Role of ferroelectric/ferromagnetic layers on the ferroelectric properties of magnetoelectric composite films derived by chemical solution deposition

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ABSTRACT

Composite thin films with $BiFeO_3$ (BFO), $CoFeO_4$ (CFO) and/or $BaTiO_3$ (BTO) layers as the components are fabricated via CSD method. XRD and Raman patterns show all the composite films can be indexed to perovskite and spinel structures. Except the interfaces between BTO and CFO layers, the other two-phase interfaces can be clearly observed. Interestingly, the BTO-CFO film has bigger polarization than BTO-BFO, especially the thickness of CFO layer is smaller than the BFO layer, implying the ferromagnetic layer has a significant impact on the ferroelectric properties of the composite films, which is too thin to be fully polarized. The variation of leakage currents show BTO-CFO film has the smallest value, corroborating the results of ferroelectric measurements. The leakage current is dominated by the space-charges-limited mechanisms according to the fitting results, and the oxygen vacancies in the BFO layers play an important role for the variations of E_{SCL} and E_{TFL} voltages.

1. Introduction

In recent years, energy and environmental issues are getting more and more attention, and multi-functional materials become the focus of current research [1–4]. Because of the coexistence of two or more ferro-properties (such as ferroelectricity, ferromagnetism, ferroelasticity) in a single structure, multiferroic materials attract now considerable attention. The coupling between magnetic and polarization orders defined as magnetoelectric (ME) effect make it having spacious application foreground [5–8]. Comparing with the single-phase multiferroics, magnetoelectric composites could achieve stronger ME coupling at room temperature, thus, researches on magnetoelectric composites have been the focus of attention for a long time [9,10].

For the magnetoelectric composites, several combinations are most widely studied, such as $BiFeO_3$ (BFO)-$CoFe_2O_4$ (CFO) [11], $BaTiO_3$ (BTO)-CFO [12], PZT-CFO [13], BTO-Ni(Co, Mn)Fe_2O_4 [14] etc. Moreover, pulsed laser deposition (PLD), magnetron sputtering (MS) and chemical solution deposition (CSD) are the most commonly used methods for the composite films preparation [5,10,15–17]. Contribute to the easy to operate for large area films on complex-shaped substrates and strictly control the stoichiometry, CSD method is more conveniently available on the fabrication of 2-2 type magnetoelectric composite films [18,19]. Nevertheless, compared to the PLD/MS-derived films, there are smaller densities and more pores for the CSD-derived films because of the natural characteristics of CSD method.

Thus, a certain thickness is often required for the CSD-derived films to obtain good performances. Tang et al. investigate the thickness effects of BFO films prepared by CSD method systematically and found that 400–600 nm is the optimized thickness range to obtain excellent properties [20]. Song et al. also reported that the thickness should be above 400 nm to obtain good ferroelectric performance for CSD-derived $Bi_6Fe_2Ti_3O_{18}$ thin films [21]. However, except the total thickness, few of the ferroelectric monolayers in composite films could have such a thickness because it is too big to enhance the ME coupling. When the thickness of monolayers cannot reach the values that can be fully polarized, the role of the ferroelectric/ferromagnetic layers on the properties of composite films is not so clear and need to be fully studied. And when the ferroelectric and ferromagnetic layers were stacked with 2-2 type, because of the changes of breakdown voltage caused by the ferromagnetic layers, the ferroelectric polarization of the composite films would be different from the single ferroelectric layers. However, compared to the ME effect, the variations of polarization caused by the ferromagnetic layers in composite films are also not so clear and fewer studies were performed in this respect.

In this paper, BFO, BTO and CFO layers were deposited on Pt/Ti/SiO_2/Si(100) substrates via CSD method with different stacking order. The microstructures, ferroelectric and leakage properties of the composite films were measured. Finally, the effect of ferroelectric/ferromagnetic layers on the ferroelectric properties of the composite films that is too thin to be fully polarized was studied and discussed.

2. Experimental details

The composite thin films studied in this work were fabricated on Pt/Ti/SiO$_2$/Si (100) substrate via CSD method. Corresponding precursor solutions with different concentrations were prepared. To the BTO precursor solution, barium acetate [Ba(CH$_3$COO)$_2$, 99% purity] and titanium butoxide [(C$_4$H$_9$O)$_4$Ti, 98.5% purity] were used as the raw materials. Acetylacetone and acetic acid were used as the solvents with a ratio of 3:2 in volume, and finally, the concentration of BTO precursor solution was 0.4 M. To the BFO and CFO precursor solutions, bismuth nitrate [Bi(NO$_3$)$_3$·5H$_2$O, 99% purity], iron nitrate [Fe(NO$_3$)$_3$·9H$_2$O, 98.5% purity] and cobalt acetate [Co(CH$_3$COO)$_2$·4H$_2$O, 99.5% purity] were used as the raw materials. 2-Methoxyethanol and acetic acid were used as the solvents with a ratio of 3:2 in volume. Specially, in order to compensate the volatilization of Bi during the heating process, 8 mol% excess amount of Bi was added in the BFO precursor solution. The final concentrations of BFO and CFO precursor solutions were 0.4 M and 0.2 M, respectively. To adjust the viscosity and enhance the stability, all solutions were added 0.5 ml ethanolamine.

The BTO solution was firstly spin-coated on substrates with a rotation speed of 6000 rpm for 20 s, and then dried on a hot plate with 100 °C for 3 min. Subsequently, the BTO gel layers were pushed into a 350 °C-preheated tube furnace for 10 min to remove the organic solvent. After 4 times coating/pyrolysis processes, the BTO precursor films were sintered for 30 min in a 700 °C-preheated tube furnace in air. The CFO solution was then deposited on the BTO layers under the same coating, pyrolysis and sintering conditions. Finally, the BFO solution was spin-coated on the CFO layers under the same preparing conditions with BTO and CFO layers except the sintering temperature, which is only 600 °C to avoid the rapid volatilization of Bi ions during the sintering process. At this point, the BTO-CFO-BFO composite film was prepared via CSD method. By the same way, the BTO-CFO, BTO-BFO and CFO-BFO composite films were fabricated, respectively. For the sake of simplicity, the composite films were defined as BT-CF-BF, BT-CF, BT-BF and CF-BF corresponding to the BTO-CFO-BFO, BTO-CFO, BTO-BFO and CFO-BFO composite films, respectively.

The crystal structure of the films was checked by a PANalytical Empyrean diffractometer with CuK$_\alpha$ radiation at room temperature. The surface morphology and thickness of the films were determined by Field emission scanning electron microscopy (FE-SEM; FEI Sirion200 type, FEI, Hillsboro, OR). To detect the polarization performance, top circular Au electrodes with a diameter of 0.2 mm were deposited on the surface of films used ion sputtering and shadow masks. A Sawyer-Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 609B) was used to measure the ferroelectric and leakage properties of the composite films.

3. Results and discussion

The XRD patterns of all the composite films are shown in Fig. 1, and the inset shows the XRD patterns of the single BFO, CFO and BTO films. As can be seen from the Fig. 1, all the peaks of the samples can be indexed to perovskite or spinel structure and no other undesirable phases appear. Due to the relatively weak diffraction intensity, the spinel peaks are not so obvious except the BT-CF sample, which has the uppermost CFO layer and can be detected directly. It is also noticed that the XRD patterns of BT-BF, CF-BF and BT-CF-BF show analogous characteristics, indicating that the different stacking manners are not seriously affect the phase formation of the composite films in this experiment.

Raman spectrum is usually used to characterize the structures and identify the chemical composition of the materials. In order to further confirm the existence of different components, the Raman spectrum of all the composite films are detected and shown in Fig. 2(a). It can be seen that the position and relative intensity of the Raman peaks are different for the films with different composite layers. According to the
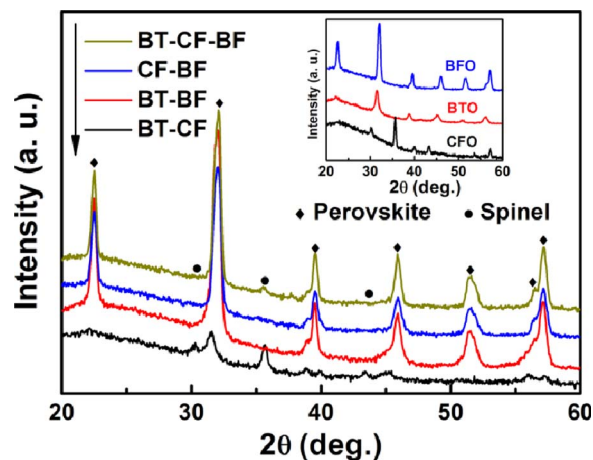

Fig. 1. XRD patterns of all the CSD-derived composite thin films. The inset shows the XRD patterns of single BFO, CFO and BTO films.
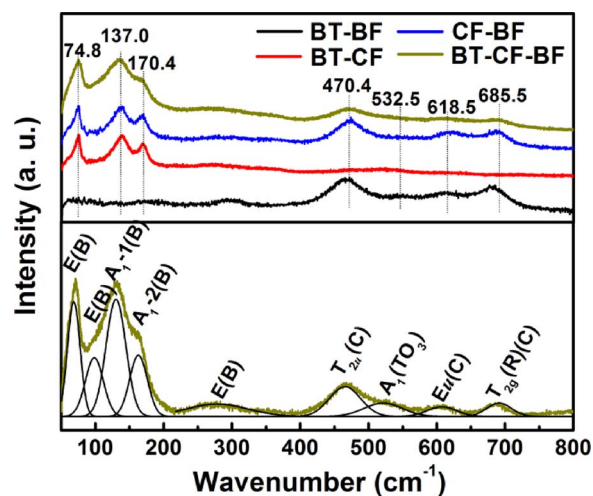

Fig. 2. (a) Raman scattering spectra of all the composite thin films measured at room temperature. (b) The well-fitted Raman spectrum of BT-CF-BF film.

comparison among the different Raman scattering spectras, it is easy to be sure that the Raman peaks below 400 cm^{-1} are the active modes of BFO layer of the composite films, and the Raman active modes of the CFO and BTO layers are all above 400 cm^{-1}. To understand the Raman spectrum more clearly, the Raman spectra of BT-CF-BF film is fitted with different Lorentz components, as shown in the Fig. 2(b). Based on the 13 Raman active phonon modes of BFO predicted by group theory and reported by several previous literatures, the Lorentz components corresponding to BFO layers can be determined as E modes (74.8, 98.2 and 277.9 cm^{-1}) and A$_1$ modes (137.0 and 170.4 cm^{-1}) [22–24]. Similarly, the Lorentz components of CFO can be determined as T$_{2u}$ (470.4 cm^{-1}), E$_u$ (618.5 cm^{-1}) and T$_{2g}$(R) (685.5 cm^{-1}), and BTO is A$_1$(TO$_3$) (532.5 cm^{-1}) [25,26]. The slight difference in relative intensity of several Raman peaks for different composite films may be attributed to the interdiffusion between the different phases during the annealing process, which will lead to some changes in ions bonding and lattice disorder, and finally reflected in the vibrational frequencies of the Raman phonon modes [27].

The cross section FE-SEM images of all the composite films are shown in Fig. 3(a)–(d). It can be detected that the thickness for the BT-CF, BT-BF, CF-BF and BT-CF-BF films are about 370 nm, 450 nm, 310 nm and 550 nm, respectively. The interfaces between the BFO and CFO layers as well as the BFO and BTO layers are clearly visible in the Fig. 3(b)–(d). Regretfully, the interfaces between the BTO and CFO layers are ambiguous as the result reported in our previous study [28].