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Effect of Rb doping on ferroelectric and piezoelectric properties of $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$ thin films

Susant Kumar Acharya [a,b], Byung-Guk Ahn [a,*], Chang Uk Jung [b], Jung-Hyuk Koh [c], In-Hwan Choi [d], Sang-Kwon Lee [d,*]

[a] Division of Advanced Materials Engineering, Hydrogen and Fuel Cell Research Center, Chonbuk National University, Jeonju 561–756, Republic of Korea
[b] Department of Physics, Hankuk University of Foreign Studies, Yongin 449-791, Republic of Korea
[c] School of Electrical and Electronics, Chung-Ang University, Seoul 156-756, Republic of Korea
[d] Department of Physics, Chung-Ang University, Seoul 156-756, Republic of Korea

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ABSTRACT

Rb doped $0.94Bi_{0.5}Na_{0.5}TiO_3$–$0.06BaTiO_3$ (BNT–BT–Rb_x) thin films with x mol% Rb (x = 0, 2.5, 5, 7.5, 10) were deposited on Pt/Ti/SiO_2/Si substrate by metal-organic solution deposition method. Experiments were conducted to investigate the effect of Rb doping on phase formation, microstructure, leakage current, and the resulting ferroelectric and piezoelectric property. It was found that substantial enhancement in structural, morphological and electrical properties can be achieved by Rb doping of BNT–BT thin films. Optimal electrical properties were obtained for 5 mol% Rb doped BNT–BT thin films, with a dielectric constant, remnant polarization, and effective piezoelectric constant of ~681, ~28.9 μC/cm^2 and ~86 pm/V, respectively. It was suggested that the enhanced electrical properties in the case of 5 mol% Rb BNT–BT thin films can be attributed to domain wall movement induced by *A*-site substitutions, large grain size, and lattice distortion.

1. Introduction

Lead zirconate titanate [$Pb(Zr,Ti)O_3$] (PZT) ceramics are among the best choice of piezoelectric materials for use in sensors, actuators, and transducers due to their excellent electromechanical properties [1]. However, waste products containing lead (Pb) can cause serious environment problems, making lead-free piezoelectric materials far more desirable than PZT [2]. Among the various lead-free piezoelectric materials, sodium bismuth titanate [$Bi_{0.5}Na_{0.5}TiO_3$] (BNT) is considered a good alternative to PZT due to its strong ferroelectricity at room temperature (remnant polarization P_r = ~38 μC/cm^2) and high Curie temperature (T_c = 320 °C) [3]. However, due to their high conductivity and large coercive fields, BNT ceramics exhibit difficulty in poling [4]. Solid solutions of BNT with $BaTiO_3$ (BT), BNT–BT, have been studied with the aim of reducing the coercive field as well as improving the dielectric and piezoelectric properties of BNT, and a morphotropic phase boundary (MPB) between a rhombohedral and a tetragonal structure was reported for 0.6–0.7 mol% BT [5,6]. BNT–BT ceramics of this composition have shown enhanced electromechanical properties. Compared to bulk composites, piezoelectric thin films exhibit unique advantages due to their potential applications in all kinds of micro-devices and integrated units such as micro-sensors, micro-electro-mechanical system (MEMS) devices, and high density information storage devices [7]. However, low remnant polarization and relatively high leakage currents of BNT–BT thin films limit their industrial applications. High leakage currents in BNT–BT thin films are basically due to the volatility of the A-site elements during thermal treatment, which creates acceptor states in the band gap and induces oxygen vacancies in order to maintain charge neutrality in the lattice [8]. This in turn weakens the electromechanical properties. Site engineering is one of the best approaches to enhance the resistivity and also to improve the ferroelectric properties of BNT–BT thin films [9]. It is well documented that small concentrations of dopants can significantly modify the properties of ferroelectric thin films such as of BNT. It has been reported that doping with different elements such as Mn, Li, Ce, Fe into the A site or B site of BNT based thin films not only decreases their leakage current but also enhances their electrical properties [8–11]. Recently, Yang et al. [12] reported that an increase in grain boundary resistivity and decrease in leakage current in Rb-doped $CaCu_3Ti_4O_{12}$ ceramics. However, no detailed studies on the effect

* Corresponding authors. Tel.: +82 2 820 5455; fax: +82 2 825 4988.
E-mail addresses: bkahn@chonbuk.ac.kr (B.-G. Ahn), sangkwonlee@cau.ac.kr (S.-K. Lee).

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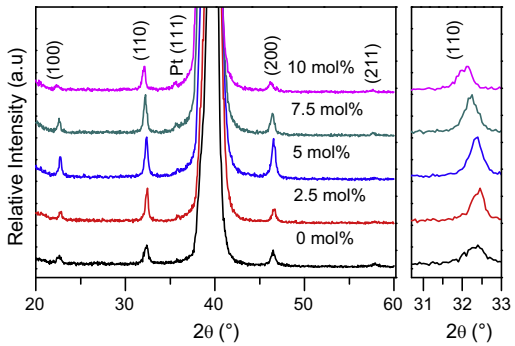

Fig. 1. X-ray diffraction patterns of the BNT–BT–Rb_x (x = 0, 2.5, 5, 7.5, 10) thin films. The diffraction of (110) plane is zoomed in to show the 2θ angle shift with increasing Rb doping.

of Rb doping on BNT–BT, neither in bulk nor in thin film form, have yet been reported.

In this paper, we report the results of our studies on x mol% Rb-doped BNT–BT (BNT–BT–Rb_x, x = 0, 2.5, 5, 7.5, 10) thin films prepared on Pt/Ti/SiO_2/Si(100) substrates by metal organic solution deposition technique. The effect of Rb content on phase formation, microstructure, leakage current, dielectric properties, ferroelectric properties, and piezoelectric properties was studied systematically.

2. Experimental details

Barium acetate [$Ba(CH_3COO)_2$], bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], sodium acetate ($NaOOCCH_3$), rubidium nitrate ($RbNO_3$), and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) were used as starting materials, while acetyl acetone, isopropyl alcohol, distilled water, and acetic acid were used as solvents. Diethanolamine [$HN(CH_2CH_2OH)_2$] was used as a ligand. The detailed method of sample preparation can be found in a previous report [13]. In brief, the stock solutions were spin-coated onto Pt/Ti/SiO_2/Si (100) substrates at a spin rate of 4500 rpm for 30 s using a commercial photoresist spinner. After each step, the gel state films were dried at 170 °C for 10 min and pyrolyzed at 450 °C for 10 min on a hot plate prior to a further annealing process. These amorphous films were then crystallized at 700 °C by rapid thermal annealing under an O_2 atmosphere with a soak time of 5 min. Deposition, drying, pyrolysis, and crystallization were repeated several times in order to acquire thicker films. X-ray diffraction (XRD, Model D/MAX–111A, Rigaku Corporation, Japan) with Cu Kα radiation was used for analysis of the phase structure of the samples. The surface and cross-sectional morphologies of the thin films were examined by a field-emission scanning electron microscope (FESEM, Model JSM-6701F, JEOL Corporation, Japan), whereas the thickness of thin film was obtained from the cross-sectional FESEM image. A NanoScope IIIa (Digital Instruments, Santa Barbara, CA, USA) and an atomic force microscope (AFM) were used to measure the surface roughness of the as-prepared thin films. The electrical properties of the BNT–BT–Rb_x thin films were evaluated using a capacitor structure of Au/BNT–BT–Rb_x/Pt, where Au electrodes with a radius of 200 μm were prepared on top of the surface through a shadow mask in a vacuum chamber using the e-beam deposition technique. The polarization versus electric–field (P–E) hysteresis loop was obtained using a TF Analyzer 2000 (aix-ACCT, Aachen, Germany) system. A precision LCR meter (HP 4284A, Agilent Technologies, CA, USA) was used to analyze the dielectric properties of the BNT–BT thin films. The leakage current through the Au/BNT–BT/Pt capacitor was measured using a programmable electrometer (Keithley 6517A, OH, USA) at room temperature. The piezoelectric properties were studied by piezo-force microscopy (PFM) (Digital Instruments, NanoScope IV, Plainview, NY, USA) incorporating a lock-in technique.

3. Results and discussion

The XRD patterns of BNT–BT–Rb_x thin films with various Rb concentrations are shown in Fig. 1. The diffraction peaks were identified by using the standard powder diffraction data of BNT–BT. The relative intensities of all the BNT–BT–Rb_x thin films were found to agree well with those given in ICDD–PDF No. 70-9852. It shows that the thin films show good crystallization and a pure perovskite structure without secondary phase. No impurity phase was detected in these Rb-doped BNT–BT samples, indicating that Rb^+ doping concentration even up to 10 mol% did not introduce any impurity. The crystallinity of the thin films increases with increasing of Rb content up to 5 mol%, and then starts decreasing with further increase in Rb content, as shown in Fig. 1. The ionic radius of Rb^+ in 12 fold co-ordination is ~0.166 nm, while the ionic radii of Na^+, Bi^{3+} and Ba^{2+} are ~0.139 nm, ~0.135 nm, and ~0.161 nm, respectively [14,15]. A close inspection of the XRD patterns showed

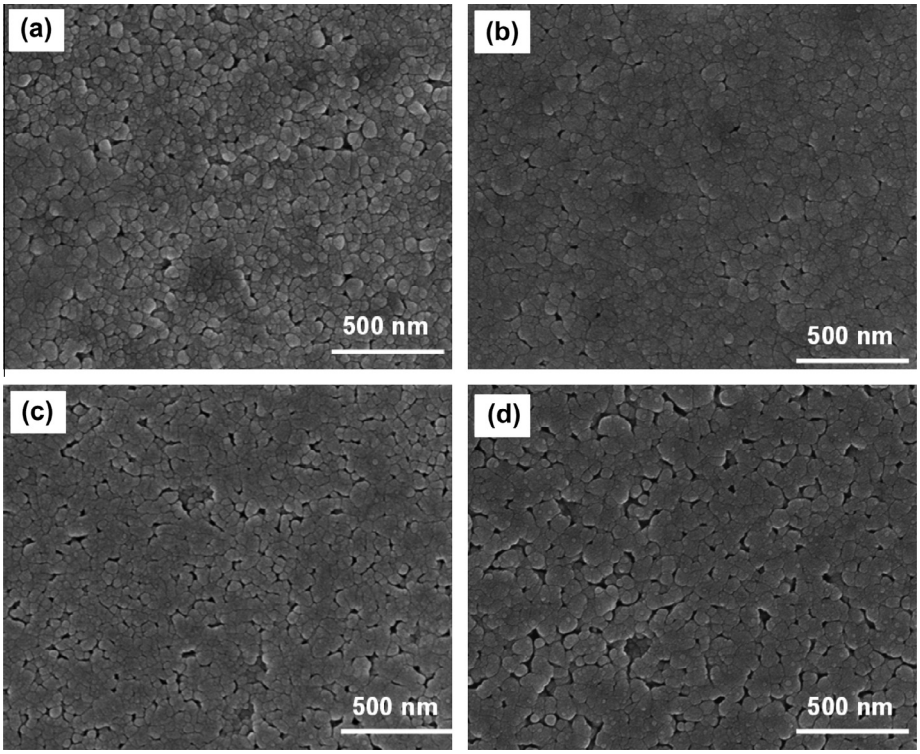

Fig. 2. (a–d) Surface morphologies of the BNT–BT–Rb_x (x = 2.5, 5, 7.5, 10) thin films as observed by FESEM images.