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Seed-layer mediated orientation evolution in dielectric Bi–Zn–Ti–Nb–O thin films

Jin Young Kim,[a)] Jun Hong Noh, Sangwook Lee, Sung-Hun Yoon, Chin Moo Cho, and Kug Sun Hong[b)]
Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

Hyun Suk Jung
School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Korea

Jung-Kun Lee
Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, USA

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Highly (*hhh*)-oriented pyrochlore Bi–Zn–Ti–Nb–O (BZTN) thin films were fabricated via metal-organic decomposition using orientation template layers. The preferred orientation was ascribed to the interfacial layer, the lattice parameter of which is similar to BZTN. High-resolution transmission electron microscopy supported that the interfacial layer consists of Bi and Pt. The (*hhh*)-oriented thin films exhibited a highly insulating nature enabling feasible applications in electronic devices, particularly voltage tunable application. The BZTN thin films did not show any apparent dielectric anisotropy and the slightly enhanced dielectric properties were discussed in connection to the internal stress and the grain boundary effect. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2806193]

Bi-based pyrochlore thin films, particularly cubic $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) thin films, have attracted great interest due to their medium permittivity (~150),[1–4] low loss (<0.0005),[2] and high tunability (40% at 1.2 MV/cm and 55% at 2.4 MV/cm).[2] Recently, $(Bi_{2-x}Zn_x)(Ti_{2-x}Nb_x)O_7$ (BZTN) solid solution thin films have been reported to exhibit higher permittivity (~250) (Ref. 5–7) than BZN thin films with similar properties. Among the various solid solutions, thin films exhibit the best properties, including the highest permittivity and tunability as well as the lowest loss when $x=0.5$ and 0.6. The BZTN thin films are usually fabricated via metal-organic decomposition (MOD) methods since the complex composition can be precisely controlled.[5–7] However, most MOD-derived BZTN thin films do not show any preferred orientation due to their lattice parameter being much larger than those of general substrates such as Pt, MgO, and STO; therefore, the orientation dependency of the dielectric properties of BZTN thin films has not been reported. In this letter, we propose an approach to control the preferred orientation of MOD-derived BZTN thin films using seed layers.

$(Bi_{1.4}Zn_{0.6})(Ti_{1.4}Nb_{0.6})O_7$ (BZTN) thin films were prepared on (111)-oriented $Pt/TiO_x/SiO_2/Si$ (Inostek, Korea) substrates via a MOD method. This composition was selected on the basis that it exhibited the best dielectric properties in our previous study, where detailed experimental procedures were also described.[5] As-deposited thin films were annealed at 750 °C under ambient atmospheres. The seed layers were grown at 400 or 700 °C by pulsed laser deposition (PLD) using a KrF excimer laser (248 nm, 2 J/cm^2, 3 Hz). The deposition was conducted at 400 mTorr of oxygen pressure. After the deposition, the thin films were cooled down at 360 Torr of oxygen pressure with a cooling rate of 10 °C/min.

The structure of the BZTN thin film was observed using x-ray diffraction (XRD) (model MX18HF-SRA, MAC Science Co., Japan), and the cross-sectional microstructures were examined using a high-resolution transmission electron microscope (HR-TEM) (model JEM-3000F, JEOL, Japan). Pt electrodes (200 μm in diameter) were sputter deposited onto the film surface using a metal mask. The dielectric properties of the Pt/BZTN/Pt capacitors were measured with an impedance analyzer (HP 4194, Hewlett-Packard, USA) in the frequency range from 100 Hz to 10 MHz, and the *I-V* characteristics were measured using a precision semiconductor parameter analyzer (Agilent 4156C, Agilent, USA).

As seen in Fig. 1(a), using only PLD methods, the highly (*hhh*)-oriented BZTN thin films could be deposited at 700 °C; however, as can be seen in Fig. 1(b), the leakage currents of the PLD-BZTN thin films (open triangles) are too high to be used in capacitor applications, particularly in voltage tunable applications. On the other hand, the MOD-BZTN thin films (open circles) maintain quite low leakage currents even under a high applied bias of 20 V. The origin of the PLD-BZTN thin film's high leakage currents is not clear and currently under investigation. In order to combine the respective merits, i.e., the highly preferred orientation of the PLD-BZTN thin films and the low leakage currents of MOD-BZTN thin films, thin PLD-BZTN layers (~20 nm) have been introduced to MOD-BZTN thin films (~400 nm) as orientation template layers. In order to form the oriented seed layers, the PLD-BZTN thin films were deposited at 700 °C for 20 s (60 pulses, 3 Hz), whereas for nonoriented seed layers, the PLD-BZTN thin films were deposited at 400 °C. As can be seen in Fig. 1(c), the preferred orientation of MOD-BZTN thin films could be controlled by

[a)]Electronic mail: dexter2@snu.ac.kr
[b)]Author to whom correspondence should be addressed. Electronic mail: kshongss@plaza.snu.ac.kr

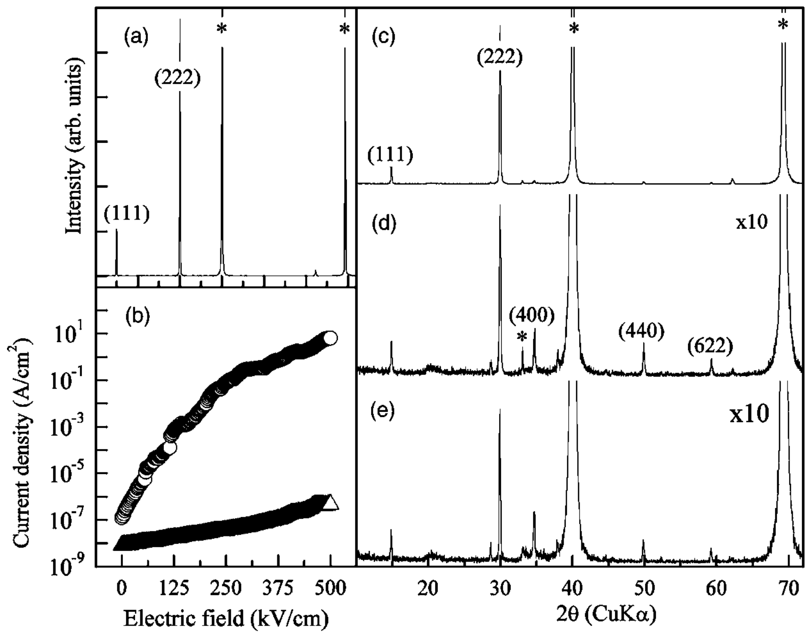

FIG. 1. (a) X-ray diffraction of BZTN thin film grown by PLD and (b) *I-V* curve of BZTN thin films grown by PLD (open triangle) and MOD (open circle), respectively. X-ray diffraction of BZTN thin films with (c) 700 °C seed layer, (d) 400 °C seed layer (magnified by ten times), and (e) no seed layer (magnified by ten times).

the PLD-seed layer. MOD-BZTN thin films with oriented seed layers (which will be denoted as "700-seed" thin films hereafter) show highly (*hhh*) orientation with negligible other diffraction peaks. In contrast, as can be seen in Fig. 1(d), MOD-BZTN thin films with nonoriented seed layers (which will be denoted as "400-seed" thin films hereafter) do not show noticeable preferred orientation. For a better comparison, the XRD pattern of MOD-BZTN thin films without any seed layers is shown in Fig. 1(e). Since no differences exist between Figs. 1(d) and 1(e), it can be concluded that the seed layers grown at 400 °C do not have any effects on the crystallographic orientation of the final thin films.

The degree of (*hhh*) orientation can be determined quantitatively through Lotgering's method.[8] According to this method, the orientation factor f can be calculated by using the following equation (where $p=\Sigma I_{hhh}/\Sigma I_{hkl}$ for the given oriented sample, $p_0=\Sigma I_{hhh}/\Sigma I_{hkl}$ for the nonoriented sample):

$$f=(p-p_0)/(1-p_0). \tag{1}$$

The results of Lotgering's method are summarized in Table I. The portion of (*hhh*) peaks (p) in the 700-seed thin film is as high as 0.95, whereas the p_0 of nonoriented bulk BZTN ceramics is 0.48.[9] On the other hand, the 400-seed thin film and MOD-BZTN thin film exhibit similar values of approximately 0.60. As a result, the calculated orientation factor of the 700-seed thin film is as high as 0.90, while those of the seed and MOD-BZTN thin films are 0.23 and 0.21, respectively.

The origin of highly preferred (*hhh*) orientation of 700-seed thin films can be investigated in greater detail through the TEM analysis. Figure 2(a) shows the high-resolution images of the 700-seed thin film. As can be seen in Fig. 2(a), there is a conspicuous interfacial layer the thickness of which is approximately 10 nm between the Pt electrode and BZTN layer. As seen in the insets of Fig. 2(a), only pure Pt and BZTN phases are found outside the interfacial layer. The lattice spacings of Pt and BZTN layers are 0.22 and 0.29 nm along the out-of-plain direction, which correspond to the d spacings of Pt (111) and BZTN (222), respectively. The selected area electron diffraction (SAED) of BZTN layer is also shown in the inset of Fig. 2(a). It is obvious that the interfacial layer plays a vital role in enhancing the preferred orientation of 700-seed thin films, since no trace of the interfacial layer exists in the nonoriented 400-seed and MOD-BZTN thin films. A similar study, which focused on the Pt-assisted phase transition and preferred orientation evolution in Bi-based layered thin films, has been reported by another research group.[10] One of the most possible reasons for the preferred orientation in this study is that the interfacial layer consists of Pt and some components of BZTN. Due to the high substrate temperature of 700 °C, highly reactive ions may possibly react with Pt to form compounds. In particular, the Bi ions may react easily with Pt because of the low melting temperature. This assumption is supported by the

TABLE I. Portions of (*hhh*) orientation and resulting orientation factors of BZTN thin films.

	700 seed	400 seed	MOD BZTN
Portion of (*hhh*), p	0.95	0.60	0.59
Orientation factor f	0.90	0.23	0.21

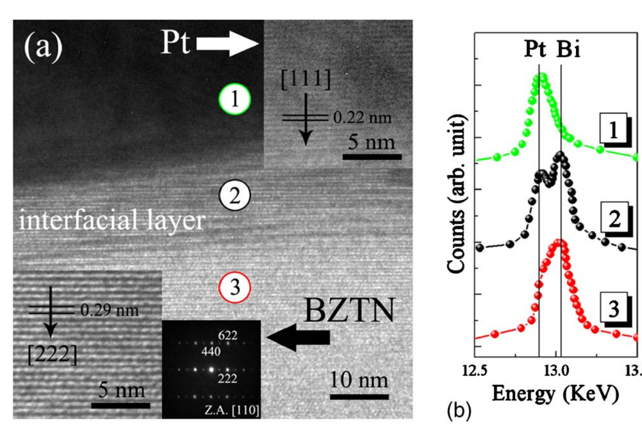

FIG. 2. (Color online) (a) TEM image of the BZTN thin film with 700 °C seed layer. The insets are high-resolution images of Pt and BZTN layers, respectively. The SAED pattern of BZTN layer is also presented. (b) EDS data of BZTN thin film with 700 °C seed layer. Circles of 1, 2, and 3 indicate Pt, interfacial, and BZNT layers, respectively.

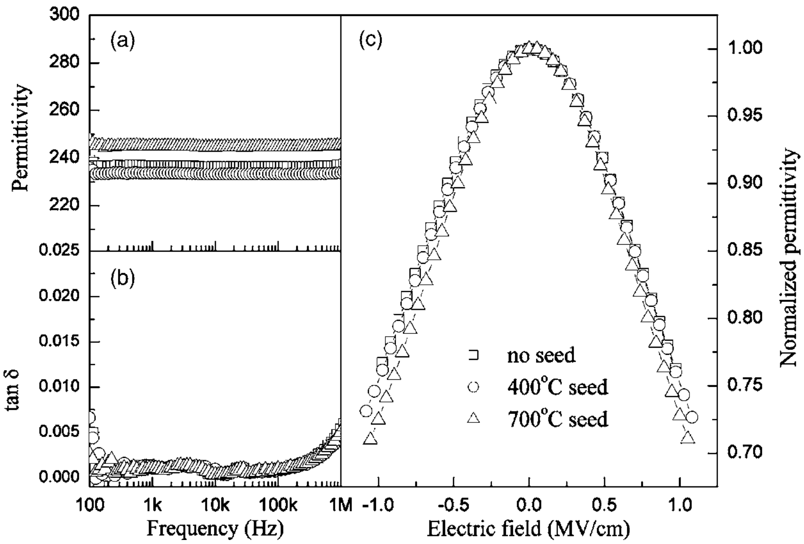

FIG. 3. (a) Dielectric permittivity, (b) dielectric loss, and (c) dielectric tunability of BZTN thin films. Open squares, open circles, and open triangles correspond to BZTN thin films with no seed layer, 400 °C seed layer, and 700 °C seed layer, respectively.

energy dispersive x-ray spectroscopy (EDS). The EDS data were collected at three different points: Pt, the interfacial layer, and BZNT, which are labeled as 1, 2, and 3 in the TEM image, respectively. Bi and Pt can be distinguished by a peak separation in the range from 12.5 to 13.5 KeV. As can be seen in Fig. 2(b), it can be confirmed that Bi and Pt coexist in the interfacial layer. Pyrochlore $Bi_2Pt_2O_7$ can be considered as the interfacial compound, since its structure and lattice parameter are almost the same with the BZTN phase.[11] As a result, the (*hhh*)-oriented $Bi_2Pt_2O_7$ interfacial layer plays a role as an orientation template layer for the (*hhh*)-oriented BZTN thin film.

The dielectric properties of the 700-seed, 400-seed, and MOD-BZTN thin films are shown in Fig. 3. In general, the 400-seed and MOD-BZTN thin films show similar dielectric properties, while the 700-seed thin films exhibit slightly superior dielectric properties. The dielectric properties of the thin films are summarized in Table II. Although the 700-seed thin films show slightly higher permittivity and tunability, it is hard to conclude that the BZTN thin films exhibit a dielectric anisotropy along the (*hhh*) direction, since the difference in the dielectric properties is much smaller than that in the orientation factors. Slightly higher permittivity and tunability of the (*hhh*)-oriented BZTN thin films can be ascribed to other factors such as the internal stress and the grain boundary effect. 700-seed thin films may be under tensile stress since the lattice parameter of BZTN phase ($a=1.035$ nm) (Ref. 9) is slightly smaller than that of the $Bi_2Pt_2O_7$ template layer ($a=1.037$ nm).[12] However, a more detailed investigation concerning the internal stress is required, since the thermal stress originating from the postannealing process also has to be taken into account. The smaller number of grain boundaries perpendicular to the out-of-plain direction in the oriented BZTN thin films may provide a reason for the higher permittivity. Physically, the metal-insulator-metal structure can be assumed to be a series of numerous high-*k* grains and low-*k* boundaries. Considering the general series mixing rule of dielectrics, it can be easily deduced that the decrease in volume fraction of low-*k* boundaries causes the increase in the permittivity.

In conclusion, the preferred orientation of highly insulating MOD-BZTN thin films could be controlled using thin template layers. Highly (*hhh*)-oriented BZTN thin films with an orientation factor as high as 0.90 can be fabricated using seed layers grown at 700 °C by PLD. The highly preferred (*hhh*) orientation in the 700-seed thin films is ascribed to the orientation template effect of the interfacial layer. The pyrochlore material containing Bi and Pt is considered as the interfacial layer (as supported by the HR-TEM image and the corresponding EDS data). In contrast to pure PLD thin films, the 700-seed thin films exhibit a highly insulating nature with a similar degree of preferred orientation. Although the 700-seed thin films show slightly higher permittivity and tunability with similar dielectric loss to other thin films, no apparent dielectric anisotropy is found in the BZTN thin films. Instead, it is suggested that the internal stress originating from the lattice mismatch between the BZTN and the interfacial layer may affect the dielectric properties, and that the reduced number of grain boundaries perpendicular to the out-of-plain direction will result to increased permittivity.

TABLE II. Dielectric properties of BZTN thin films.

	Permittivity ε at 100 kHz	tan δ at 100 kHz	Tunability[a] (%) at 1 MV/cm
700 seed	245	0.000 75	28
400 seed	234	0.000 72	24.5
MOD BZTN	236	0.000 84	24

[a]Tunability (%) $=[(\varepsilon_0-\varepsilon_{1\ \mathrm{MV/cm}})/\varepsilon_0]\times 100$.

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