films was confirmed by the in-plane alignment with respect to the major axis of the LAO substrate. Fig. 2(a), (b), and (c) show the φ -scans measured on LSMO {220}, LCMO {220}, and LAO {220}. In the φ -scans, four peaks with an

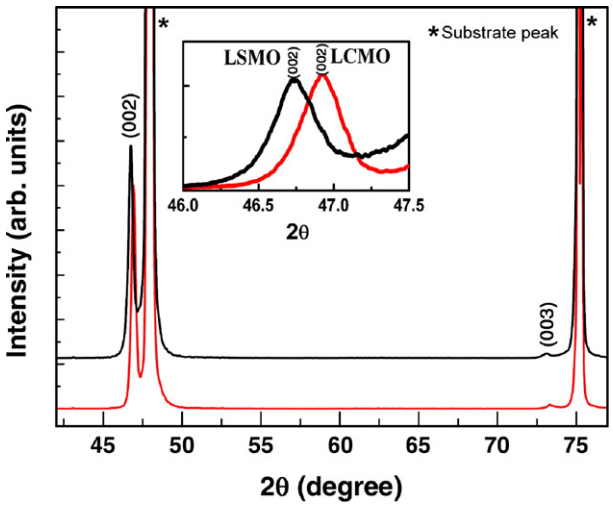

Fig. 1. XRD θ–2θ scans of LSMO and LCMO films on $LaAlO_3$ substrate. Inset of the figure shows the (002) peaks of LSMO and LCMO.