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Synthesis and Properties of Nd-substituted Bismuth Titanate Polycrystalline Thin Films with *a-/b*-axes Orientations

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Polycrystalline $Bi_{4-x}Nd_xTi_3O_{12}$ (BNT, x=0.25, 0.50 and 0.75) thin films with preferred *a-/b*-axes orientations were grown on $IrO_2(101)/SiO_2/Si(100)$ substrates from chemical solution route. Insulating characters and ferroelectric properties in 250-nm-thick BNT (x=0.25) thin films with *a-/b*-axes orientations were investigated at room temperature. Fair range in leakage current density of $J=10^{-7}$~10^{-8} A/cm^2 at 100 kV/cm without the contribution from Bi_2O_2 blocking layers and well-defined value of remnant polarization ($2P_r$=37 μC/cm^2 at 400 kV/cm) were recorded. This range of J suggests the further possibility in reducing the film thickness suitable for low-voltage drive using *a-/b*-axes-oriented BLSF thin films.
Key words: BLSF, CSD, Orientation control, Polycrystalline film, Lanthanoids

1. INTRODUCTION

Bismuth layer structured ferroelectrics (BLSF) have been intensively investigated as the most competitive candidate materials for non-volatile ferroelectric random access memory (Nv-FeRAM) because of lead-free compositons and especially for high fatigue endurance [1]. Among wide structural and compositional range of BLSF, bismuth titanate $Bi_4Ti_3O_{12}$ (BIT) crystal has attracted particular interest due to that large value of spontaneous polarization P_s was reported [2]. In the pseudo-orthorhombic BIT unit with the lattice parameters a, b and c of 0.5448, 0.5410 and 3.284 nm, respectively [3], the ferroelectric activity appears with spontaneous polarization P_s of 50 and 4 μC/cm^2 along *a*- and *c*–axis, respectively [4]. Recently, in addition, modifications into BIT lattice by lanthanoids such as La, Nd and Sm have been conducted along the site engineering concept and remarkable improvement of ferroelectric polarization properties were reported [5-7]. Among them, $Bi_{4-x}Nd_xTi_3O_{12}$ (BNT) has been receiving great attention because of its superior value of remnant polarization in epitaxial and polycrystalline films [8-9]. Furthermore, the possibility of the enhancement in P_s by Nd substitution was suggested [10].

The *a-/b*-axes-oriented BIT-type epitaxial thick films have been achieved by utilizing bottom electrode layers of simple perovskite [11] and rutile-type structure [12], in order to align the polar-*a*-axis along the film normal. In addition, polycrystalline $Bi_{4-x}Pr_xTi_3O_{12}$ (BPT) thick films with polar-*a*-axis orientation grown on the oxidized IrO_2 layers exhibited almost complete value of spontaneous polarization measured in single crystalline BIT [13].

However, the BLSF films of *a-/b*-axes orientations with the film-thickness below 400 nm have never been reported so far [10-14], because Bi_2O_2 blocking layers allign parallel to the applied electric field [15], and the electric conductivity parallel to Bi_2O_2 layers is higher than that of perpendicular direction [16]. And also larger film thickness causes too high drive voltage. Therefore, it is significant to evaluate insulating character of BNT thin films with the electrical field parallel to the Bi_2O_2 layers using *a-/b*-axes orientations for practical applications.

In present work, we report the electrical properties in BNT polycrystalline thin films with *a-/b*-axes orientations and the film thickness of 250 nm.

2. EXPERIMENTAL PROCEDURE

(101)-oriented IrO_2 conducting oxide layers were deposited on $SiO_2/Si(100)$ wafers by reactive RF sputtering as bottom electrodes with the thickness of 100 nm. Coating solutions with nominal compositions $Bi_{4-x}Nd_xTi_3O_{12}$ (BNT, x=0.25, 0.50 and 0.75) were prepared by dissolving hygroscopic starting materials of Bi-acetate, Nd-acetate-hydrate and Ti-iso-propoxide (Aldrich, 99.99+, 99.9 and 99.999 % in purity, respectively) in anhydrous 2-methoxyethanol (99.8 %, Aldrich). The thermal decomposition behavior of the coating solution was examined in air with the rate of 10 °C·min^{-1} by thermo-gravimetry and differential thermal analysis [(TG-DTA), Thermoplus TG8120, Rigaku]. The coating solutions were spin-coated on the substrates, followed by a calcination process for direct crystallization of BNT on a hot-plate at 530~570 °C repeatedly. Subsequent annealing by rapid thermal annealing was performed at 720 °C for grain growth. The crystal structure and orientation behavior of deposited films were investigated by x-ray diffraction [(XRD), X'pert Pro, PANalytical] of CuK$_\alpha$ radiation. Film thickness and surface morphology were observed by field-emission scanning electron microscope [(FE-SEM), S-5000, Hitachi]. Electrical property measurements were conducted at room temperature with ferroelectric testing system [RT-66A, Radiant] and leakage current density measurement [4140B, Agilent

Technology], after depositting Pt top electrode layers with the diameter of 200 μm through metal mask.

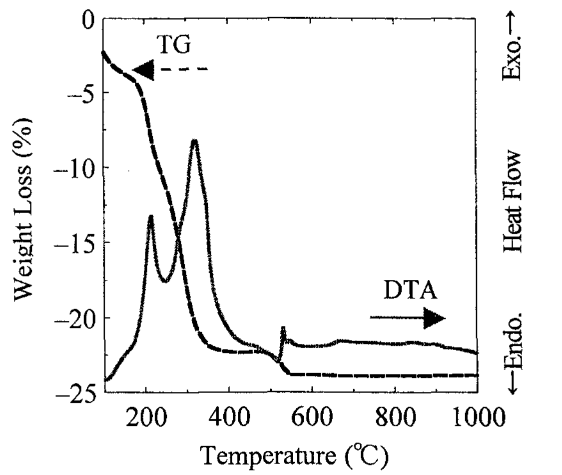

Fig.1: TG-DTA curves of BNT(x=0.25) powder.

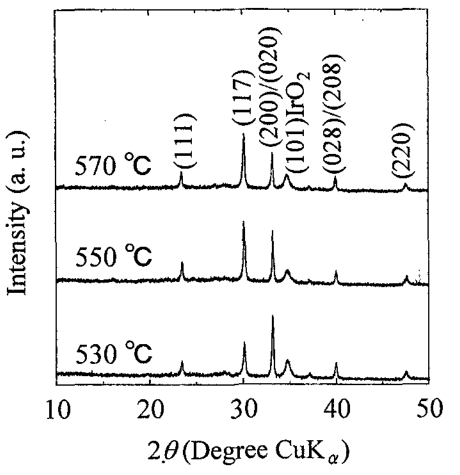

Fig.2: XRD profiles of $Bi_{3.75}Nd_{0.25}Ti_3O_{12}$ (T_{cr} = 530~570 °C) polycrystalline thin films deposited on (101)$IrO_2/SiO_2/Si$.

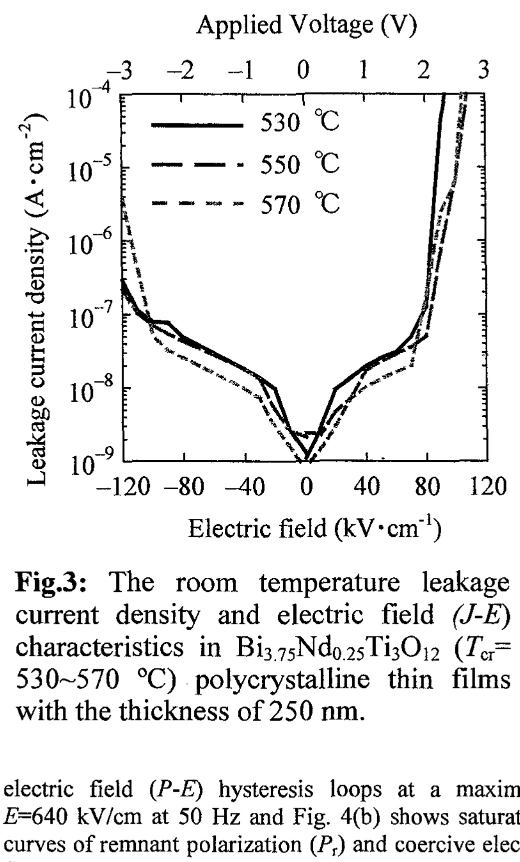

Fig.3: The room temperature leakage current density and electric field (J-E) characteristics in $Bi_{3.75}Nd_{0.25}Ti_3O_{12}$ (T_{cr}= 530~570 °C) polycrystalline thin films with the thickness of 250 nm.

3. RESULTS AND DUSSCUSSION

Figure 1 shows the TG-DTA curves of BNT(x=0.25) powders derived from chemical solution by drying at 150 °C in air. The TG-DTA curves revealed complete thermal decomposition of the solution was fulfilled at about 530 °C. Therefore, the crystallization temperature (T_{cr}) was decided over 530 °C for inheriting the atomic arrangement of IrO_2 layer during crystallization in BNT films.

Figure 2 shows the XRD profiles of BNT (x = 0.25) films with varying T_{cr}. The BNT film of T_{cr} = 530 °C exhibited dominant (200)/(020) orientations surpassing (117) orientation, while the films of higher T_{cr} = 550 and 570 °C exhibited higher intensity of (117) than those of (200)/(020). In addition, not shown here, but films of T_{cr} under 500 °C exhibited dominant (117) orientation with some c-axis orientation components. These different orientaion behaviors upon T_{cr} might derive from the rates of grain growth among (200)/(020) and (117) planes. At this range of T_{cr}, these rates of grain growth might be the most competitive, and which required very narrow process window within ΔT_{cr} = 20 °C for growing the preferred a-/b-axes-oriented BNT films.

Figure 3 shows the room temperature characteristics of leakage current density (J) as function of electric field (E) in BNT (x=0.25) thin films with the film thickness of 250 nm (solid , dashed and dotted lines respectively indicate T_{cr} = 530, 550 and 570 °C). All of 250-nm-thick BNT films with different orientations exhibited similarly fair values of J=10^{-7}~10^{-8} A/cm^2, although relatively higher J was observed in the film with a-/b-axes orientations. This range of J suggests the further possibility in reducing the film thickness suitable for low-voltage drive without the contribution on insulating property from Bi_2O_2 blocking units along the DC electrical field. Relatively poor values of DC breakdown field (~100 kV/cm), on the other hand, were observed. These values should be improved for practical applications.

Figure 4(a) shows the room temperature polarization electric field (P-E) hysteresis loops at a maximum E=640 kV/cm at 50 Hz and Fig. 4(b) shows saturation curves of remnant polarization (P_r) and coercive electric field (E_c) in BNT (x=0.25) thin film of T_{cr}=530 °C. Good saturation behaviors of P_r and E_c were achieved below 10 V. Since the thermal expansion coefficient of Si is much smaller than that of oxide ionic crystals, in-plane tensile strain is introduced during cooling and leads to a-/b-axes mixed orientations [17]. Considering the continuous saturation curves, the rotation of a-/b-domains was unlikely even at E>700 kV/cm. The somewhat poor value of observed P_r compared with that of BIT single crystals may be derived from a-/b-axes mixed orientations.

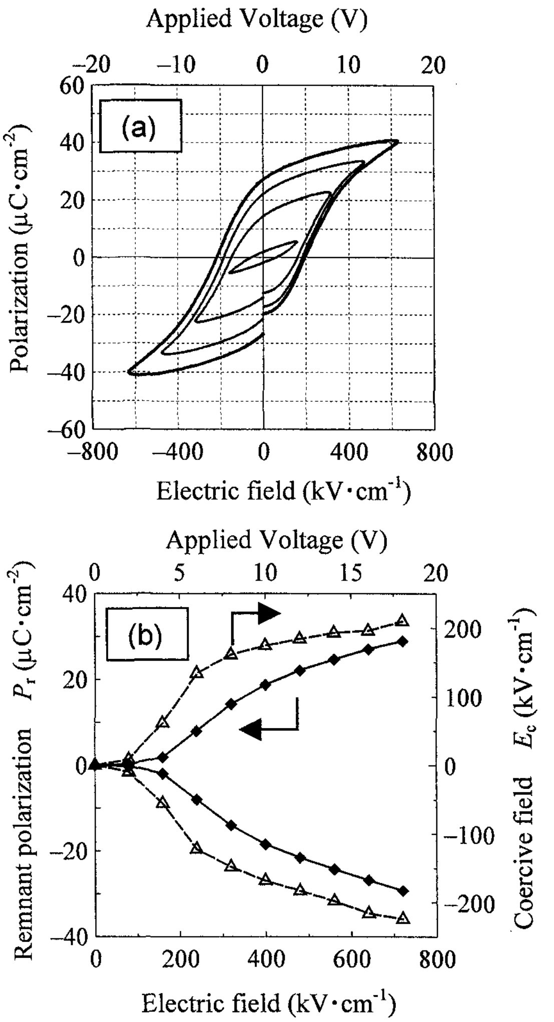

Fig.4: Room temperature ferroelectric properties in 250 nm-thick BNT thin film of x=0.25 and T_{cr}=530 °C. (a) *P-E* hysteresis loops and (b) Saturated curves of P_r and E_c.

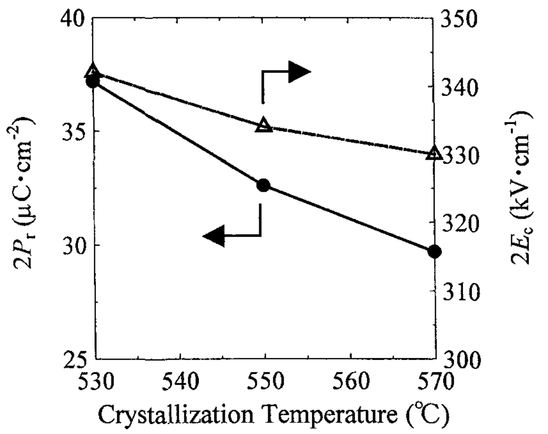

Fig.5: The T_{cr} dependence of measured $2P_r$ and $2E_c$ under the electric field of 400 kV/cm (10 V) at 50 Hz in 250 nm–thick BNT(x=0.25) films.

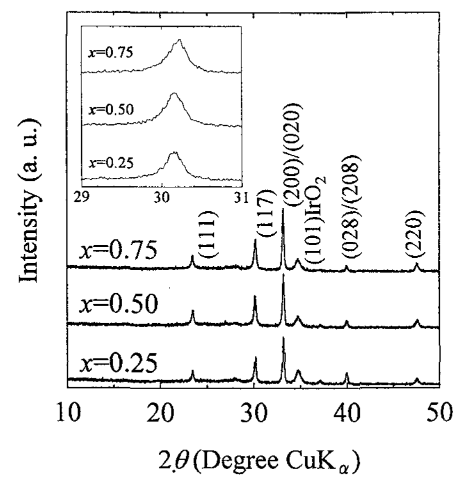

Fig.6: XRD profiles of 250 nm-thick BNT (x=0.25~0.75) polycrystalline thin films deposited on (101)IrO_2/SiO_2/Si.

Table.1: Ferroelectric polarization properties of 250 nm-thick BNT films.

x	$2P_r$ (μC·cm^{-2})	$2E_c$ (kV·cm^{-1})
0.25	37	337
0.50	31	320
0.75	25	296

Figure 5 shows T_{cr} dependence of $2P_r$ and $2E_c$ under E =400 kV/cm (10 V) at 50 Hz in 250 nm-thick BNT (x=0.25) thin films. The maximum values were $2P_r$=37 μC/cm^2 and $2E_c$=342 kV/cm for T_{cr}=530 °C, respectively. The values of $2P_r$ continuously decreased with increasing T_{cr}. This trend may reflect the orientation behavior upon T_{cr}.

Since most of reported works on BNT thin films have been concentrated in Nd-substitution content x in the range of $0.50<x<0.85$, [8-10,18,19] we also investigated ferroelectric properties in BNT thin films of x=0.50 and 0.75 with preferred *a*-/*b*-axes orientations

Figure 6 shows XRD profiles of BNT films with Nd-substitution content x. The inset shows the monotonous shift of (117) peak position toward higher 2θ with increasing x, indicating that Nd ion was incorporated into BIT lattice. Similar orientation behaviors of BNT thin films were achieved for all of x. This result suggests that the concept of long-range lattice matching between oblong (101) plane in rutile-type structure and *a*-*c*/*b*-*c* planes in BIT is valid for the present wide range of x=0.25-0.75. We found that, furthermore, the process window of crystallization for preferred *a*-/*b*-axes orientations expanded to ΔT_{cr}=50 and 60 ℃ for x=0.50 and 0.75.

Table I shows a list of $2P_r$ and $2E_c$ in 250 nm-thick BNT thin films of x=0.25, 0.50 and 0.75 under E=400 kV/cm (10 V). Similarly good saturation behaviors of P_r and E_c were achieved below 10 V for all x. The $2P_r$ and $2E_c$ values decreased continuously with increasing x. Based on thermal and structural analyses for BNT crystalline powders, we have observed monotonous decreases both in Curie temperature T_c and orthorhombic anisotropy a/b with increasing x. [20]. The observed monotonous decrease in $2P_r$ of BNT thin films with the increase of x may be related to the bulk properties of T_c and a/b in BNT crystal.

4. CONCLUSION

We synthesized polycrystalline BNT (x=0.25, 0.50 and 0.75) thin films with a-/b-axes orientations and the thickness of 250 nm on $IrO_2(101)/SiO_2/Si(100)$ substrates by chemical solution deposition method. By optimizing the heat treatment conditions, low leakage current density of J=10^7~10^{-8} A/cm^2 at 100 kV/cm was achieved in BNT (x=0.25) thin films without the Bi_2O_2 blocking units along the DC electrical field due to the a-/b-axes orientations. From the measurement of ferroelectric properties at room temperature, well-saturated P-E hysteresis loops and fair value of remnant polarization ($2P_r$=37 μC/cm^2 at 400 kV/cm) were measured in BNT thin films of x = 0.25. These results could promote the application of lead-free BLSF thin films with a-/b-axes orientations for Nv-FeRAM devices.

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