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Photovoltaic enhancement based on improvement of ferroelectric property and band gap in Ti-doped bismuth ferrite thin films

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ABSTRACT

Ti-doped bismuth ferrite thin films were prepared via sol–gel spin-coating method. The effects of titanium on the microstructure, optical, leakage, ferroelectric and photovoltaic characteristics have been investigated systematically. The result shows that bismuth ferrite thin films doped with 0–8 at.% Ti are rhombohedral distortion perovskite structure. The addition of titanium inhibits the grain growth and enhances the thickness uniformity and can decrease the band gap of bismuth ferrite thin films. The leakage current of bismuth ferrite thin films is effectively reduced by adding a certain amount of titanium and the leakage mechanism has been investigated. Addition of titanium increases the remnant polarization of the films. As titanium content increases, the short circuit photocurrent density decrease first and then increase, while the open circuit photovoltage increase first and then decrease. The power conversion efficiency of Ti-doped bismuth ferrite thin films increases as titanium content increases, which can be explained as a result of the increased remnant polarization and decreased band gap.

1. Introduction

The ferroelectric photovoltaic effect (FE-PV) was discovered about half a century ago in variety of ferroelectric materials with non-centrosymmetry. It is generally thought that the ferroelectric photovoltaic effect originates from the electric polarization or ferroelectric domain wall in ferroelectric materials [1–3]. Ferroelectric photovoltaic effect has two unique characteristics: (1) the anomalous photovoltaic (APV) effect, i.e. the output open circuit photovoltage (V_{OC}) can be several orders of magnitude larger than the band gap of ferroelectric materials [2,4], (2) the photocurrent direction can be switched by changing the polarization of ferroelectric materials with the electric field [4,5]. To date, the photovoltaic effect in the $LiNbO_3$ [6], $BaTiO_3$ [7], $Pb(Zr,Ti)O_3$ [8], $(Pb,La)(Zr,Ti)O_3$ [4], $(K,Na)(Nb)O_3$ [9] and $(Bi_{3.7}Nd_{0.3})Ti_3O_{12}$ [10] has been widely investigated, but these wide band gap ferroelectric materials ($E_g > 3$ eV) cannot absorb visible light effectively so that the intrinsic photovoltaic characteristics of ferroelectrics are unsatisfactory. Although recently discovered novel ferroelectric materials with narrow band gap such as $KBiFe_2O_5$ (E_g is about 1.6 eV) [11] and $[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$ (E_g can be adjusted to 1.1 eV by changing its composition) [12] can effectively absorb visible light, the polarization of these materials is too low. Bismuth ferrite ($BiFeO_3$, short for BFO) is the only single phase multiferroic materials that simultaneously show magnetic (antiferromagnetic) and ferroelectric properties at room temperature. Because of its large polarization ($P_S \sim 90\ \mu C/cm^2$) and magnetoelectric coupling effect, BFO is widely studied over the last few years [13,14]. In recent years, the photovoltaic characteristics of BFO have gained widely attention because of its narrow band gap (2.3–2.7 eV) and large polarization [15–22]. But these practical applications for BFO have been restricted because of its large leakage current as a result of difficulty in fabricating single phase BFO and oxygen vacancy originating from reduction of Fe^{3+} ions and volatilization of Bi. To stabilize the perovskite phase and enhance the electric properties of BFO, a wide variety of dopants (such as La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Pr^{3+}, Dy^{3+}, Ba^{2+}, Co^{3+}, and Ce^{3+} [23–26]) have been applied. Among them, Ti^{4+} is an important dopant to improve the electric properties of BFO [27–31]. Wang and Nan [27] and Juan and Liu [30] found that the leakage current of BFO thin films can be improved effectively by adding Ti. Liu et al. found that addition of Ti^{4+} can increase the remnant polarization and decrease the coercive field of BFO thin films [31]. The improved ferroelectric properties caused by addition of Ti^{4+} may result in the enhancement of photovoltaic characteristics for BFO materials. But the effects of Ti^{4+} on photovoltaic properties of BFO thin films have not been studied. Therefore, we prepared

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Ti-doped BFO thin films by sol–gel spin-coating method and studied systematically the effects of Ti^{4+} content on microstructure, optical, ferroelectric and photovoltaic properties of BFO thin films.

2. Experimental

Ti-doped BFO thin films were prepared by sol–gel spin-coating method. Bismuth nitrate ($[Bi(NO_3)_3 \cdot 5H_2O]$, ⩾99.0%, Sinopharm Group Co., Ltd.), iron nitrate ($[Fe(NO_3)_3 \cdot 9H_2O]$, ⩾99.0%, Sinopharm Group Co., Ltd.) and tetrabutyl titanate ($[C_{16}H_{36}O_4Ti]$, ⩾99.0%, Aladdin Reagent) were used as raw materials. Acetic acid (CH_3COOH, short for HAc, ⩾99.0%, Sinopharm Group Co., Ltd.) and 2-Ethoxyethanol ($C_2H_5OCH_2CH_2OH$, ⩾99.0%, Sinopharm Group Co., Ltd.) were used as solvent. Firstly, $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in the mixed solvent of 2-Ethoxyethanol and HAc (the volume ratio of 2-Ethoxyethanol to HAc was 4:1) to form Fe precursor solution. The solution was continuously stirred at 60 °C for 30 min to make sure $Fe(NO_3)_3 \cdot 9H_2O$ could been dissolved completely. In the similar way, Bi precursor solution was prepared. Secondly, tetrabutyl titanate was dissolved in acetic acid to form Ti precursor solution. And the concentration of Ti precursor solution was adjusted to be 1 mol/L by adding 2-Ethoxyethanol. Thirdly, Fe precursor solution was added to Bi precursor solution in a molar ration of Fe: Bi = 1:1.05 (5 at.% excess Bi) and stirred constantly for 30 min at 25 ºC to form the mixture. Then, Ti precursor solution (mole ratio of Fe: Ti is 1:0, 1:0.02, 1:0.04 and 1:0.08, respectively) was added to the above-mentioned mixture. The pH value of the precursor solution is adjusted to be about 3 by adding ethanolamine ($[HOCH_2CH_2NH_2]$, ⩾99.0%, Chengdu Kelong Chemical Reagent Factory). Then acetylacetone ($[CH_3COCH_2COCH_3]$, ⩾99.0%, Sinopharm Group Co., Ltd.) was added to control the hydrolysis rate. Finally, the concentration of the precursor solution was adjusted to 0.3 mol/L by adding a certain amount of 2-Ethoxyethanol. The obtained precursor solution was transparent and homogeneous. After aging the precursor solution for 24 h at room temperature, thin films were deposited on Pt (100 nm)/Ti (30 nm)/SiO_2 (500 nm)/Si (500 μm) substrate by spin-coating method. Then, the thin films were annealed at 600 °C for 10 min in oxygen atmosphere.

The crystal structure was identified by X-ray diffraction (DX-2700 model, Dandong Fangyuan, China, Cu target with a working voltage of 30 kV and a current of 20 mA) in a scanning rate of 3°/min. The surface morphology of the films was observed by atomic force microscopy (AFM, NTEGRA Prima, NT-MDT, Russia). The thickness of Ti-doped BFO thin films is about 250 nm determined by step profiler (Dekatk 150, Veeco, USA). The optical transmission characteristics of the films were measured using a double beam ultraviolet–visible (UV–vis) spectrophotometer (TU1810, Persee, China) in the wavelength range of 200–1100 nm. To measure the electric properties and photovoltaic characteristic, translucent Au top electrodes with a diameter of 200 μm and a thickness of 50 nm were deposited on the thin films using DC magnetron sputtering (JGP280, SKY, China). The ferroelectric property and leakage current were determined by ferroelectric test system (TF2000e, aixACCT, Germany). The current–voltage (*I*–*V*) curves were characterized by a current source meter (2400, Keithley, USA) when the thin films were illuminated with the solar simulator (Newport, Oriel instrument, USA).

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the XRD patterns of BFO thin films with different titanium contents. Firstly, it is observed that the main diffraction peaks in BFO thin films doped with 0–8 at.% Ti are indexed as a rhombohedral distortion perovskite structure ($BiFeO_3$, *R3m* space group, JCPDS card no. 74-2016). There is no secondary phase observed in all the samples. It indicates that Ti^{4+} ions have entirely entered into BFO lattice. Secondly, the diffraction peaks of the thin films shift to the lower angle region with the increase of titanium content, which indicates that the interplanar distance increases according to Bragg equation. The calculated lattice parameters of Ti-doped BFO thin films are shown in Table 1. It is seen that the lattice constant (a, b, c) of the thin films increases as titanium content increases. It is because that Ti^{4+} ions with larger ionic radius (0.068 nm) substitutes for Fe^{3+} ions with relative smaller ionic radius (0.064 nm) on B sites, which leads to the lattice expansion. Moreover, the axis angle (α, β, γ) of the samples decreases with the increase of titanium content. Thirdly, the average grain size of the films can be calculated according to the full width at half maximum (*FWHM*) data in XRD patterns by the Scherrer formula:

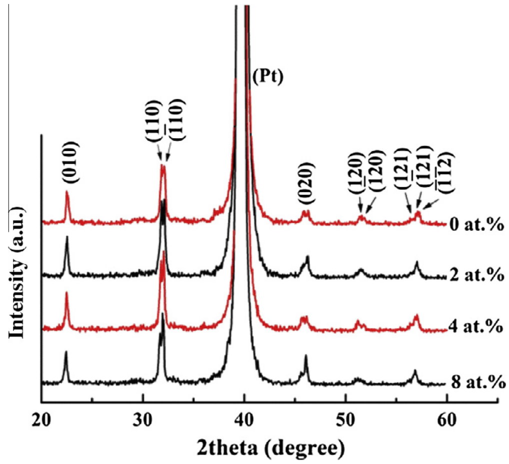

Fig. 1. XRD patterns of BFO thin films with different titanium contents.

$$D = \frac{K\lambda}{\beta COS\,\theta} \tag{1}$$

where D is the grain size (nm), K is the shape factor (0.89), λ is the wavelength of the X-rays ($\lambda = 0.15406$ nm for Cu Kα radiation), β is the width of the diffraction peak at half maximum for the diffraction angle 2θ. According to Eq. (1), the calculated average grain size of BFO thin films doped with 0, 2, 4, 8 at.% Ti is 48 nm, 35 nm, 30 nm and 26 nm, respectively. It indicates that the addition of titanium can inhibit the grain growth.

Fig. 2 shows the AFM images of BFO thin films with different titanium contents. Firstly, it is found that the pure and Ti-doped BFO thin films are crack-free and dense. Secondly, the average grain size of BFO thin films with 0 at.%, 2 at.%, 4 at.% and 8 at.% Ti is 100 nm, 90 nm, 68 nm and 50 nm, respectively. It indicates that the addition of titanium can inhibit the grain growth of BFO thin films. The result is similar with the above calculated results according to the Scherrer formula. There are two primary reasons for the grain-refining effect of Ti^{4+} on BFO thin films. On the one hand, Ti^{4+} ions dissolve into BFO lattice to substitute for Fe^{3+} ions on the B sites and lead to lattice distortion. Lattice distortion shall consume some energy, but if appearance of solute segregation will not consume the energy, therefore, Ti^{4+} ions are prone to segregate on the grain boundary. Ti^{4+} ions located in the grain boundary can hinder motion of the grain boundary and accordingly inhibit the grain growth of BFO thin films. But the second phase related to titanium has not been observed in XRD patterns and it is probably because that the amount of second phase related to titanium is too low to be detected by XRD. On the other hand, oxygen vacancies appear because of variable valence of $Fe^{3+} \rightarrow Fe^{2+}$ or volatilization of Bi^{3+} in the fabrication process of BFO thin films. The grain growth is affected by grain boundary mobility which is affected by oxygen vacancy concentration. The grain boundary mobility decreases as the concentration of oxygen vacancy decreases [32]. Ti^{4+} ions substitute for Fe^{3+} ions on B sites and lead to the suppression of oxygen vacancies, which results in the decrease of grain boundary mobility. Therefore, addition of titanium inhibits the grain growth of BFO thin films. Moreover, the root mean square roughness (RMS)

Table 1
Lattice parameters of Ti-doped BFO thin films.

Titanium content (at.%)	Lattice parameters	
	$a = b = c$ (nm)	$\alpha = \beta = \gamma$ (°)
0	0.3952	89.678
2	0.3954	89.653
4	0.3955	89.621
8	0.3959	89.583