



Electrical behavior of chemically grown lanthanum ferrite thin films

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Abstract

Perovskite structured oxides are important functional materials often used for the development of modern devices. To extend their applicability, these materials need to be scalably and efficiently grown in the form of thin films. In this work, perovskite structured thin films of nanograined LaFeO₃ (LFO) were chemically grown using polymeric precursors on Pt substrates. The thin films were characterized by X-ray diffraction, field-emission scanning electron microscopy, atomic force microscopy, and transmission electron microscopy. The electrical properties of the films were also measured. The homogeneous LFO thin films synthesized at a sintering temperature of 500 °C in 2 h contained grains with lateral dimensions of about 68 nm and 356 nm in thickness. The dielectric permittivity and dielectric loss measurements of the sample indicated only a slight dispersion in the frequency because of the lower two-dimensional stress in the plane of the film. The nanograined LFO semiconductor thin films showed a room temperature magnetic coercive field, which rendered them magnetically soft. The electrical characterization of the films, including temperature-dependent conductivity and thermopower confirmed *p*-type conduction and the mobility activation energy was measured to be 0.96 eV. A strong magnetization with a remnant magnetization of ~60 emu/g was observed in the LFO films, indicating the uncompensated spin magnets moments of the Fe³⁺ ions.

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1. Introduction

Multiferroic (MF) materials, which exhibit simultaneous coexistence of magnetic (ferro/antiferromagnetic) and electric (ferro/antiferro electric) orderings have gained widespread interest because the onset of magnetoelectric coupling in these materials occurs in the same phase. MFs have various potential applications in solid oxide fuel cells, non-volatile magnetic memory devices, and ultrasensitive magnetic read-heads of modern hard disk drives [1–3]. The coexistence of ferroelectricity and ferro/antiferromagnetism and the unique coupling behavior renders MFs potential candidates for the design of new functional sensors and multistate devices [4]. High-quality nanocrystalline rare earth orthoferrites, especially LnFeO₃ (Ln = a lanthanide element),

have drawn much attention because of their unique physical and chemical properties for various applications [5]. Most ferroelectrics and multiferroic materials are oxide perovskites with a general stoichiometry ABO₃. In perovskite structured materials, the small cations (B) are at the center of an octahedron of oxygen anions and the large cations (A) are at the unit cell corners. The high local internal electric field produces spontaneous polarization, leading to the onset of ferroelectric ordering. Further, the cation B-oxygen-cation-B angle is nearly 180°, which induces superexchange interaction, leading to the onset of magnetic ordering in the same system. Many compounds with the ABO₃ stoichiometry crystallize with an orthorhombic distortion in the perovskite structure and LaFeO₃ (LFO) is a prototype of this series. The crystal structures of these materials are derived from the standard cubic structure by the distortion of the BO₆ octahedral. These perovskites are of particular interest because of their relatively simple crystal structure in combination with

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excellent magnetic, piezoelectric, optical, catalytic, and dielectric properties [6].

LFO is a semiconducting perovskite oxide [7,8], which has been extensively studied because of its potential applicability in gas sensors, electrodes of solid-state fuel cells, spin valves, and other exchange bias applications in magnetic memory, or for oxygen sensing [4,7–15]. LFO with antiferromagnetic characteristics [9,10] crystallizes in an orthorhombically distorted perovskite structure with lattice parameters $a=5.557 \text{ \AA}$, $b=5.5652 \text{ \AA}$, and $c=7.8542 \text{ \AA}$ [14]. The Néel temperatures of thin film and bulk LFO are as high as 670 and 740 K, respectively [10]. The antiferromagnetism and an extremely high ordering temperature (T_N) of LFO are very promising for its application in the storage industry, spin valves, exchange bias applications, and heterostructures of magnetic/magnetic and magnetic/electric films [11]. In this work, we have used a solution-based method widely used to prepare thin oxide films for the preparation of LFO thin films. Solution-based preparation methodologies involve either sol–gel processing or decomposition of organometallics. Various types of sol–gel processing include colloidal sol–gel processing, synthesizing inorganic polymeric gels from organometallic compounds, and formation of an organic polymeric complex which originates the polymeric precursor method (PPM). PPM can involve [16–18] in situ polymerization of organometallic monomers or the preparation of a viscous solution containing metal ions, polymers, and a solvent. This viscous solution can be easily converted into a thermoplastic gel at high polymer concentrations. In situ PPM has been used extensively to obtain ceramic powders with small particles and a single phase [19].

This method was originally developed by Pechini [20] and is based on the chelation of a metallic cation by a carboxylic acid (such as citric acid) and further polymerization, which is promoted by the addition of ethylene glycol, leading to polyesterification. To obtain crack-free films, process parameters, including solution viscosity and ionic concentration, substrate–film adhesion, heating conditions, preparation atmosphere, substrate, and withdrawal speed need optimization. Differences between the thermal expansion coefficients of the film and the substrate also influence PPM [21,22]. In this paper, we report, to the best of our knowledge, the first systematic study on the structural, morphological, and electrical characteristics of LFO thin films obtained by PPM. We have also investigated the magnetic behavior of orthorhombic LFO structures deposited on Pt/Ti/SiO₂/Si substrates by PPM.

2. Experimental procedure

The LFO thin films were prepared by the PPM, as described elsewhere [23]. The precursor solutions of lanthanum and iron were prepared by adding and stirring the raw materials (La₂CO₃-Merck 99.5% and Fe(NO)₃·9H₂O- Merck 99.9%) in to ethylene glycol and concentrated aqueous citric acid under heating. Appropriate quantities of the solutions of La and Fe were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was set to 20 cP by adjusting the water content using a Brookfield viscometer. The films were

spin-coated from the deposition solution onto a Pt (111)/Ti/SiO₂/Si substrate. The LFO films completely crystallized after annealing for 2 h at 500 °C. Multilayered films were obtained by spin-coating the deposition solution 10 times on the surface of the substrate at 5000 rpm. The films were annealed at 300 °C for 1 h at a heating rate of 3 °C/min in a conventional furnace and later crystallized at 500 °C for 2 h in static air environment. The number of layers was set as a function of the desired thickness to achieve the desired electrical properties. The films were analyzed by X-ray diffraction (XRD) at room temperature (using a Rigaku-DMax 2000PC diffractometer) with Cu-K α radiation in the 2θ range 20–60° at 0.3°/min. The crystallite size (d) of the films was calculated using the Scherrer equation $d=k\lambda/\beta \cos \theta$, where k is a constant, λ is the X-ray wavelength, and β is the full width at half maximum (FWHM) of the maximum reflection measured from a slow scan, and θ is the diffraction angle of the main peak. The thickness of the annealed films was measured using scanning electron microscopy (SEM, Topcom SM-300) by imaging the transverse section using backscattered electrons. Three measurements were acquired to obtain the average thickness, which was ~ 300 nm. The microstructural characterization of the films was carried out using transmission electron microscopy (TEM, Philips CM-20). The surface morphology of the thin films was characterized by atomic force microscopy (AFM) in the tapping mode (Nanoscope IIIa-Bruker).

Further, X-ray photoelectron spectroscopy (XPS, PHI-5702 multifunction instrument) was carried out on the samples using an Al-K α X-ray source with a passing energy of 29.35 eV. The pressure in the chamber during the experiments was about 4.5×10^{-9} Torr. The binding energy calibration scale was controlled using the O 1s peak, which appears in the XPS profiles of the as-grown samples.

For electrical measurements, a top Au electrode (0.5 mm in diameter) was sputtered through a shadow mask at room temperature. After the deposition of the top electrode, the film was annealed in a tube furnace under oxygen at 300 °C for 1 h to decrease the oxygen vacancies. The electrical properties of the capacitor (Au/LFO/Pt/Ti/SiO₂/Si) were measured on a Radiant Technology RT6000 A tester equipped with a micrometer probe station in a virtual ground mode at 60 Hz. The dielectric properties of the capacitor were measured with an HP4192A impedance/gain phase analyzer under zero bias at room temperature as a function of frequency in the range from 10 kHz to 1 MHz. The magnetization measurements were carried out using a vibrating sample magnetometer (VSM, Quantum Design™). The electrical conductivity (ρ) measurements were obtained in air using a PC-controlled four-probe direct current (DC) equipment. The ρ value was obtained in the temperature (T) range room temperature. The thermopower was evaluated using K-thermocouples (which measured the applied temperature gradient) and platinum electrodes (which measured the resulting voltages).

3. Results and discussion

Fig. 1 shows the XRD pattern of the LFO thin films deposited on Pt/Ti/SiO₂/Si (100) substrates. The polycrystalline film exhibited a

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