Characterization of Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/BiFeO$_3$ multilayer thin films prepared by a sol-gel method

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Multiferroic Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/BiFeO$_3$ multilayer thin films were fabricated by the spin-coating method on Pt/Ti/SiO$_2$/p-Si(100) substrates alternately using Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ and BiFeO$_3$ metal alkoxide solutions. The PZT/BFO multilayer thin films show the formation of layers and a change of lattice constant caused by different structure of each other. The coating and heating procedure was repeated several times to form Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/BiFeO$_3$ multilayer films. All films showed the typical XRD patterns of the perovskite polycrystalline structure without the presence of a second phase such as Bi$_2$FeO$_4$. Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/BiFeO$_3$ multilayer films showed a uniform and small grain size rather than pure Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ and BiFeO$_3$ films. We think that the crystal growth of the upper BiFeO$_3$ layers can be influenced by the lower Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ layers and, choosing the initial Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/BiFeO$_3$ layer or a seeding layer has controlled the microstructural behavior of the resultant film. Leakage current density of the Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$/BiFeO$_3$ multilayer film was $5.74 \times 10^{6}$ A/cm$^2$ at 150 kV/cm.

Key words : BiFeO$_3$, Pb(Zr, Ti)O$_3$, Multiferroic, Thin film, Sol-gel method.

Introduction

Thin films of multiferroic materials have attracted a lot of attention primarily due to their potential applications in electronic devices and spintronic devices such as capacitors of dynamic random access memories, piezo micro actuators and pyroelectric infrared detectors [1]. BiFeO$_3$(BFO) is one such material, and is of particular interest in terms of practical applications, because its electrical and magnetic ordering both occur above room temperature (Curie temperature of 850 °C and Neel temperature of 370 °C) [2]. The ferroelectricity of a BFO single crystal has been confirmed at liquid-nitrogen temperature early in 1970 by Reague et al. [3]. But the spontaneous polarization was very small because of the high leakage current in the specimen. The origin of the large leakage current is the presence of a small number of Fe$^{2+}$ ions and oxygen vacancies [4]. In order to solve the leakage current problem, a substitution technique, such as La and Nd atoms for Bi atoms and Mn, Nb, Ti and Cr atoms for Fe atoms [5, 6], has been utilized. And, in recent years, some groups researched magnetoelectric multilayers, which are constructed by a ferroelectric layer and a ferromagnetic or magnetoelectric layer. These multilayer films can provide higher remanent polarization and better leakage current properties than a single BFO thin film. Many researchers have studied the structural and electrical properties of multilayer BFO films with Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT), as a familiar ferroelectric material, especially [7]. Pt/Ti/SiO$_2$/Si multilayer substrates have been frequently used for ferroelectric thin film deposition. A Pt electrode has been used to guarantee excellent chemical stability during the deposition layer. However, during the high annealing temperature process in the fabrication of multilayer films using a plantinized Si substrate, the formation of an unfavorable interfacial layer or the oxidation of the Ti layer were reported [8]. However, there are only a few reports on the syismatic study of these subjects for BFO multilayer films, although it is believed that the structural and electrical properties of multilayer films are greatly affected by the film/substrate or film/film interfacial layer.

In this study, multiferroic PZT/BFO multilayer thin films were fabricated by the sol-gel method, which were spin-coated onto the Pt/Ti/SiO$_2$/Si substrate alternately using BFO and PZT metal alkoxide solutions. We investigated the role of the lower layer in the crystallization of the upper layer and the structural characteristics of the interface in PZT/BFO multilayer thin films.

Experiments

BiFeO$_3$(BFO) and Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$(PZT) solutions were prepared by a sol-gel method. BFO with excess Bi-nitrate 10 mol% precursor solutions were prepared from Bi-nitrate pentahydrate [Bi(NO$_3$)$_3$·5H$_2$O], Fe-nitrate nonahydrate [Fe(NO$_3$)$_3$·9H$_2$O] as starting materials, and acetic acid as solvent. And, PZT with excess Pb-acetate 10 mol% precursor solutions were prepared.

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from Pb-acetate trihydrate \([\text{Pb(CH}_3\text{CO}_2\text{)}_2 \cdot 3\text{H}_2\text{O}]\), Zr n-propoxide \([\text{Zr(OCH}_2\text{CH}_2\text{CH}_3\text{)}_4]\) and Ti iso-propoxide \(\{\text{Ti(OCH(CH}_3\text{)}_2\text{)}_4\}\) as starting materials and 2-methoxyethanol as solvent. The PZT precursor solution was passed through a syringe filter and spin-coated on the Pt(200 nm)/Ti(10 nm)/SiO\(_2\)(100 nm)/p-Si(100) substrates using a spinner operated at 3000 rpm for 20 s to form the first layer. These PZT films were dried at 300 °C for 15 minutes to remove the organic materials, and sintered at 600 °C for 30 minutes to crystallize them into the perovskite structure. And then, the BFO precursor solution was spin-coated and dried on the PZT films under the same conditions, and sintered at 600 °C for 10 minutes to form the second BFO layer. This procedure was repeated several times, and PZT/BFO multilayer thin films were fabricated. The crystalline structure of PZT/BFO multilayer films was analyzed by X-ray diffraction (XRD) with CuK\(_\alpha\) emission. The surface and cross-sectional morphologies of films were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The compositional depth profile was analyzed by secondary ion mass spectroscopy (SIMS). For leakage current measurements, Pt films were DC sputter-deposited on the PZT/BFO films as the top electrode with a diameter of 200 µm. The leakage current properties were measured using a digital electrometer (Keithley 6517A).

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of (a) PZT film, (b) BFO film and (c) PZT/BFO multilayer thin films. All films showed the typical XRD patterns of the perovskite polycrystalline structure, and a second phase such as \(\text{Bi}_2\text{Fe}_4\text{O}_9\) or preferred orientation was not observed. The XRD peaks of pure PZT and BFO films are indexed using a rhombohedral structure. However, the PZT/BFO multilayer film (Fig. 1(c)) showed the (101)/(110), (002)/(200) and (112)/(211) XRD peaks split at diffraction angles of 2θ = 32°, 44° and 56°, respectively. It can be assumed that BFO film grown on a rhombohedral PZT film showed a similar constituent phase to the strain-free powders, suggesting that no chemical reactions occurred between PZT film and BFO film during the sintering of PZT/BFO multilayer films.

Fig. 2 shows the surface SEM micrographs of morphologies of PZT/BFO multilayer films. Many pores were observed in a pure PZT film (Fig. 2(a)) and the average grain size was about 48 nm. And the pure BFO film (Fig. 2(b)) showed a dense grain structure with a grain size of 93.2 nm. However, the PZT/BFO multilayer films showed a smaller grain size than the pure PZT and BFO films, especially, the BFO/PZT/BFO/PZT multilayer film showed a fine and void-free grain structure with an average grain size of about 66 nm. We think that the crystal growth of the upper BFO layers can be influenced by the lower PZT layers, and choosing the initial PZT layer or a seeding layer has controlled the microstructural behavior of the resultant film.

Fig. 3 shows the SIMS depth profile for the element of PZT/BFO/PZT multilayer thin film and substrate. Pb, Zr, Ti, Bi and Fe elements showed a non-uniform
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profile with the depth of the film due to the difference of their compositions. The regions with a higher Pb, Zr and Ti peaks corresponded to the PZT layer. Pb diffusion into the Pt bottom electrode was observed. From these results, we inferred that the mixed phase of the PZT and BFO compositions were formed at each interface of PZT/BFO films and the Pb-deficient interfacial layer was formed at the layer adjacent to the bottom electrode [9]. The SiO_2 layer is incorporated with the diffused Pt and Ti. For a more detailed investigation on the microstructure of a PZT/BFO/PZT multilayer film and interfacial layer, a TEM study was performed. Fig. 4 shows the selected area electron diffraction (SAED) pattern (Fig. 4(a)) and the TEM cross-sectional image (Fig. 4(b)) of the PZT/BFO/PZT multilayer film, respectively. The appearance of the spot-pattern on the diffraction obtained from the PZT layer indicates the perovskite phase. The average thickness of the film after one cycle of drying/sintering was approximately 33-37 nm. PZT/BFO multilayer films showed a uniform and small grain size rather than the pure PZT and BFO films. It can be assumed that the crystal growth of the upper BFO layers can be influenced by the lower PZT layer. Pb diffusion into the Pt bottom electrode was observed. The SiO_2 layer is incorporated with the diffused Pt and Ti. The leakage current densities of a PZT/BFO multilayer films were superior to those of single composition BFO films and those values were less than 7 \times 10^{-6} \text{A/cm}^2 at an applied electric field range of 0-150 kV/cm.

Conclusions

In this study, PZT/BFO multilayer films, which were spin-coated on Pt/Ti/SiO_2/Si substrates, were prepared by the sol-gel method. All films showed the typical XRD patterns of the perovskite polycrystalline structure, and a second phase such as Bi_2FeO_4 or preferred orientation was not observed. The average thickness of the film after one cycle of drying/sintering was approximately 33-37 nm. PZT/BFO multilayer films showed a uniform and small grain size rather than the pure PZT and BFO films. It can be assumed that the crystal growth of the upper BFO layers can be influenced by the lower PZT layer. Pb diffusion into the Pt bottom electrode was observed. The SiO_2 layer is incorporated with the diffused Pt and Ti. The leakage current densities of a PZT/BFO multilayer films were superior to those of single composition BFO films and those values were less than 7 \times 10^{-6} \text{A/cm}^2 at an applied electric field range of 0-150 kV/cm.

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