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Enhancement of electrical properties of (Gd, V) co-doped $BiFeO_3$ thin films prepared by chemical solution deposition

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Abstract

Pure $BiFeO_3$ (BFO) and $(Bi_{0.9}Gd_{0.1})(Fe_{0.975}V_{0.025})O_{3+\delta}$(BGFVO) thin films were prepared on Pt(111)/Ti/SiO_2/Si(100) substrates by using a chemical solution deposition method. The improved electrical properties were observed in the BGFVO thin film. The leakage current density of the co-doped BGFVO thin film showed two orders lower than that of the pure BFO, 8.1×10^{-5} A/cm^2 at 100 kV/cm. The remnant polarization ($2P_r$) and the coercive electric field ($2E_c$) of the BGFVO thin film were 54 μC/cm^2 and 1148 kV/cm with applied electric field of 1100 kV/cm at a frequency of 1 kHz, respectively. The $2P_r$ values of the BGFVO thin film show the dependence of measurement frequency, and it has been fairly saturated at about 30 kHz.

Keywords: Electrical properties; Ferroelectric properties; Grain size; Perovskites

1. Introduction

$BiFeO_3$ (BFO) is a well-known multiferroic material with a high Curie temperature (T_c) and high Neel temperature (T_N). It has been therefore widely investigated for several applications in multiferroic devices. However, the main problem in BFO, which limits the various applications, is its large leakage current density at room temperature. The reasons of high leakage current density could be explained from the structural defects, the presence of impurity phase and its non-stoichiometric composition due to the high volatility of bismuth [1,2]. Above all, as it has been reported that site engineering is effective in reducing the leakage current, A- and B-sites of the co-doped BFO thin film have been widely investigated recently, in which Bi^{3+} in the A-site was partially substituted by Gd^{3+} or Nd^{3+}, while Fe^{3+} in the B-site was partially substituted by high-valence Mn^{4+}, V^{5+}, or Mo^{6+} simultaneously [3,4]. According to the reports [5–7], A- and B-sites co-doping would lower the leakage current and increase the resistance by eliminating secondary phases and oxygen vacancies, and thus improves the ferroelectric properties of the BFO.

In this paper, we studied the co-doping effects of rare earth (Gd) and transition metal (V) ions in BFO thin film. The pure BFO and $(B_{0.9}Gd_{0.1})(Fe_{0.975}V_{0.025})O_{3+\delta}$(BGFVO) thin films have been deposited on Pt(111)/Ti/SiO_2/Si(100) substrates by using a chemical solution deposition method. The electrical properties of the thin films were investigated by leakage current density measurement and polarization–electric field (*P–E*) hysteresis loops measurements, which were measured at frequencies from 1 kHz to 40 kHz. It has been already known that the ionic radius of Gd^{3+} (1.107 Å) is much small than that of Bi^{3+} (1.45 Å), and V^{5+} for the B-site has higher-valence cations. Therefore, we could expect improved electrical properties due to larger structural distortions.

2. Experiments

The pure BFO and $(B_{0.9}Gd_{0.1})(Fe_{0.975}V_{0.025})O_{3+\delta}$ (BGFVO) thin films were prepared by using chemical solution deposition method. Bismuth nitrate pentahydrate, gadolinium nitrate hexahydrate, iron nitrate nonahydrate and vanadium oxytripropoxide were used as starting

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materials. A mixture of 2-methoxyetahnol (2-MOE) and ethylene glycol was used as a solvent and acetic acid was used as a catalyst. A mixture of 2-MOE and ethylene glycol was stirred at 40 °C in a water bath for 30 min to make a homogeneous solution. For the BGFVO precursor solution, bismuth nitrate pentahydrate (5 mol% excess) was dissolved in the above solution and stirred for 30 min. Gadolinium nitride hexahydrate and iron nitrate nonahydrate were added to the above Bi solution and stirred for 30 min. Seperately, 2-MOE and acetylacetone were mixed at room temperature in a glove box for 30 min. Vanadium oxytripropoxide was dissolved in 2-MOE–acetylacetone and stirred for 1.5 h. The vanadium solution was added to the bismuth–iron–gadolinium solution with continuous stirring for 3 h at room temperature. The concentration of final solution was adjusted to approximately 0.1 M. The BFO precursor solution was prepared in the same way.

The thin films, such as BFO and BGFVO, were prepared on Pt(111)/Ti/SiO_2 substrates with angular speed of 3500 rpm for 25 s by using a spin coating method. After spin coating, the coated films were prebaked at 360 °C for 10 min on a hotplate. The coating and the prebaking were repeated 12 times to obtain the desired thickness. Finally, the thin films were annealed at 550 °C for 30 min by using a conventional annealing process under a nitrogen atmosphere for crystallization.

The crystal structures of the thin films, which are the electronic structure and the surface morphology, were investigated by using an X-ray diffractometer (Rigaku, MiniFlex II) and a scanning electron microscope (Tescan, MIRA II LMH). Gold electrodes with area of 1.54×10^{-4} cm^2 were deposited on the top surfaces of the thin films by using a metal shadow mask to form a capacitor structure. Ferroelectric hysteresis loops and leakage current densities were measured by using a standardized ferroelectric test system (Modified sawyer-tower circuit with oscilloscope) and an electrometer (Keithley, 6517A).

3. Results and discussion

Fig. 1(a) shows X-ray diffraction (XRD) patterns of the BFO and co-doped BGFVO thin films measured with Cu Kα_1 radiation. The major peaks of the thin films are $BiFeO_3$ phase with the polycrystalline distorted rhombohedral perovskite structure with *R3c* space group and no secondary phases were observed in the thin films [1,2]. Fig. 1(b) and (c) show the magnified XRD peaks in the vicinities of 2θ values of 22.5° and 32°. As shown in Fig. 1(c), the (110)/(1$\underline{1}$0) diffraction peaks in the BGFVO thin film shift to the higher angle. The shift is resulting from the relatively small ionic radius of the Gd^{3+} (1.107 Å) ion compared to that of Bi^{3+} (1.45 Å) ion [8]. No significant lattice distortion was observed by the V doping.

Fig. 2 shows the surface morphologies of the BFO and co-doped BGFVO thin films. The co-doped BGFVO thin film shows relatively dense structure and improved uniformity of grain size and slightly increased grain size compared to the pure BFO thin film. The grain size of the co-doped BGFVO thin film is about 130–180 nm, while that of the BFO thin film is about 60–100 nm. The thicknesses of the BFO and co-doped BGFVO thin films are about 300 nm and 400 nm, respectively. In general, it is well known that there are more defects in grain boundaries, therefore the increase of grain size could reduce defects at the grain boundaries, which may improve the ferroelectric properties [9]. Therefore, on the basis of the improved surface morphology and the increase of grain size for the co-doped BGFVO thin film, better ferroelectric properties can be expected compared to the pure BFO thin film.

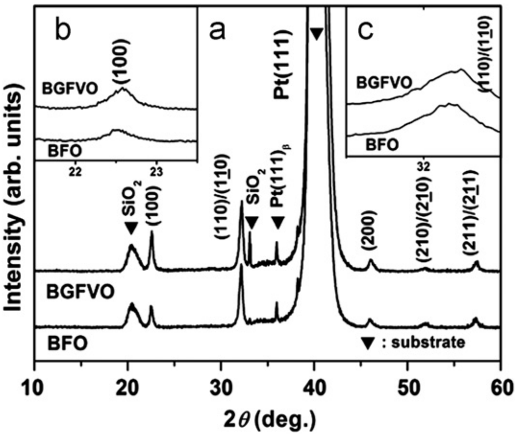

Fig. 1. (a) X-ray diffraction (XRD) patterns of the BFO and BGFVO thin films deposited on Pt(111)/Ti/SiO_2/Si(100) substrates. (b)Magnified XRD patterns in the vicinity of $2\theta = 22.5°$ corresponding to (100) plane. (c)Magnified XRD patterns in the vicinity of $2\theta = 32°$ corresponding to (100)/$(1\,\overline{1}\,0)$ planes.

As shown in Fig. 3, the leakage current densities (*J*) with applied electric field (*E*) for the BFO and co-doped BGFVO thin films were measured at room temperature. The leakage current density of the co-doped BGFVO thin film shows much lower than that of the BFO thin film. For the BFO thin film, the leakage current density was 2.58×10^{-3} A/cm^2 at an applied electric field of 100 kV/cm. The BGFVO thin film showed a lower leakage current density, which is 8.1×10^{-5} A/cm^2 at an applied electric field of 100 kV/cm. It is about two orders lower than that of the BFO thin film.

The substitution of Gd^{3+} ion for Bi site could effectively reduce the formation of oxygen vacancies by Bi volatility [10,11]. Since the bond-energy of Gd–O (716 ± 17 kJ/mol) is about two times larger than that of Bi–O (343 ± 6 kJ/mol), Gd–O bonds could not be easily broken compared to Bi–O. And the formation of defect complexes in the co-doped BGFVO thin film could lead to the improvement in the ferroelectric properties of the co-doped BGFVO thin film [3,5–7].

As high-valence V^{5+} ions were introduced as donor ions, it can be express as [12]

$$V_2O_5 \leftrightarrow 2V_{Fe}^{\bullet\bullet} + 5O_o + 4e$$

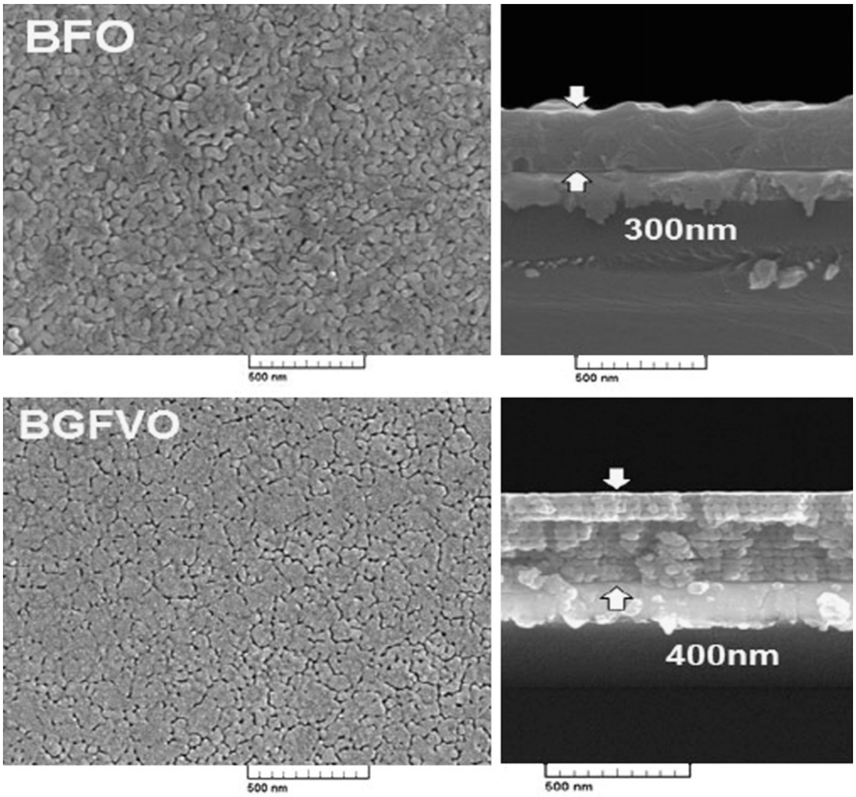

Fig. 2. FE-SEM morphologies of the BFO and BGFVO thin films with cross-sectional micrographs.

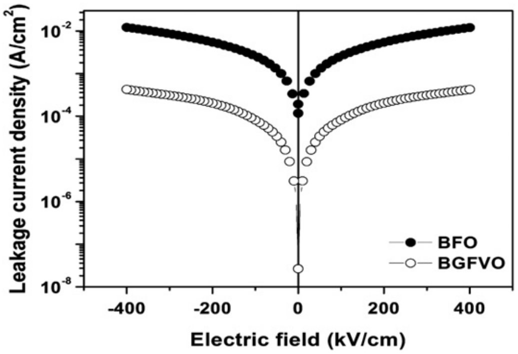

Fig. 3. Leakage current densities of the BFO and BGFVO thin films measured at room temperature.

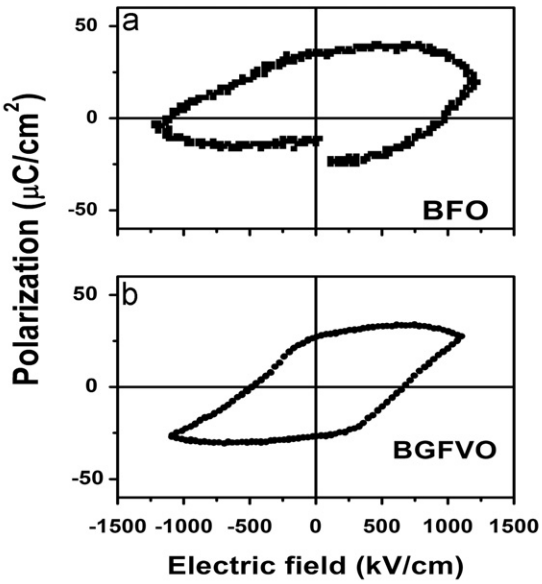

Fig. 4. *P–E* hysteresis loops of the (a) BFO and (b) BGFVO thin films measured at 1 kHz.

$$1/2O_2 + V_o^{\bullet\bullet} + 2e \leftrightarrow O_o$$

where $2V_{Fe}^{\bullet\bullet}$ is V ion with +2 effective charge at the core site of an oxygen octahedron, $V_o^{\bullet\bullet}$ is oxygen vacancies with 2+ effective charge, O_o is oxygen ion in the lattice, and 2e formed for the charge compensation.

Fig. 4 shows the polarization–electric field (*P–E*) hysteresis loops for the BFO and co-doped BGFVO thin films. The loops were measured with a maximum electric field of 1100 kV/cm at frequency of 1 kHz. The BFO thin film in Fig. 4(a) shows a leaky hysteresis loop, while the co-doped BGFVO thin film shows relatively improved hysteresis loop. The remnant polarization ($2P_r$) and the coercive electric field ($2E_c$) of the co-doped BGFVO thin film were 54 μC/cm^2 and 1148 kV/cm at applied electric field of 1100 kV/cm, respectively. The improved ferroelectric properties of the co-doped BGFVO thin film are mainly ascribed to the suppression of oxygen vacancies and improved microstructure by Gd and V co-doping [5–7]. The lattice distortion might be one of the reasons for the large ferroelectric polarization of the sample.

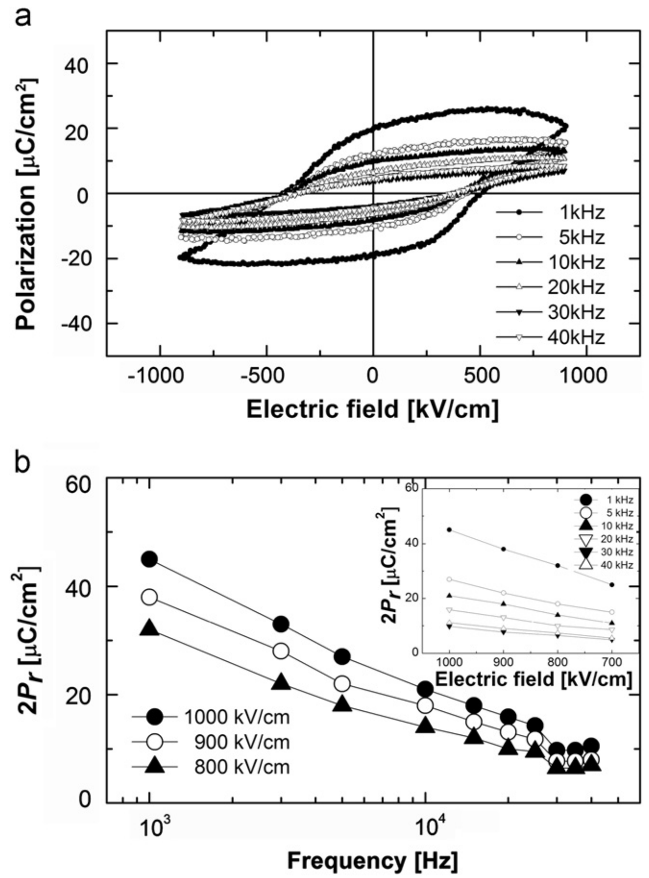

Fig. 5. (a) *P–E* hysteresis loops with measurement frequency from 1 kHz to 40 kHz at 900 kV/cm. (b) The values of the $2P_r$ of the BGFVO thin film measured with measurement from 1 kHz to 40 kHz at 800, 900 and 1000 kV/cm. Inset shows the $2P_r$ with applied electric field from 1 kHz to 40 kHz.

Fig. 5(a) shows the dependence of *P–E* hysteresis loops on frequencies at a maximum electric field of 900 kV/cm. The decrease in the polarization is clearer in the low frequency region, but it is not clear in the high frequency region. Fig. 5(b) shows the dependence of the $2P_r$ value of the BGFVO thin film as a function of frequency at applied electric fields of 800 kV/cm, 900 kV/cm and 1000 kV/cm. In the low frequency range from 1 to 25 kHz, the $2P_r$ value rapidly decreased due to the reduction of leakage current density [11,13]. However, it did not largely decrease above 30 kHz. In the low frequency range, the $2P_r$ value was largely increased with increasing applied electric field from 800 kV/cm to 1000 kV/cm. The inset in Fig. 5 shows the dependence of the $2P_r$ value as a function of the applied electric field with frequency. The $2P_r$ rapidly decreased in the low frequency region with larger electric field.

4. Conclusions

We investigated the effects of Gd and V co-doping in BFO thin film by comparing with the pure BFO thin film for the first time. The co-doped BGFVO thin film exhibited improved electrical properties, which are lower leakage current density and increased remnant polarization value. These results could be explained by the polycrystalline distorted rhombohedral perovskite structure, the dense structure and the improved uniformity of grain size and the effective reduction of oxygen vacancies with doping effect of Gd and V. In addition, we could confirm that the remnant polarizations ($2P_r$) were fairly saturated about above frequency of 30 kHz for the co-doped BGFVO thin film by the reduction of leakage current density. We expect saturation frequencies could be changeable with doping types. In future, we plan to confirm saturation frequencies with several doping types. On the basis of the above results, we can conclude that the (Gd, V) co-doped BGFVO thin film can be a good candidate for new devices and applications.

Acknowledgments

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