Rare Metal Materials and Engineering
Volume 45, Issue 6, June 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(6): 1449-1454.

ARTICLE

Effect of Different Annealing Atmosphere on Ferroelectric Properties of 0.7BiFeO3-0.3PbTiO3 Thin Films

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Abstract: 0.7BiFeO$_3$-0.3PbTiO$_3$ (BFPT7030) thin films were deposited on LaNiO$_3$/SiO$_2$/Si substrate by sol-gel process. The thin films were annealed in air, O$_2$ flow, air flow and N$_2$ flow in air environment by a rapid thermal annealing technique. Films annealed in air, O$_2$ flow and air flow were fully crystallized and showed highly (100) preferred orientation. BFPT7030 thin film annealed in N$_2$ flow could not obtain hysteresis loops because of the bad crystallization. The BFPT7030 thin films annealed in air showed the largest P_r of 30 μC·cm^{-2} and the lowest leakage current density, while the film annealed in air flow showed the lowest P_r of 13 μC·cm^{-2} and the largest leakage current. XPS results demonstrate that the Fe^{3+}:Fe^{2+} is 2.09:1, 1.65:1 and 1.5:1 for films annealed in air, O$_2$ flow and air flow, respectively, and the Bi and Pb relative content in the films annealed in O$_2$ flow and air flow is less than that of the film annealed in air. Fluctuation of Fe ions valence state and the volatilization of Bi are the main reasons for the generation of oxygen vacancies. Adding O$_2$ gas is helpful to prevent the generation of oxygen vacancies. Although volatilization of Pb would lead to inferior microstructure, no oxygen vacancies is generated during the process of volatilization of Pb.

Key words: annealing atmosphere; BiFeO$_3$-PbTiO$_3$; ferroelectric; sol-gel

BiFeO$_3$ has attracted much attention from perspectives of both fundamental physics and practical applications[1-4] because of its unique ferroelectric and antiferromagnetic ordering at room temperature[5-7]. BiFeO$_3$ has a very high Curie temperature of about 1100 K[8], which indicates that it possesses a high spontaneous polarization. Moreover, the first-principle study of spontaneous polarization in BiFeO$_3$ suggests that it has a large ferroelectric polarization of 90～100 μC·cm^{-2} [9]. However, both past and contemporary measurements showed much less polarization than predicated, especially in bulk form[10-14]. BiFeO$_3$ has a distorted perovskite structure which makes it unstable. To overcome this obstacle, the BiFeO$_3$-ABO$_3$ solid solution systems have attracted great attention as a solution for improved structural stability[15-17]. Among those perovskite ABO$_3$ compounds, PbTiO$_3$ is a stable ferroelectric perovskite oxide[18]. A (1-x)BiFeO$_3$-xPbTiO$_3$(BFPT100x) system is expected not only to provide the desired structural stabilization, but also exhibits a morphotropic phase boundary (MPB). According to the previous studies, the MPB of the BFPT100x system is located around the x≈0.3 composition, in which the tetragonal (T) and rhombohedral (R) phases coexist[19-22]. Although BFPT system showed relatively better structural properties. its ferroelectric polarization still exhibit not much high properties, Liu et al reported a remnant polarization (P_r) of 2.0 μC·cm^{-2} for BFPT100x (x=0.3) films prepared by a sol-gel method[23]. Sakamoto et al synthesized BFPT100x thin films by chemical deposition which showed a high ferroelectric polarization of 60 μC·cm^{-2}, but it was measured at –190 ºC[24]. Saturated P-E loops were not observed at room temperature due to the large leakage current in the high

Received date: June 24, 2015
Foundation item: Academic Level Pass of Southwest Petroleum University (201131010051); Set Sail Project of Southwest Petroleum University (2014QHZ022); Important Program of Education Department of Sichuan Province (14ZA0046)
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electric field.

BFPT-based thin films suffered from large leakage which is believed to result from oxygen vacancies arising from the hopping electrons from Fe^{3+} to Fe^{2+}. Oxygen vacancies act as a bridge between the Fe^{3+} to Fe^{2+} and leads to electron conduction[25]. And the volatilization of Pb and Bi, which leads to non-stoichiometry, would also increase the density of oxygen vacancies and increase the electron conduction. Since the leakage current of BFPT100x system mainly comes from oxygen vacancies and results in poor ferroelectric properties, this arouse our interest to assess the effect of annealing atmosphere (air, O_2 and N_2) on the ferroelectric properties. In the present paper, four $0.7BiFeO_3$-$0.3PbTiO_3$ (BFPT7030) thin films were deposited on $LaNiO_3/SiO_2/Si$ substrates via a sol-gel process by a rapid thermal technique (RTA). The as-deposited BFPT7030 thin films were annealed in air, O_2 flow, air flow and N_2 flow in the air environment. The microstructure and electric properties of these films were investigated The result analysis can be used as reference for preparing high quality BFPT100x thin films.

1 Experiment

BFPT7030 thin films were prepared on $LaNiO_3/SiO_2/Si$ substrates by a sol-gel process. The raw materials were bismuth nitrate pentahydrate [$Bi(NO_3)_3 \cdot 5H_2O$], iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$], lead acetate [$Pb(CH_3COO)_2 \cdot 3H_2O$], and tetrabutyl titanate [$Ti(OC_4H_9)_4$].

Bismuth nitrate and iron nitrate were mixed with a mole ratio of 1:1 and incompletely dissolved in a small amount of acetic anhydride and acetic acid, then ethylene glycol was added, and stirred at room temperature for 3 h until bismuth nitrate and iron nitrate were completely dissolved. This solution was named solution A. Tetrabutyl titanate (stabilized by acetyl acetonate) was dissolved in ethylene glycol, stirred at 45 ºC for 50 min; at the same time, lead acetate was dissolved at room temperature in ethylene glycol, stirred for 20 min and then added with diethanolanine, stirred for 30 min; then mixed tetrabutyl titanate solution and lead acetate solution, and stirred at 45 ºC for 3 h. This solution was named solution B, lead acetate and tetrabutyl titanate were mixed with a mole ratio of 1:1. Finally solution B was mixed with solution A, and stirred at 45 ºC for 16 h to form BFPT7030 sol. Diethanol amine was added to the final sol to increase the viscosity. The final concentration of lead acetate was 0.3 mol/L.

Four BFPT7030 thin films were prepared by depositing BFPT7030 sol for eight times. The films were annealed in air, O_2 flow, air flow and N_2 flow in the air environment. The depositions process was carried out by spin coating at 3000 r/min for 30 s in a super clean room. Each deposition layer was dried at 150 ºC for 1 min and 200 ºC for 3 min, followed by annealing at 700 ºC for 90 s by rapid thermal annealing (RTA) technique with heating rate of 1 $ºC \cdot s^{-1}$.

X-ray diffraction (XRD, DX-1000, Dandong, China) with Cu Kα radiation (λ=0.154 056 nm) in the mode of θ-2θ scan was used for the phase analysis of the films. The surface morphology of the BFPT7030 thin films was analyzed using a field emission-scanning electron microscope (FE-SEM, HITACHI S4800, Japan). The ferroelectric properties of the films were measured using Au as top electrodes, which were directly evaporated on the annealed films through a shadow mask with a diameter of 0.5 mm by DC sputtering, forming an $Au/BFPT/LNO/SiO_2/Si(100)$ stacked capacitor. The $LaNiO_3$ (LNO) layer of the $LaNiO_3/SiO_2/Si$ substrates was used as a bottom electrode. LNO was deposited on SiO_2/Si substrate by RF magnetron sputtering at the substrate temperature of 450 ºC with the ratio of oxygen and argon of 10:40 SCCM (SCCM denotes cubic centimeter per minute at STP) under a working pressure of 2.0 Pa. The hysteresis loops of polarization (P) as a function of applied electric field (E) (P-E curve) and leakage current properties of the BFPT7030 thin films were evaluated by the Radiant Precision Ferroelectric Measurement System (RT2000 Tester, USA). X-ray photoelectron spectroscopy (XPS) were used to analyze Bi, Pb relative content and Fe oxidation state.

2 Results and Discussion

2.1 Microstructure of the BFPT7030 thin films

Fig.1 shows the XRD patterns of BFPT7030 thin films. All the films demonstrate a perovskite phase and fully crystallized except for the BFPT7030 films annealed in N_2 flow, which is quite different from other reports[26,27]. Very weak peaks are found in the BFPT7030 films annealed in N_2, indicating that the BFPT7030 thin films crystallize badly. This result may be attributed to the rapid thermal annealing (RTA) technique and the annealing temperature which is not much higher. The total time of heat treatment is less than 2 min, while in other literatures[26,27], the total time of the heat treatment of BFPT-based films is more than 1 h. Other films annealed in air and O_2 are completely crystallized and exhibit highly (100) preferred orientation. The preferential orientation parameter, α_{hkl}, can be calculated by the following formula:

$$\alpha_{hkl}=I_{hkl}/\sum I_{hkl} \quad (1)$$

where I_{hkl} is the relative intensity of the corresponding diffraction peak. The calculated preferential orientation α_{100} of the BFPT7030 thin films annealed in air, O_2 flow and air flow is 0.71, 0.77 and 0.75, respectively, indicating that BFPT7030 thin films are highly (100) oriented. Although the α_{100} of BFPT7030 thin film annealed in O_2 flow and air flow atmosphere is a little higher than that of the film annealed in air atmosphere, the peak height of BFPT7030 thin film annealed in O_2 flow and air flow atmosphere is much less than that of the film annealed in air, meaning that