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Ferromagnetic, ferroelectric and magnetoelectric properties of (001)-oriented $Pb(Zr_{0.52}Ti_{0.48})O_3/La_{0.67}Sr_{0.33}MnO_3$ composite films deposited on Si substrates using chemical solution deposition

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ABSTRACT

Using (001)-oriented $LaNiO_3$ (LNO) as a buffer layer, the ferromagnetic-ferroelectric layered composite film of $Pb(Zr_{0.52}Ti_{0.48})O_3/La_{0.67}Sr_{0.33}MnO_3$ (PZT/LSMO) with a (001) orientation was deposited on a Si (100) substrate through a chemical solution deposition (CSD) method. The LNO buffer layer promotes the (001) preferential orientation and the columnar growth of the overlying LSMO and PZT layers. The oriented PZT/LSMO/LNO film has soft ferromagnetism characteristics, and a higher saturated magnetization (750.9 emu/cm^3) compared with the non-oriented one. The effects of the orientation and the selection of the bottom electrode (BE) on ferroelectric properties of PZT/LSMO/LNO composite films were investigated. Using LNO as the BE, the oriented PZT/LSMO/LNO film exhibits the highest remnant polarization (Pr) of 30.0 μC/cm^2 and the lowest leakage current density of 10^{-6} A/cm^2 at 300 kV/cm. The oriented PZT/LSMO/LNO film also exhibits a good magnetoelectric (ME) effect and shows the maximum ME voltage coefficient α_E of 125.9 mV/cm·Oe at room temperature. Our investigation provides an effective way to replace the expensive single-crystal substrates, and to promote the application of ferromagnetic-ferroelectric composite films into the Si-based microelectronic field.

1. Introduction

Magnetoelectric multiferroic materials whose ferroelectric and ferromagnetic orders coexist have attracted much attention due to their potential applications in sensors, data storage, actuators, spintronics, and microelectro-mechanical systems [1–4]. These materials have not only ferroelectric and ferromagnetic properties, but also the "magnetoelectric (ME) effect", by which an induced electrical polarization and magnetization can be controlled by applying a magnetic and electric field, respectively. However, the available magnetoelectric multiferroic materials with single-phase are scarce in nature and only exhibit weak ME effect at low temperature. It has greatly driven forward the growth of magnetoelectric composite materials combining ferromagnetic and ferroelectric substances, and ferromagnetic-ferroelectric layered composite films in particular, since the thickness, composition, connectivity and crystal orientation of the ferromagnetic-ferroelectric layered composite films can be modulated or controlled at the microscopic scale, and their heterostructures can easily be achieved. For ferromagnetic-ferroelectric layered composite films, ferromagnetism, ferroelectricity and ME effect have something do with the film orientation. The oriented/epitaxial films are expected to exhibit better properties compared with the non-oriented counterparts [5,6]. Recently, many oriented (or epitaxial) ferromagnetic-ferroelectric layered films, such as $BaTiO_3/(La,Sr)MnO_3$ [6–8], $Pb(Zr,Ti)O_3/(La,Sr/Ca)MnO_3$ [9–12], $BaTiO_3/(Ni/Co)Fe_2O_4$ [13,14], $Pb(Zr,Ti)O_3/CoFe_2O_4$ [15,16], $Bi_{3.25}Nd_{0.75}Ti_3O_{12}/La_{0.7}Sr_{0.3}MnO_3$ [17] have been reported. However, the oriented (or epitaxial) ferromagnetic-ferroelectric layered films usually must be fabricated onto the expensive $SrTiO_3$, $LaAlO_3$ or MgO single-crystal substrates. However, single-crystal substrates can only provide a small-sized geometry, which is not suitable for the Si technology that requires the low-cost and large-area. Since the Si-based

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technology continues to dominate the microelectronics market, the researchers are digging their way to find a new method to combine Si with ferromagnetic or ferroelectric materials to develop new devices [5]. For this, the buffer layer has been used to mediate the orientation of ferromagnetic or ferroelectric materials. Within buffer layers, $LaNiO_3$ (LNO) is a very attractive candidate since its pseudocubic lattice parameter (of 0.384 nm) matches with most ferromagnetic and ferroelectric perovskites materials [18,19]. Using LNO as a buffer layer, it is beneficial for the crystallization, orientation and consequently the improvement of ferromagnetic or ferroelectric properties [19,20]. Furthermore, LNO can be used as a low-resistive electrode material in the capacitors, improving fatigue properties compared with conventionally-used Pt electrodes [21]. However, little attention has been paid to the fabrication of highly oriented ferromagnetic-ferroelectric layered composite films with LNO buffered Si substrates.

Common techniques to deposit ferromagnetic/ferroelectric films mainly include pulsed laser deposition (PLD) [5–7,9,10,12–17], magnetron sputtering [11] and molecular beam epitaxy (MBE) [22]. However, those methods have several disadvantages such as the high cost and the limited deposition area. The chemical solution deposition (CSD) is an appealing alternative method to prepare functional thin films. It has been extensively adopted to fabricate ferromagnetic/ferroelectric films, due to its low cost, effectiveness to cast onto the large-area substrates, and ease to control the stoichiometry and microstructure of the films [8,19,20,23].

In this work, a (001)-oriented LNO layer was firstly deposited onto the Si substrate, and then used as a template for the growth of the overlying $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) and $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) layers. All layers were prepared by CSD method. The LNO buffer layer could replace the single-crystal substrates and promoted the (001) preferential orientation and the columnar growth of the overlying LSMO and PZT layers. The ferromagnetic and ferroelectric properties of the as-prepared oriented PZT/LSMO/LNO composite film were investigated, and compared with those of a non-oriented counterpart and some epitaxial PZT/LSMO films deposited on single-crystal substrates. Furthermore, the ME effect of the oriented PZT/LSMO/LNO composite film was also discussed. It was demonstrated that our approach was both effective and practical for the fabrication of highly oriented ferromagnetic-ferroelectric layered composite films onto Si substrates.

2. Experimental

(001)-oriented LNO buffer layers were deposited onto the Si (100) substrate referring to a CSD procedure previously reported [24]. The LNO precursor solution with a total metal ionic concentration of 0.4 M was prepared using lanthanum nitrate and nickel acetate as raw materials in a mixed solvent of 2-methoxyethanol and 2-aminoethanol. A dip-coater was used to deposit the film in a drawing rate of 0.5 mm/s. The films were successively dried at 150 °C for 10 min, then heated up to 700 °C in a heating rate of 15 °C/s, and finally annealed for 10 min, by using a rapid thermal annealing furnace. In order to obtain highly conductive films, the dip-coating, drying and annealing processes were repeated for 5 times. The final thickness of the LNO buffer layer was about 154 nm. To further enhance the film conductivity, the LNO film was re-annealed at 700 °C for 1 h in a tube furnace with an oxygen flux of 100 mL/min. The resistivity of the LNO film measured by a four-probe tester was 2.64×10^{-3} Ω cm.

The LSMO layer was also fabricated onto the as-prepared LNO film by a CSD method [25]. The starting reagents for the preparation of the LSMO precursor solution were lanthanum nitrate, strontium acetate, and manganese acetate with a concentration of 0.4 M. Acetyl acetone and methanol were used as the stabilizer and the solvent, respectively. After the dip-coating process, the precursor film was pre-annealed in air at 350 °C for 5 min, and then heated at 750 °C in a conventional box-type resistance furnace for 10 min to remove any organic residuals. The dip-coating, drying, and annealing processes were repeated 5 times to obtain the LSMO/LNO film. The thickness of LSMO layer was about 107 nm. The LSMO perovskite phase was crystallized in air at 750 °C for 30 min.

The PZT layer, with a composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$, was synthesized referring to the procedure described elsewhere [26]. Starting precursor materials were Zirconium n-butoxide, butyl titanate and lead acetate. 2-methoxyethanol and acetyl acetone were respectively used as solvent and stabilizer. A 10% excess of lead acetate was used to compensate for the loss of Pb occurring during the annealing process. The total concentration of metal ions was 0.4 M. The PZT layer was deposited onto the top of the LSMO/LNO film by dip-coating. Subsequently, the film was dried at 200 °C for 15 min, then pre-annealed at 400 °C for 15 min and finally crystallized at 650 °C for 30 min in the conventional box-type resistance furnace in air. For the preparation of the PZT layer, the increase of the thickness at each coating-annealing cycle was about 29.6 nm. After repeating the dip-coating, drying and annealing processes for 5 cycles, the PZT layer reached about 148 nm.

In order to investigate the effect of the orientation on the ferromagnetic and ferroelectric properties of the PZT/LSMO/LNO film, a non-oriented PZT/LSMO/LNO film was prepared using the same approach, but the heat treatment process of the LNO layer. In the preparation of the non-oriented LNO layer, the dip-coated LNO precursor sol film was pre-annealed at 350 °C for 10 min, and finally annealed at 700 °C for 30 min using the conventional box-type resistance furnace in air. The overlying LSMO and PZT layers did not grow with a preferential orientation due to the non-orientation of the LNO buffer layer.

The crystalline structure of LNO, LSMO/LNO and PZT/LSMO/LNO films were characterized by X-ray diffraction (XRD, Shimadzu, XRD-7000, Cu Kα radiation, $\lambda = 1.5406$ Å) with the sampling pitch of 0.02°. The surface morphologies of the films were characterized by field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL). The specimens were prepared by conventional grinding and polishing, and then examined using high resolution transmission electron microscopy (TEM, JEM-3010) with a lattice resolution of 0.14 nm. The magnetic hysteresis loops of the composite films were performed using a vibrating sample magnetometer (VSM) in a physical property measurement system (Versalab, Quantum Design). The plane of the films was fixed to be parallel to the magnetic field. The ferroelectric and leakage behaviors of the PZT layer were characterized using a ferroelectric tester (TF-Analyzer 2000, aixACCT). The ME effect of the composite film was measured by using a ME measuring device (Super-ME, Quantum Design China).

3. Results and discussion

The low-angle XRD analysis was performed in reflection geometry by fixing 1° between incident X-ray beam and film surface, and rotating the detector angle. It was carried out to determine the phase purity and evaluate the structural quality of each layer of the PZT/LSMO/LNO composite film. XRD patterns from LNO, LSMO/LNO and PZT/LSMO/LNO films are shown in Fig. 1. Diffraction peaks from the LNO film are satisfactorily indexed on the base of a cubic cell (according to the JCPDS standards, Card No. 33–0710). Peaks from the LSMO/LNO film are indexed by adding a rhombohedral cell for LSMO (Card No. 50–0308). The PZT/LSMO/LNO pattern is indexed by adding a tetragonal cell for the PZT (Card No. 33–0784). The