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Effects of substitution of Ti for Fe in $BiFeO_3$ films prepared by sol–gel process

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Abstract

Ti substituted $BiFe_{1-x}Ti_xO_{3+\delta}$ films have been prepared on indium–tin oxide (ITO)/glass substrates by the sol–gel process. The films with $x = 0.00$–0.20 were prepared at an annealing temperature of 600 °C. X-ray diffraction patterns indicate that all films adopt R3m structure and the films with $x = 0$ and 0.10 show pure perovskite phase. Cross-section scanning shows the thickness of the films is about 300 nm. Through 0.05 Ti substitution, the $2P_r$ increases to 8.30 μC/cm^2 from 2.12 μC/cm^2 of the un-substituted $BiFeO_3$ film and show enhanced ferroelectricity at room temperature. The $2P_r$ values are 2.63 and 0.44 μC/cm^2 for the films with $x = 0.01$ and 0.2, respectively. Moreover, the films with $x = 0.05$ and 0.10 show enhanced dielectric property since the permittivity increases near 150 at the same measuring frequency. Through the substitution of Ti, the leakage conduction is reduced for the films with $x = 0.05$–0.20.

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1. Introduction

In recent years, there has been an increasing interest in a new class of materials in which both electrical and magnetic ordering can coexist. They are called magnetoelectric materials and exhibit coexistence of magnetic and ferroelectric ordering in a certain temperature range. These materials, therefore, have the potential for applications in magnetic as well as ferroelectric devices. Besides, the fundamental physics of magnetoelectric materials is rich and fascinating [1,2]. Unfortunately, a choice for such material is very limited since hardly any material exhibits coexistence of ferroelectric and ferromagnetic properties at room temperature. Bismuth ferrite ($BiFeO_3$) compound, with its perovskite structure, is one of the very few known magnetoelectric systems. It exhibits antiferromagnetic ordering ($T_N = 380$ °C) and ferroelectric behavior with high ferroelectric Curie temperature ($T_C = 830$ °C) [3]. Its X-ray and neutron diffraction study results reveal that $BiFeO_3$ has a rhombohedrally distorted perovskite structure with space group R3c [4].

However, one of the major problems of earlier $BiFeO_3$-based materials is that a low electrical resistivity has prevented practical application of the material as either piezoelectric or magnetoelectric functional components. The main cause is well established to originate from the oxygen vacancies produced by the valence fluctuation of Fe^{3+} to Fe^{2+} [5]. In our previous work, we reported $BiFeO_3$ films deposited in indium–tin oxide (ITO)/glass substrates by sol–gel process. Although clear electric hysteresis loops have been obtained by the improvement of preparation technology, there is no substantial improvement in the large leakage conduction. B site substitution with high valence ions such as Ti^{4+} may be an applicable method to reduce the leakage conduction. Matsui et al. [6] have reported improvement of magnetic and leakage current properties of $BaFeO_3$ film by Zr substitution prepared by pulsed laser deposition method. On the other

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hand, remnant polarization (P_r) is a key criterion for the applications of ferroelectric materials in memory device. In general, it is thought that the $2P_r = 10\,\mu C/cm^2$ is the lower limit for the application in memory device and it is necessary to enhance the ferroelectricity of some weak ferroelectrics. Moreover, larger P_r means more work charge in a storage unit and it makes stored information more intense and readable. Therefore, extensive efforts are focused on the improvement of ferroelectricity. B site substitution with different ions is an effective method to increase the P_r value.

For the above reasons, Ti substituted $BiFe_{1-x}Ti_xO_{3+\delta}$ (BFTO) films were prepared on ITO/glass substrates by sol–gel process in the present work. The films showed enhanced ferroelectricity by substitution of Ti. Furthermore, dielectric property was improved and leakage conduction was also reduced substantially by the substitution.

2. Experimental procedure

The BFTO films were prepared on ITO/glass substrates by sol–gel process, before spin coating the ITO/glass substrates were cleaned by ultrasonication in alcohol and acetone repeatedly. The BFTO precursor solutions were prepared using bismuth nitrate $[Bi(NO_3)_3 \cdot 5H_2O]$ and iron nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ and Ti-isopropoxide $[Ti(C_4H_9O_4)_4]$ as staring materials. Bismuth nitrate and iron nitrate were mixed with a proper molar ratio and dissolved at room temperature in 2-methoxyethanol and stirred for 30 min. Their molar percent ratios of Ti were determined according to the composition formula $BiFe_{1-x}Ti_xO_{3+\delta}$, in which $x = 0.00$ (pure BFO), 0.05, 0.10 and 0.20. The molar ratios of Fe to Ti are 1:0, 95:5, 9:1 and 8:2, respectively. Then Ti-isopropoxide was added under constant stirring. Last, sufficient acetic anhydride was added to dehydrate and ethanolamine was added to adjust the viscosity under constant stirring. The concentration of the stock solutions was adjusted to 0.3 M by adding 2-methoxyethanol. The above processes were performed in an ambient atmosphere at room temperature. The depositions were carried out by spin coating at 6000 rpm for 15 s. The as-deposited wet films were pre-annealed at 350 °C for 3 min and followed by an annealing at 600 °C in air. The spin coating and annealing process were repeated eight times to obtain the desired thickness.

The structure of the films was analyzed by XRD. The XRD patterns were recorded with X-ray diffractometer with Cu Kα radiation. The morphology was analyzed by scanning electron microscopy. For electrical measurements, Pt dots of 0.1 mm^2 were deposited through a mask on the film by sputtering. Before measuring, the films were annealed at 300 °C for 10 min to get full contact with the electrodes. Dielectric property was measured with a HP 4284A LCR meter. Ferroelectricity loops were obtained using a precision workstation.

3. Result and discussion

The crystalline nature of the films was identified by XRD. Fig. 1(a) shows the XRD patterns of the BFTO films on ITO/glass substrates annealed at 600 °C; the pattern of the $BiFeO_3$ ($x = 0\%$) film is identified according to ICCD 20-0169. The film is fully crystallized since high intense peaks are evident and no peaks of impure phases such as $Bi_2Fe_4O_9$ and $Bi_{46}Fe_2O_{72}$ phases are spotted. In addition, a rhombohedral perovskite structure was identified for the films with $x = 0$. With the x increasing to 0.2, the intensity and width of the peaks are decreased and increased, respectively, and it suggested that the film is relatively poorly crystallized. It is easy to see that all films are randomly oriented and the result is similar to our previous work [7]. According to our work, the $BiFeO_3$ annealed at 600 °C adopted random orientation and (1 1 0) preferred orientation is adopted by the film annealed at 500 °C on ITO/glass substrates. We attribute the random orientation

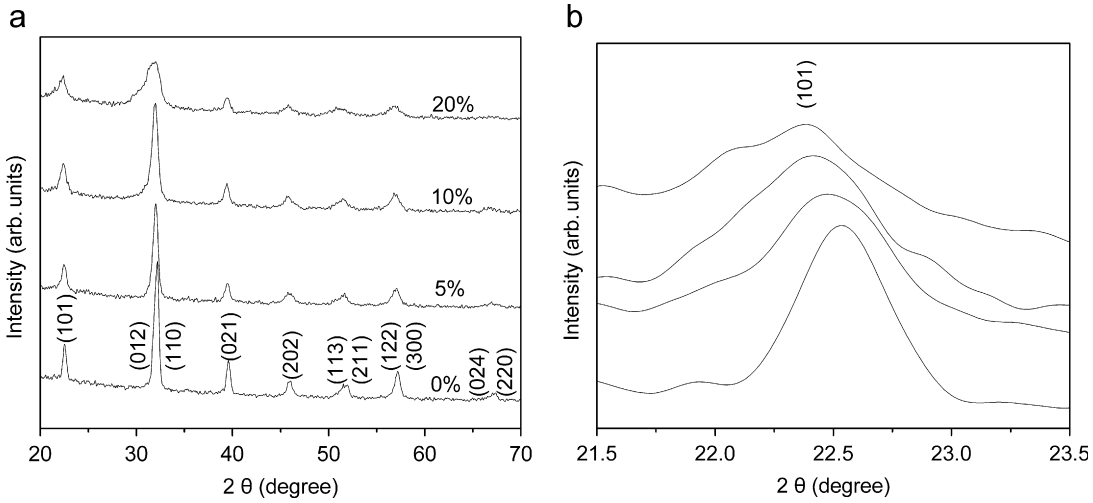

Fig. 1. (a) XRD patterns of BFTO films prepared at 600 °C. (b) Magnified XRD patterns of BFTO films.