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Multiferroic and magnetoelectric properties of lead-free $Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O_3$-$Ni_{0.8}Zn_{0.2}Fe_2O_4$ composite films with different deposition sequence

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ABSTRACT

$Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O_3/Ni_{0.8}Zn_{0.2}Fe_2O_4$(BN) and $Ni_{0.8}Zn_{0.2}Fe_2O_4/Ba_{0.8}Sr_{0.2}Ti_{0.9}Zr_{0.1}O_3$ (NB) composite film were deposited on $Pt/Ti/SiO_2/Si$ substrates by the sol-gel method and spin-coating method. The results show that the deposition sequences of the composite films have significant influence on the ferroelectric, ferromagnetic and magnetoelectric properties of the composite films. Two composite films possess not only good ferroelectric and ferromagnetic properties but good magnetoelectric properties as well. The NB composite film has clear interface between the ferroelectric film and ferromagnetic film and possesses greater magnetoelectric coupling effect than the BN composite film under the same H_{bias}. The maximum value of α_E is 70.14 mV cm^{-1} Oe^{-1} was obtained in the NB composite film when H_{bias} is 638 Oe.

1. Introduction

Magnetoelectric materials possess both ferromagnetic properties and ferroelectric properties [1,2]. Coexistence of ferromagnetism and ferroelectricity may result in the magnetoelectric effect [2,3]. Magnetoelectric materials have recently attracted scientific and technological interest because of their potential applications in novel multi-functional devices, such as spintronics, actuators, sensors, multiple state memory elements [4–7]. The magnetoelectric effect is a spontaneous electric polarization induced by an external magnetic field [8–11], which is characterized by magnetoelectric voltage coefficient, $\alpha_E = \delta E/\delta H$ (where E is the induced electric field and H is the applied magnetic field) [12]. Magnetoelectric effect can occur either in single phase materials or composite films in which ferroelectric and ferromagnetic phases are mechanically coupled [13,14]. However, at room temperature, magnetoelectric effect of single phase materials is too weak for practical devices [2,3,8]. Therefore, researchers focus on the magnetoelectric composite films to acquire large magnetoelectric effect. Compared with single phase materials, the composite films have some unique advantages. For example, the composite films have much lower interface loss and higher magnetoelectric coupling effect and the artificial film can thus be achieved to modify the magnetoelectric behavior, such as lattice strain or inter-layer interaction. Furthermore, the magnetoelectric effect can be controlled in nanoscale and enhanced magnetoelectric effect can be obtained [11,15,16].

Generally speaking, the magnetoelectric composite films have three different structures including 0-3, 1-3 or 2-2 type [1,10,17]. It is found that great magnetoelectric effect can be obtained in 0-3 and 1-3 structured films owing to a leakage problem, which results from the low resistance of the ferromagnetic phase in the ferroelectric matrix [17]. In addition, it is not easy to control growth of the composite films with 0-3 or 1-3 type structures [1,8,15]. Noticeably, the leakage currents of magnetoelectric composite films with 2-2 type or layered structures can be reduced significantly by isolating the low resistive ferromagnetic phases with insulating ferroelectric phases [18]. As a consequence, great magnetoelectric effect can be obtained in 2-2 or layered composite films. In addition, it is easy to control growth of composite films with 2-2 type structures [13]. Therefore, the 2-2 type composite films have become potential candidates for magnetoelectric applications [14]. The magnetoelectric composite films with 2-2 type structure are composed of ferromagnetic films and ferroelectric films. Nowadays, it is well known that the magnetoelectric effect in these composite films arises from coupling between the magnetostrictive effect in ferromagnetic films and piezoelectric effect in ferroelectric films [1,2,5,8]. 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 phase, resulting in an electric polarization [5,12]. Thus, the

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magnetoelectric coupling effect in composite films depends on the ferromagnetic and ferroelectric properties of the composite films and coupling interaction across the interfaces between ferreoelectric and ferromagnetic films [8,13,14]. In order to enhance magnetoelectric coupling effect, ferromagnetic phases with large magnetostrictive effect and ferroelectric phases with large piezoelectric effect were commonly adopted [13,14,19]. For instance, predominant ferromagnetic phases in magnetoelectric composite films are $CoFe_2O_4$ or $NiFe_2O_4$(NFO) for their high magnetostrictive coefficient [1]. As $NiFe_2O_4$ possess mall magnetic anisotropy in comparison with $CoFe_2O_4$, $NiFe_2O_4$ has thus been considered to be the promising ferromagnetic phase in the magnetoelectric composite films. What's more, transition metal, such as Zn and Mn, were doped to $NiFe_2O_4$ to improve ferromagnetic properties. Therefore, $Ni_{1-x}Zn_xFe_2O_4$ (NZFO) was used as ferromagnetic phase in this work. In this way, we intend to investigate the impact of doping of Zn^{2+} on the ferroelectricity and determine the optimized doping amount of Zn^{2+}. On the other hand, it is known that $PbZr_{1-x}Ti_xO_3$ (PZT) have been widely used as main ferroelectric phases in the magnetoelectric composite films due to their excellent ferroelectric and piezoelectric properties [8]. However, as Pb as a main constituent element in PZT has brought about environment pollution and serious damage to human's health [8,20,21], it is necessary to investigate lead-free ferroelectric materials to replace PZT. Nevertheless, up to date, lead-free piezoelectric materials generally have inferior piezoelectricity and ferroelectricity compared with PZT. Liu and Ren [18] prepared Ca and Zr doped $BaTiO_3$ (BTO) which exhibits excellent piezoelectric behavior (d_{33} =620 pC/N). Luo et al. [22,23] pointed out that doping of Ca^{2+}, Sr^{2+} or Zr^{4+} to $BaTiO_3$ will improve the piezoelectric properties [17]. Thus, $Ba_{1-X}Sr_XTi_{0.9}Zr_{0.1}O_3$ (BSTZO) was used as ferroelectric phase in this work. We will investigate impact of doping of Sr^{2+} on the ferromagneticity and determine the optimized doping amount of Sr^{2+}. Besides, there has not been systematic investigation on the relationship between the deposition sequence in the composite films and magnetoelectric properties of the composite films. As magnetoelectric properties of the composite films depend not only on the intrinsic properties of ferreoelectric and ferromagnetic films but also on the structures of the composite films which influence coupling interaction across the interfaces between ferreoelectric and ferromagnetic films [21], therefore, it is necessary to investigate the relationship between 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 BSTZO films or NZFO 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 $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $Ba_{1-X}Sr_XTi_{0.9}Zr_{0.1}O_3$ precursor solutions alternately on the substrate. By changing the deposition sequence of two precursor solutions, the composite films with the structure of $Ba_{1-X}Sr_XTi_{0.9}Zr_{0.1}O_3$-$Ni_{0.8}Zn_{0.2}Fe_2O_4$-substrate (BN) and $Ni_{0.8}Zn_{0.2}Fe_2O_4$- $Ba_{1-X}Sr_XTi_{0.9}Zr_{0.1}O_3$-substrate(NB) were prepared. The impact of deposition sequence on the phase compositions, microstructures and properties of the magnetoelectric composite films was investigated in detail.

2. Experimental

In order to prepare the $Ba_{1-X}Sr_XTi_{0.9}Zr_{0.1}O_3$ (x = 0,0.1, 0.2, 0.3) precursor solution, barium acetate and strontium acetate were dissolved in glacial acetic acid and then stirred at 55 °C until complete dissolution to obtain the first solution. The tetrabutyltitanate (Ti$(C_4H_9O)_4$) and tetrabutylzirconate (Zr$(C_4H_9O)_4$) were dissolved in ethylene glycol methyl ether ($C_3H_8O_2$) and stirred at room temperature to obtain the second 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 $Ba_{1-X}Sr_XTi_{0.9}Zr_{0.1}O_3$ (BSTZO). The precursor solution was spin-coated on Pt/Ti/SiO_2/Si substrates at a spinning rate of 3200 rpm for 30 s to obtain one-layered precursor films. The BSTZO precursor films were dried at 120 °C for 10 min, then pre-annealed at 450 °C for 10 min and annealed at 700 °C for 20 min to obtain BSTZO films. Finally, four-layered BSTZO films were prepared by repeating spin-coating, pre-annealing process and annealing process for three times.

In order to prepare $Ni_{1-x}Zn_xFe_2O_4$ (x = 0, 0.1, 0.2, 0.3) precursor solution, nickel acetate and zinc acetate were dissolved in glacial acetic acid and then stirred at 55 °C until the solution was completely dissolved to obtain solution A. The ferric nitrate was dissolved in ethylene glycol methyl ether to obtain solution B. The polyvinylpyrrolidone was dissolved in acetic acid and then stirred at room temperature to obtain solution C. Finally, solution A, B and C were mixed and stirred at 60 °C for 3 h to obtain a sol precursor solution of $Ni_{1-x}Zn_xFe_2O_4$(NZFO). The NZFO precursor solution was spin-coated on Pt/Ti/SiO_2/Si substrates at a spinning rate of 3200 rpm for 30 s. The NZFO precursor films were dried at 120 °C for 10 min, then pre-annealed at 500 °C for 10 min and annealed at 650 °C for 20 min to obtain BSTZO films. Finally, three-layered NZFO films were prepared by repeating spin-coating, pre-annealing process and annealing process two times.

The composite films were prepared by spin-coating $Ba_{1-x}Sr_XTi_{0.9}Zr_{0.1}O_3$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ precursor solution alternately on the substrate. By changing deposition sequence of films of $Ba_{1-x}Sr_XTi_{0.9}Zr0.1O_3$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$, the BN and NB composite films were prepared.

The phase compositions and crystal structures of the films were perform by means of X-ray diffractometer (X'Pert, PRO, MPD, PANalytical, B.V., Holl) with CuKα radiation. The morphologies of surface and cross-section of films were observed by field-emission scanning electron microscopy (FESEM, SU8020, Hitachi, Japan). The ferromagnetic hysteresis loops of the films were studied by vibrating sample magnetometer (S-VSM, Quantum, Design, USA). The ferroelectric behavior of the films was characterized by a ferroelectric test system (Precision, LC, Radiant Technologies Inc, USA). The magnetoelectric effect of the composite films was measured by a measuring device designed by the superconducting magnetic laboratory of University of Science and Technology of China and manufactured by Quantum Design China (test accuracy of voltage, 1μV).

3. Results and discussion

The XRD pattern of single $BaTiO_3$ film and $Ba_{1-X}Sr_XTi_{0.9}Zr_{0.1}O_3$ (BSTZO) films with different x (mole fraction of doping Sr^{2+}) are displayed in Fig. 1. It can be seen that all of the three BSTZO films are composed of the main phase, $BaTiO_3$ and Pt from the substrate without any secondary phase or impurity phase, indicating that Sr^{2+} and Zr^{2+} have dissolved into the lattice of $BaTiO_3$ to form a solid solution. It is

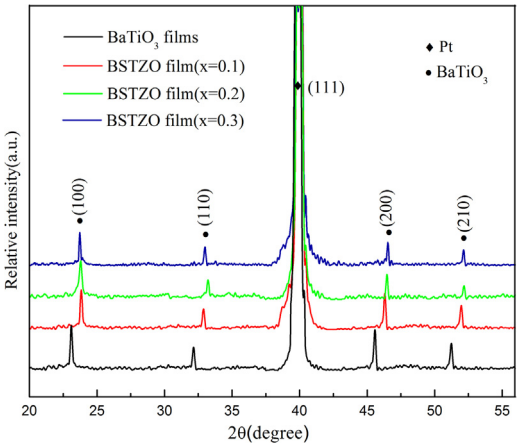

Fig. 1. XRD patterns of $BaTiO_3$ and BSTZO films with different x, mole fraction of doping Sr^{2+} (x = 0.1, 0.2, 0.3).