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Lead-free BLTO/NMFO magnetoelectric composite films prepared by the sol-gel method

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ABSTRACT

The lead-free ferroelectric films of $Bi_{4-x}La_xTi_3O_{12}$(BLTO) and ferromagnetic films of $Ni_{1-x}Mn_xFe_2O_4$(NMFO) were prepared on $Pt/Ti/SiO_2/Si$ substrate by means of the sol-gel and spin-coating method. The lead-free magnetoelectric composite films with the structure of $Bi_{3.4}La_{0.6}Ti_3O_{12}/Ni_{0.7}Mn_{0.3}Fe_2O_4$/substrate (BN) and $Ni_{0.7}Mn_{0.3}Fe_2O_4/Bi_{3.4}La_{0.6}Ti_3O_{12}$/ substrate (NB) were also deposited on $Pt/Ti/SiO_2/Si$ substrate. The X-ray diffraction results show that two composite films possess BLTO and NMFO phases without any intermediate phase. The SEM images show that two composite films exhibit layered structure, clear interface and no transition layer between BLTO and NMFO films. Two composite films exhibit both good ferromagnetic and ferroelectric properties, as well as magnetoelectric coupling effect. The deposition sequence of ferroelectric and ferromagnetic films in the composite films has significant influence on the ferroelectric, ferromagnetic and magnetoelectric coupling properties of the composite films. The values of magnetoelectric voltage coefficient of the BN composite films are higher than those of the NB composite films at any fixed H_{bias}.

1. Introduction

Generally, the magnetoelectric materials exhibit ferroelectric properties and ferromagnetic properties, as well as magnetoelectric coupling effect, which is a spontaneous electric polarization induced by an external magnetic field [1–3]. Nowadays, the magnetoelectric materials have attracted growing interest due to their potential application in novel multi-functional devices, such as spintronics, transducers, sensors, and four-state logic memories [1,2,4]. However, it is known that single-phase materials, e.g., $BiFeO_3$, possess very poor magnetoelectric coupling effect at room temperature and thus their applications are limited [5–8]. As a consequence, more and more researchers focused on the composite materials to acquire large magnetoelectric effect [5]. Compared with the single-phase materials, the magnetoelectric composite films possess some unique advantages [9]. Firstly, different phases could combine at atom-level in the composite films, which makes it easy to understand the mechanism of magnetoelectric coupling effect at atomic scale. Secondly, the phase composition and connectivity can be controlled at nanometer scale. Nowadays, it is well known that the magnetoelectric coupling effect in composite films arises from coupling between the magnetostrictive effect in ferromagnetic films and piezoelectric effects in ferroelectric films [10]. The magnetoelectric coupling effect is a coupled electrical and magnetic phenomenon via elastic interaction. That is, when a magnetic field is applied to a composite film, strain was generated in the magnetic film due to magnetostriction. The strain is then passed to the ferroelectric film through the interface between the ferromagnetic and ferroelectric phases, resulting in an electric polarization [11]. Thus, the magnetoelectric coupling effect in composite films depends on the ferromagnetic and ferroelectric properties of the composite films and coupling interaction across the interfaces [12]. In order to enhance magnetoelectric coupling effect, ferromagnetic phases with large magnetostrictive effect and ferroelectric phases with large piezoelectric effect were commonly adopted [10]. For instance, predominant ferromagnetic phases in magnetoelectric composite films are referred to as $CoFe_2O_4$(CFO) or $NiFe_2O_4$(NFO) for their high magnetostrictive coefficients. As NFO materials have small magnetic anisotropy in comparison with CFO materials, NFO materials have thus been considered to be the promising ferromagnetic phase in the magnetoelectric composite films. What's more, transition metals, such as Ni and Mn, were doped to prepare $Ni_{1-x}Mn_xFe_2O_4$ (NMFO) with enhanced ferromagnetic properties in the magnetoelectric composite films. On the other hand, it is known that $PbZr_{1-x}Ti_xO_3$ (PZT) materials have been widely used as the main ferroelectric constituent in a magnetoelectric composite film for their excellent piezoelectric properties [13], nevertheless, as a main constituent element in PZT, lead(Pb) have brought about pollution to environment and exert serious damage to human's brain and nervous system [14,15]. Therefore, in view of environmental protection and human health, it is

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rather urgent to develop lead-free ferroelectric based composite films. Recently, what is noticeable is that lead-free ferroelectric $Bi_4Ti_3O_{12}$ (BTO) materials are expected to be used in the next-generation magnetoelectric composite films. As ferroelectric property of BTO materials are poor, La was usually doped to BTO ($Bi_{4-x}La_xTi_3O_{12}$ (BLTO)) to enhance the ferroelectric properties. However, up to date, the relevant researches mostly focused on $Bi_{4-x}La_xTi_3O_{12}$ ceramics and there are rather few researches on preparing $Bi_{4-x}La_xTi_3O_{12}$ films in the magnetoelectric composite system. And few reports on the relationship between the structures and magnetoelectric properties of the composite films are available now. Therefore, we aim to investigate the relationship between the structures and magnetoelectric properties of the composite films by modifying the deposition sequence in the composite films in order to acquire the composite films with enhanced magnetoelectric coupling effect.

Based on the above discussion, the ferroelectric BLTO films and ferromagnetic NMFO films were prepared on $Pt/Ti/SiO_2/Si$ substrate by using the sol-gel and spin-coating method firstly. Then, the layered composite films were prepared by spin-coating the BLTO and NMFO precursor solutions alternately on the $Pt/Ti/SiO_2/Si$ substrate. By changing the deposition sequence of BLTO and NMFO precursor solutions, we obtain the composite films with the structure of BLTO/NMFO/substrate (BN) and NMFO/BLTO/substrate (NB). The impact of deposition sequence on the phase compositions, microstructures and properties of the magnetoelectric composite films was investigated in detail.

2. Experimental

BLTO, NMFO films and BLTO-NMFO composite films were deposited on $Pt(100)/Ti/SiO_2/Si$ substrate via the sol-gel and spin-coating method. For the preparation of the BLTO precursor solution, bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) (5 wt% excess Bi to compensate for the volatilization of Bi), lanthanum nitrate hydrate ($La(NO_3)_3{\cdot}6H_2O$) were dissolved in glacial acetic acid($C_2H_4O_2$) to obtain one solution. Tetrabutyl titanate ($Ti(C_4H_9O)_4$) were dissolved in ethylene glycol monomethyl ether($C_3H_8O_2$) to obtain another solution. Then the above two solutions were mixed while adding acetylacetone ($C_5H_8O_2$) as stabilizer and stirred at 60 °C to obtain a sol precursor solution of BLTO (0.3 mol L^{-1}). The BLTO precursor solution was then spin-coated on the $Pt/Ti/SiO_2/Si$ substrate to form one-layered BLTO precursor films at a spinning rate of 3500 rpm for 30 s. The BLTO precursor films were dried at 120 °C for 10 min to evaporate water and organic solvent, then pre-annealed at 400 °C for 15 min to decompose organic components and annealed at 700 °C for 20 min to obtain BLTO films. Finally, three-layered BLTO films were prepared by repeating the spin-coating, pre-annealing and annealing process twice.

For the preparation of the NMFO precursor solution, nickel acetate ($C_4H_6NiO_4{\cdot}4H_2O$) and manganese acetate ($C_4H_6MnO_4{\cdot}4H_2O$) were dissolved in glacial acetic acid ($C_2H_4O_2$) to obtain the first solution. Ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) were dissolved in ethylene glycol monomethyl ether ($C_3H_8O_2$) to obtain another solution. Then the above solutions were mixed while adding polyvinylpyrrolidone ($(C_6H_9NO)_n$) as stabilizer and stirred at 60 °C to form a sol NMFO precursor solution (0.1 mol L^{-1}). The NMFO precursor solution was then spin-coated on the $Pt/Ti/SiO_2/Si$ substrate to form one-layered NMFO precursor films at a spinning rate of 3500 rpm for 30 s. The NMFO precursor films were dried at 120 °C for 10 min to evaporate water and organic solvent, pre-annealed at 500 °C for 15 min to decompose organic components and annealed at 700 °C for 20 min to obtain pure NMFO films. Finally, two-layered NMFO films were prepared by repeating the spin-coating, pre-annealing and annealing process once.

The layered composite films of BLTO/NMFO were prepared by spin-coating the BLTO and NMFO precursor solutions alternately on the substrate. By changing deposition sequence of precursor films of BLTO and NMFO, we prepared the composite films with two different layered structures: BLTO/NMFO/substrate (BN) and NMFO/BLTO /substrate (NB).

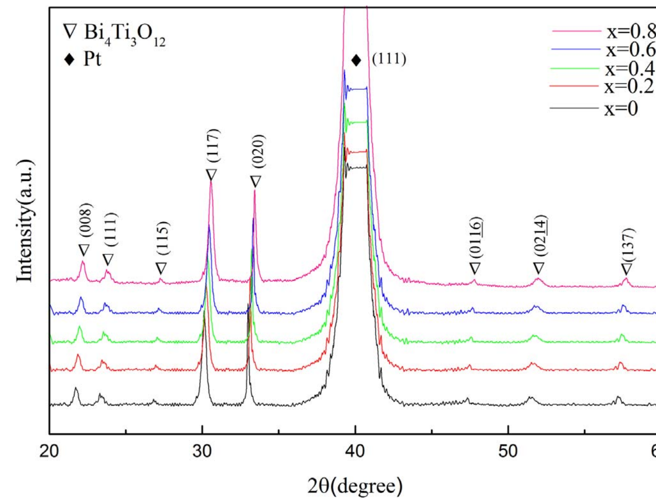

Fig. 1. XRD patterns of the BLTO films under different x, mole fraction of doping La.

The phase compositions of the films were determined by X-ray diffractometer (X′Pert PRO MPD, PANalytical B.V., Holland) with CuKa radiation. The morphology of the surfaces and cross-sections of the films was observed with a field emission scanning electron microscope (SU8020, Hitachi, Japan). The ferromagnetic behavior of the films was detected by a vibration sample magnetometer(S-VSM, Quantum Design, USA). The polarization versus electric field (P-E) hysteresis loops of films were characterized by a ferroelectric test system (Precision LC, Radiant Technologies Inc, USA). Magnetoelectric effect of the composite films was measured via a measuring device designed by superconducting and magnetism laboratory, University of Science and Technology of China. Ag electrodes with a diameter of 150 μm were deposited through a shadow mask on the BLTO and composite films before testing the ferroelectric and magnetoelectric coupling property.

3. Results and discussion

The XRD patterns of $Bi_{4-x}La_xTi_3O_{12}$ (BLTO) films and pure $Bi_4Ti_3O_{12}$ (BTO) films were presented in Fig. 1. It reveals that both the BTO film and BLTO films are evidently polycrystalline structure without any preferred orientation. On the other hand, the XRD peaks from BLTO films are all composed of those from the main phase ($Bi_4Ti_3O_{12}$) and Pt from the substrate, which is in good agreement with pure BTO films. This implies that, for BLTO films, La has dissolved into the lattice of $Bi_4Ti_3O_{12}$.

The ferroelectric polarization-electric field (P-E) hysteresis loops of the BLTO films doped with different mole fraction of doping La were displayed in Fig. 2. The variation of the saturation polarization (Ps) and coercive field (Ec) of the BLTO films with different mole fraction of doping La was shown in the inset of Fig. 2. It is observed that P-E hysteresis loops for the BLTO films and pure BTO film exhibit well-saturated shape. It can be seen that four BLTO films possess greater values of Ps, and smaller values of Ec than those of the pure BTO film ($x = 0$), implying that the doping of La is helpful to improving the ferroelectric properties. From the inset of Fig. 2, it is clear that, with the increase of mole fraction of doping La, the values of Ps of BLTO films increase firstly, reach the maximum (when $x = 0.6$), then decrease. However, with the increase of mole fraction of doping La, the values of Ec of BLTO films decrease firstly, reach the minimum (when $x = 0.6$), then increase. It is clear that, when mole fraction of doping La is 0.6, the BLTO films possess greatest value of Ps and smallest value of Ec, which is corresponding to the best ferroelectric properties. So, in this

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