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Growth of c-axis-oriented $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ thin films for ferroelectric memory applications

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Abstract

Highly c-axis-oriented $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNdT) thin films were grown on $Pt/TiO_2/SiO_2/Si$ (1 0 0) substrates using the method of metalorganic sol decomposition by optimizing the parameters such as excess bismuth concentration, crystallization temperature, film thickness and crystallization ambient. The BNdT film capacitor with a top Pt electrode showed a large remnant polarization ($2P_r$) of 80 μC/cm^2 at an applied voltage of 10 V and exhibited a fatigue-free behaviour up to 2×10^9 switching cycles at a frequency of 1 kHz. These experimental results reveal that Nd-substituted $Bi_4Ti_3O_{12}$ thin films can be used as capacitors in ferroelectric access memories.

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1. Introduction

There have been extensive research efforts to enhance the reliability of perovskite-based ferroelectric thin films for use in nonvolatile ferroelectric random access memory (NvRAM) devices [1–4]. $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films of various compositions have been extensively studied as the promising FeRAM candidate material. Despite having advantages such as low processing temperature and large remnant polarization (P_r), PZT films with metal electrodes were found to exhibit ferroelectric fatigue. Although the application of conductive oxide electrodes greatly improves the fatigue resistance of PZT, it also increases the processing complexity and causes larger leakage current. Also, due to the toxicity of lead, it is desired that lead-free materials be used in memory applications from the view point of environmental protection [5,6]. A serious effort in searching for lead-free materials having essentially fatigue-free behaviour has led to the advent of a new generation of ferroelectric thin films with bismuth oxide-layered structure. Lanthanum-substituted

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bismuth titanate, $(Bi_{4-x}La_x)Ti_3O_{12}$, is an attractive lead-free material for ferroelectric random access memory (FeRAM) application because of its relative large remnant polarization and fatigue-free character [7,8]. According to the proposition made by Park et al. [9], the fatigue free behavior of BLT can be attributed to the enhanced stability of oxygen in the Ti–O octahedron layer. Accepting this proposition, it is expected that the substitution of a stable trivalent cation can enhance the fatigue resistance provided it stabilizes the oxygen in the octahedron layer and its ionic radius is similar to that of bismuth having a higher volatility. Hence an attempt has been made to study the effect of substitution for Bi of Nd [$r(Nd^{3+}) = 1.27$ Å] [10] with a smaller ionic radius than La [$r(La^{3+}) = 1.36$ Å] in the pseudoperovskite layer. The main purpose of this study is to demonstrate highly *c*-axis-oriented Nd-substituted $Bi_4Ti_3O_{12}$ (BNdT) thin films having fatigue free characteristics as well as improved remnant polarizations useful for FeRAM applications.

2. Experimental procedure

The precursor solution for BNdT was prepared by dissolving appropriate amounts of bismuth acetate [$Bi(CH_3COO)_3$] and neodymium acetate [$Nd(CH_3COO)_3$] into an aqueous acetic acid solution at room temperature. Stoichiometric amount of titanium isopropoxide solution {Ti [$(CH_3)_2OCH]_4$} was slowly added to the mixed precursor solution to get clear yellowish sol. The BNdT films were fabricated onto $Pt/TiO_2/SiO_2/Si$ substrates by repeated coating/drying cycles. The amorphous films deposited on the substrates were subsequently crystallized by thermal annealing at various temperatures in air atmosphere. The crystalline structure and surface morphology of the films were characterized by X-ray diffraction (XRD) and atomic force microscopy. Chemical composition of the BNdT films was determined using dispersive X-ray and electron microprobe analysis. For the fabrication of BNdT capacitors, top Pt electrodes were deposited by radio frequency magnetron sputtering. The typical area of a top electrode was $10^{-4}\,cm^2$. Ferroelectric and dielectric properties of the fabricated capacitors were measured using a ferroelectric analyzer (RT6000S, Radiant Technology, Albuquerque, NM) and an impedance analyzer (HP4194A, Hewlett Packard) equipped with a micrometer probe station, respectively.

3. Results and discussion

Fig. 1 shows the XRD scan results of BNdT films with different excess bismuth concentrations (0, 4 and 8 mol%) annealed at 650 °C in air atmosphere. All the XRD patterns can be readily identified and indexed using standard XRD data for the perovskite bismuth titanate (BT) compiled in JCPDS card. This indicates that BNdT film maintains a pseudoperovskite-layered structure similar to perovskite BT. Interestingly, it was found from XRD pattern that the crystal orientation of the BNdT thin films was strongly influenced by excess bismuth concentration. The films obtained from stoichiometric sol were found to be polycrystalline, while the films prepared from sols with 4% and 8% excess bismuth concentration showed *c*-axis-oriented preferential growth. The degree of orientation is much higher in the case of films prepared from sols with 8 mol%

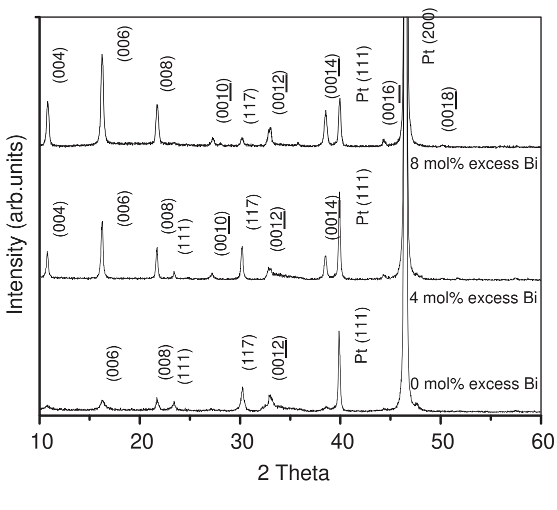


Fig. 1. XRD patterns of BNdT films grown on $Pt/TiO_2/SiO_2/Si$ (1 0 0) substrates with different excess bismuth concentrations (0, 4 and 8 mol%) annealed at 650 °C.

excess bismuth concentration with only a minor fraction of (1 1 7) orientation as calculated by Lotgering's [11] orientation factor. A possible explanation for the growth of *c*-axis oriented films with higher Bi/Ti ratio can be given by considering the crystal structure of BT. BT consists of $(Bi_2O_2)^{+2}$ layers interleaved with $(Bi_2Ti_3O_{10})^{-2}$ layers. The *c*-axis is perpendicular to these layers. At initial stages of the film growth, higher Bi/Ti ratio allows more Bi-atoms to be adsorbed on the substrate surface. The higher concentration of bismuth may form $(Bi_2O_2)^{+2}$ layer parallel to the substrate, inducing the film growth with *c*-axis orientation [12]. In BNdT thin films, due to the volatile nature of bismuth at higher temperatures, the 8 mol% excess bismuth leads to stoichiometric composition and thereby favour the growth of highly *c*-axis-oriented BNdT thin films.

XRD patterns were taken for the BNdT films with prepared at two different conditions: in the first one, films were heated at 350 °C for 10 min and spin coated again until desired thickness was reached. In this case, each layer was amorphous and all layers were crystallized at 650 °C called *intermediate amorphous*. In the second case, each layer was heated at 350 °C for 10 min and immediately crystallized at 650 °C before next spin coating called intermediate crystallized. From the XRD results it was found that the *c*-axis orientation decreases in the first case but at the same time the degree of *c*-axis orientation becomes higher in the second case and the degree of (0 0 l)-type preferential growth as estimated using Lotgering's orientation factor was above 96%. These differences in the crystallization of the films prepared by the two different routes are mainly due to the difference in nucleation mechanism. For the intermediate crystallized route, each intermediate crystallized layer acts like a nucleation site to the next layer to be crystallized. In the case of intermediate amorphous, the nucleation starts from the interface between the film and substrate and hence the possibility of random orientation [13].

Microstructure examination of the films showed that films were crack-free, dense and adhered well on the substrates. Fig. 2 shows the AFM image of the film surface with roughness of about 15 nm.

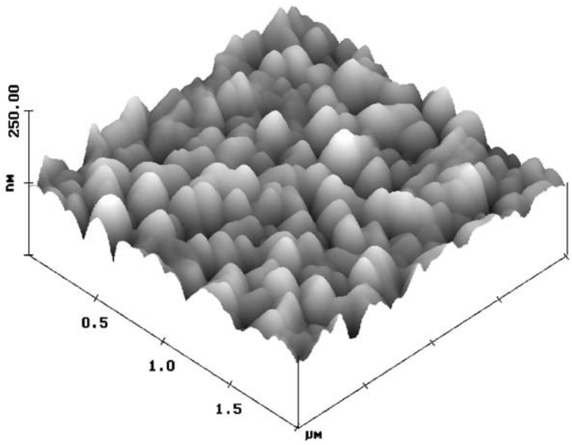
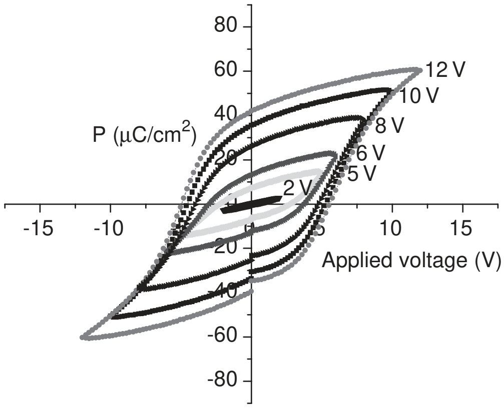


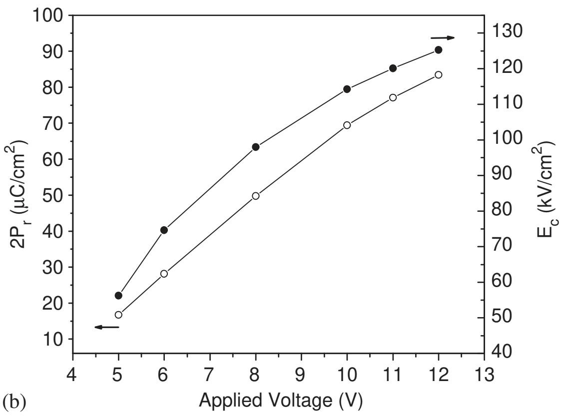
Fig. 2. AFM image of BNdT film surface taken over the scanning area of $2 \times 2\,\mu m^2$.

Film thickness examination using a field-emission scanning electron microscope (FE-SEM) showed fine-sized, uniform grains for the film thickness of approximately 400 nm. The chemical composition of the BNdT film as determined by energy dispersive X-ray and electron microprobe techniques is found to be Bi:Nd:Ti = 3.16:0.84:3.01. Considering the importance of fatigue-free capacitors with highly *c*-axis orientation, the electrical properties were studied on the BNdT films with 8 mol% of excess bismuth concentration.

The ferroelectric properties are related to stoichiometric content, grain size and crystallinity of the film [14]. Fig. 3(a) shows the *P–E* hysteresis loops of BNdT thin films annealed at 650 °C and measured at various applied voltages ranging between 2 and 12 V. Hysteresis curves for ferroelectric thin films often exhibit horizontal shifts along the voltage axis due to built-in bias fields or along the vertical *P*-axis due to asymmetric electrodes and /or space charge accumulation at one of the electrode interfaces due to the oxygen vacancy concentration near the electrodes [15]. This space-charge accumulation has been overcome in BNdT thin films by annealing the capacitor in O_2 for 10 min at 450 °C. The capacitor was characterized by well-saturated *P–E* switching curves without any shifts along the voltage axis. The remanent polarization ($2P_r$) of the capacitor was 40 $\mu C/cm^2$ at an applied voltage of 5 V, and



(a)



(b)

Fig. 3. (a) Hysteresis loops measured at various applied voltages ranging from 2 to 12 V. (b) Variations of $2P_r$ and E_c values of Pt/BNdT/Pt capacitor for different applied voltages.

increased to 80 μC/cm^2 at 10 V. These values are substantially higher than those of highly *c*-axis-oriented BLT and BSmT [16,17] thin films which range between 27 and 49 μC/cm^2 at 10 V. The higher P_r value in the BNdT thin films are due to the increased lattice distortion. In addition to this, the *P–E* curve did not show any noticeable asymmetric behaviour resulting in imprint failures. Fig. 3(b) shows the variation of $2P_r$ and E_c with applied voltage. From the figure it is found that these values increase rather steeply at a low voltage and there is no appreciable change beyond 10 V. The capacitor is nearly saturated at an applied field of 12 V.

The relative dielectric permittivity [$\varepsilon'(\omega)$] and the dissipation factor [$\varepsilon''(\omega)/\varepsilon'(\omega) = \tan\delta$] of the capacitor were measured at 25 °C as a function of frequency. The relative permittivity and the dissipation factor are 587 and 0.087 at a frequency of 1 MHz, respectively. These values are comparable to PZT, SBT and BLT capacitors [18,19]. Although the dielectric permittivity decreases steadily with increasing frequency, there is no sudden change with increasing frequency up to 1 MHz. The dielectric loss improves slightly with increasing frequency up to 1 MHz. All these indicate that the observed *P–E* hysteresis behaviour of the BNdT capacitor originates from the ferroelectric polarization switching of bound charges, not from the response of freely moving charges.

The fatigue of ferroelectric thin films is exhibited in the loss of switchable polarization with repeated switching cycles. This loss of switchable polarization limits the life time of the ferroelectric device applications, where both write and read cycles rely on ferroelectric switching. The fatigue-free characteristics of the BNdT capacitor are summarized in Fig. 4. The capacitor shows little change both in the switching polarization (P_{sw}) and in the non-switching polarization (P_{ns}) up to 2×10^9 switching cycles at a frequency of 1 kHz.The values of non-volatile charge [(i.e. $(+P_{sw})-(+P_{ns})$ or $(-P_{sw})-(-P_{ns})$)] are approximately 26 μC/cm^2 and remains constant throughout the switching

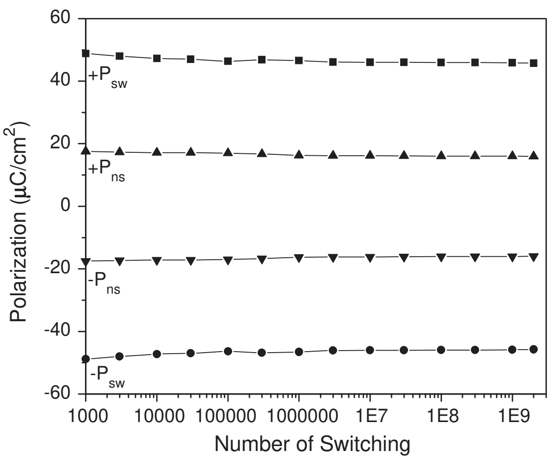


Fig. 4. Fatigue characteristics of BNdT film for 10^9 switching cycles.

cycles. Besides, the *P–E* curves do not show any noticeable asymmetric behaviour resulting in imprint failures, even after being subjected to 2×10^9 cycles.

4. Conclusions

Highly *c*-axis-oriented $Bi_{4-x}Nd_xTi_3O_{12}$ ($x = 0.85$) thin films have been grown on Pt/TiO_2/SiO_2/Si (1 0 0) substrates using the method of metalorganic sol decomposition. The orientation of the films was controlled by varying the excess bismuth concentration in the precursor mixture. Single-phase BNdT thin films were obtained with 8 mol% of excess bismuth concentration and annealing the films in air atmosphere. Ferroelectric studies on the films show a large $2P_r$ value (80 μC/cm^2), which is larger than that of Sm and La-modified $Bi_4Ti_3O_{12}$ films at an applied voltage of 10 V. Moreover, BNdT thin films showed a fatigue-free character up to 2×10^9 switching cycles at a frequency of 1 kHz. As a result, lead-free BNdT films having good ferroelectric properties are useful candidates for ferroelectric random access memory applications.

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