Ferroelectric properties of $\text{NaNbO}_3\text{--BaTiO}_3$ thin films deposited on $\text{SrRuO}_3/(001)\text{SrTiO}_3$ substrate by pulsed laser deposition

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$(\text{NaNbO}_3)_{1-x}(\text{BaTiO}_3)_x$ (NN- x BT) thin films with low BaTiO_3 (BT) concentrations x ($x = 0.05$ and 0.10) were fabricated on $\text{SrRuO}_3/(001)\text{SrTiO}_3$ (SRO/(001)STO) substrate by pulsed laser deposition (PLD). X-ray diffraction pattern (XRD) and transmission electron diffraction pattern (TED) showed that NN-0.10BT thin film was epitaxially grown on SRO/(001)STO substrate with a crystallographic relationship of $[001]_{\text{NN-}x\text{BT}} \parallel [001]_{\text{STO}}$. From reciprocal space maps, the lattice parameters of the out-of-plane direction of NN- x BT thin films became larger with an increase in BT concentration, although the lattice parameter of the in-plane was hardly changed by the BT concentration. The value of relative dielectric constant ϵ_r of the NN- x BT thin films were increased with BT concentration. The ϵ_r and the dielectric loss $\tan\delta$ of NN-0.10BT were 1220 and 0.02 at 1 kHz, respectively. The P - E hysteresis loops of the NN- x BT thin films showed clear ferroelectricity. Although the value of remanent polarization P_r decreased with the BT concentration, the behaviors of ϵ_r , P_r , and coercive electric field E_c of the NN- x BT thin films against the BT concentration accorded with those of NN- x BT ceramics, in which NN-0.10BT ceramics exhibited the largest piezoelectric property. Therefore, the NN-0.10BT thin film is expected to show high piezoelectricity.

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Key-words : NaNbO_3 , BaTiO_3 , Thin film, Ferroelectric, Piezoelectric, Pulsed laser deposition, Epitaxial

[Received August 28, 2008; Accepted October 16, 2008]

1. Introduction

The study of ferroelectric thin films is important for applications to micro sensors and actuators in micro-electro-mechanical systems (MEMS). $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) thin films have been widely used as piezoelectric materials due to their excellent piezoelectric properties.^{1,2)} However, PZT-based materials contain a large concentration of harmful lead in their components. From an environmental point of view, it is desirable to develop lead-free piezoelectric materials with high piezoelectric properties that are comparable with PZT. Therefore, such lead-free piezoelectric materials as $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN),³⁻¹²⁾ $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT)^{10,13-16)} and BaTiO_3 (BT)¹⁷⁻¹⁹⁾ have been studied for their good piezoelectric properties. However, the thermal stability of BNT-based materials is low, and their depolarization temperature ($< 200^\circ\text{C}$) is much lower than their Curie temperature. The biggest problem with KNN-based materials is the poor sinterability. Easy volatilization of K_2O at sintering temperature is one reason why fabricating a dense KNN is difficult. This poor sinterability affects the piezoelectricity. For example, piezoelectric strain constant (d_{33}) for KNN calcined in air is almost half of that fabricated by hot-press method.³⁾ Therefore, replacing KNbO_3 (KN) with another compound with similar structure and properties to KN would enable the fabrication of sintered ceramics with high piezoelectricity. Recently, Zeng et al. reported that $(\text{NaNbO}_3)_{1-x}(\text{BaTiO}_3)_x$ (NN- x BT) ceramics with low BT concentrations show large d_{33} values.¹⁴⁾ Among NN- x BT ceramics, NN-0.10BT with a Curie temperature of 230°C exhibits the largest d_{33} value of 147 pC/N. However, there are no reports about studies of NN- x BT thin films with low BT con-

centrations.

Previously, we reported that high-quality epitaxial NN thin films can be fabricated on $\text{SrRuO}_3/(001)\text{SrTiO}_3$ (SRO/(001)STO) substrate by pulsed laser deposition (PLD).²⁰⁾ The (001) SRO film was epitaxially grown on the (001)STO substrate, and the NN film was also epitaxially grown on the SRO/(001)STO substrate. The NN thin film showed that remanent polarization P_r and coercive electric field E_c were $6.4 \mu\text{C}/\text{cm}^2$ and $40 \text{ kV}/\text{cm}$, respectively.

In this study, we fabricated NN- x BT ($x = 0.05, 0.10$ and 0.15) thin films using similar PLD techniques and evaluated the NN- x BT thin films. The NN- x BT targets used in this study were prepared by a solid-state reaction method. We successfully fabricated NN-0.05BT and NN-0.10BT thin films on SRO/(001)STO substrate. The fabricated NN- x BT thin films were characterized by X-ray diffraction pattern (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), transmission electron diffraction pattern (TED) and atomic force microscopy (AFM). Additionally, the dielectric and ferroelectric properties were characterized to investigate the nature of the NN- x BT thin films.

2. Experimental

2.1 Preparation of NN- x BT targets

NN- x BT targets ($x = 0.05, 0.10$ and 0.15) were prepared by a solid-state reaction method. Na_2CO_3 (99.5%), BaCO_3 (99%), Nb_2O_5 (99.9%) and TiO_2 (99.9%) of high-purity grade were used as starting materials. They were mixed in a stoichiometric ratio of well-blended compositions by grinding for 1.5 h using an agate mortar and a pestle. The well-mixed powders were casted as a disk and calcined at 950°C for 4 h in air. The calcined samples were re-grinded by an agate mortar and a pestle for 1.5 h, followed by the compression moulding of the grinded powders.

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The pressed disks were fired at 1260°C for 1 h in air. The structures of the obtained NN-*x*BT targets were identified by powder X-ray diffraction analysis (Rigaku Co., RINT2000). The chemical compositions of the NN-*x*BT targets were analyzed by X-ray fluorescence (Rigaku Co., RIX2000). The densities of these targets were determined by their weights and volumes.

2.2 Deposition of SRO layer

The SRO bottom electrode was deposited on the (001)STO substrate by PLD (laser: Lambda Physik COMPex 201 and associated vacuum chamber: Neocera pulsed laser deposition systems) using a SRO ceramic target. The SRO target with a relative density of *ca.* 77% was prepared in accordance with previous work.²¹⁾ A KrF excimer laser with a UV wavelength of 248 nm was focused on the SRO target. Initially, the base pressure of the vacuum chamber was *ca.* 6.7×10^{-4} Pa. The following were the fabrication conditions of the SRO layer on the (001)STO substrate: laser repetition rate of 10 Hz, distance of 90 mm between the target and the substrate, energy density of 0.9 J/cm², O₂ partial pressure of *ca.* 27 Pa, substrate temperature of 750°C, and 10,000 laser shots. Fabricated SRO thin film with a thickness of *ca.* 150 nm was epitaxially grown on a (001)STO substrate.

2.3 Fabrication of NN-*x*BT thin films on SRO/(001)STO substrate

NN-*x*BT thin films were fabricated on the prepared SRO/(001)STO substrate by PLD using the prepared NN-*x*BT targets. As a laser source, a KrF excimer laser with a wavelength of 248 nm was used and also focused on the NN-*x*BT targets. After the chamber (in which the targets and substrates were fixed) was vacuated until *ca.* 6.7×10^{-4} Pa, NN-*x*BT thin films were deposited on the SRO/(001)STO substrate. The following were the deposition conditions: laser repetition rate of 10 Hz, distance of 90 mm between the target and the substrate, energy density of 0.9 J/cm², O₂ partial pressure of *ca.* 30 Pa, substrate temperature of 850°C, and 300,000 laser shots.

2.4 Characterization of NN-*x*BT thin films

The phases of the fabricated NN-*x*BT thin films were identified by XRD analysis. Crystallographic analysis of the thin films was performed from the results of a conventional $\theta/2\theta$ scan and a rocking curve. The reciprocal space map was recorded by high resolution X-ray diffraction (Philips X' Pert-MRD) to analyze the crystallographic relationship between the deposited NN-*x*BT thin films and the SRO/(001)STO substrate to determine the lattice parameters of the grown films.

The surfaces of the NN-*x*BT thin films were observed by AFM (SII SPA300 SPI-3700). Their microstructures were observed by SEM with ultimate analysis (SEM-EDX, JEOL Ltd., JSM-5410). The cross-sections of the thin films were also observed to determine their thickness. Additionally, the cross-sectional microstructures of the films were observed by TEM (JEOL Ltd., JEM-40000EX) operated at 400 keV, and part of the films was analyzed by TED.

Before investigations of the dielectric and ferroelectric properties, Pt upper electrodes with 0.07 cm² were deposited on the NN-*x*BT thin films by a conventional sputter technique. The ϵ_r and the $\tan\delta$ values were recorded using an inductance-capacitance-resistance (LCR) meter (Agilent 4284A). *P-E* hysteresis loops were recorded using a ferroelectric tester, TF2000FE (aixACCT Systems GmbH).

3. Results and discussion

3.1 Characterization of NN-*x*BT targets

Figure 1(a) shows the XRD patterns of the prepared NN-*x*BT ceramics targets (*x* = 0.05, 0.10 and 0.15) with NN (ICSD#23239) and BT (ICSD#30617) ceramics. NN and BT possess orthorhombic and tetragonal crystal systems, respectively. The obtained XRD patterns indicate that a single-phase perovskite structure was formed in all NN-*x*BT targets whose crystal structures is orthorhombic crystal and resembles NN. Figure 1(b) shows the expanded XRD patterns of the targets and NN and BT ceramics in the region of 2θ from 30° to 34°. The peaks that appeared at 32.1° and 32.5° are attributed to 020 and 114 diffractions, respectively. The peak of 114 diffraction was shifted to a lower angle with the increase in *x* (concentration of BT) and was near the peak of the 101 diffraction of BT. Moreover, the peak of the 114 diffraction was close to that of the 020 diffraction, and no difference between the diffraction angles of 114 and 020 was observed for the NN-0.10BT and NN-0.15BT targets. These changes against the addition of BT agree with the results reported by Zeng et al.¹⁴⁾ The above results show that NN-*x*BT solid solutions can be prepared. Table 1 shows the relative densities and the chemical composition ratio of NN-*x*BT targets. All targets have a high relative density of *ca.* 90%. Since the determined chemical compositions of the targets agree with the weighed composition, the desired NN-*x*BT targets (*x* = 0.05,

Fig. 1. (a) X-ray diffraction patterns: (I) NaNbO₃ (ICSD#23239, space group: *Pbcm*, lattice parameters: *a* = 0.5506 nm, *b* = 0.5566 nm, *c* = 1.552 nm), (II) NaNbO₃-0.05BaTiO₃ target, (III) NaNbO₃-0.10BaTiO₃ target, (IV) NaNbO₃-0.15BaTiO₃ target and (V) BaTiO₃ (ICSD#30617, space group: *P4mm*, lattice parameters: *a*, *b* = 0.3994 nm, *c* = 0.4038 nm), and (b) enlarged XRD patterns indicating shift of 020 and 114 diffractions.

0.10 and 0.15) with high density could be obtained.

3.2 Structural analysis of fabricated NN-*x*BT thin films on SRO/(001)STO substrate

We fabricated NN-*x*BT (*x* = 0.05, 0.10 and 0.15) thin films. However, we could not fabricate the NN-0.15BT thin film with good quality in crystallinity. Therefore, in the present study we investigated the crystal structures and the dielectric and ferroelectric properties the NN-0.05BT and NN-0.10BT thin films. **Figure 2** shows the $2\theta/\theta$ XRD patterns of the NN-*x*BT thin films deposited on the SRO/(001)STO substrate. The large peaks near $2\theta = 23^\circ$ and 46° (●) in the two thin films are attributed to the 001 and 002 diffractions of the pseudo-tetragonal perovskite structure, respectively. Some small peaks attributed to the other diffractions of the pseudo-tetragonal perovskite were observed in these films. The peaks appeared at 32° (■) are assigned to the 110 diffraction, and it appears at 39° , 111 diffraction. The intensities of the 001 and 002 diffractions of the NN-*x*BT thin films are much larger than those of the other diffractions, and the ratio of the diffraction intensity of both NN-*x*BT thin films is quite different from that of these ceramics, as shown in Fig. 1. These indicate that the NN-*x*BT thin films are grown with 001 orientation. The peaks, which appeared at 16° and 29° (▼), are attributed to an impurity phase and can be attributed to a pyrochlore phase, such as Na₂Nb₄O₁₁.²²⁾

The rocking curves were recorded to evaluate the crystallinity of these thin films. **Figure 3** shows the rocking curves of the NN-*x*BT layers on the SRO/(001)STO substrate. The obtained

values of the full width at half maximum (FWHM) of NN-0.05BT and NN-0.10BT are 0.24° and 0.19° , respectively. These results indicate that the fluctuations of the crystalline orientation of these thin films are very small. Additionally, the fabricated NN-0.10BT thin film has higher crystallinity than the NN-0.05BT thin film.

The reciprocal space maps were also recorded to analyze the crystallographic relationship between the fabricated NN-*x*BT films and the SRO/(001)STO substrate and to determine the lattice parameters of the thin films. **Figure 4** shows the XRD reciprocal space map of the NN-0.05BT and NN-0.10BT films near the 103 diffraction of the STO substrates. Clear spot patterns of the 103 diffraction of NN-0.05BT, NN-0.10BT, and STO were observed. Any diffractions derived from the SRO bottom electrode could not be clearly identified. SRO has a pseudocubic perovskite structure with a lattice parameter of $a = 0.3910$ nm, which is very close to the lattice constant of cubic STO ($a = 0.3905$ nm). Additionally, the SRO layer is much thinner than the other films. Therefore, the SRO spot overlaps the STO substrate. This result agrees with our previous report.⁷⁾ In Fig. 4, the Q_x values of the 103 spot for the NN-0.05BT and NN-0.10BT thin films almost correspond with those of the STO substrate. Therefore, the *a*-axis lengths of the pseudo-tetragonal unit cells of the NN-0.05BT and NN-0.10BT thin films equal the STO substrate. On the other hand, the *c*-axis lengths of these films are larger than the STO substrate. The obtained pseudo-tetragonal lattice parameters of the NN-0.05BT are $a_p = 0.3907$ nm and $c_p = 0.3927$ nm, and those of the NN-0.10BT are $a_p = 0.3908$ nm and $c_p = 0.3936$ nm. The lattice parameters of the NN powder are a ($= b$) = 0.3915 nm and $c = 0.3880$ nm. From the XRD results in Fig. 1, the lattice parameters of NN-*x*BT ceramics are gradually enlarged with an increase in the BT concentration. If the deposited NN-*x*BT thin films do not come under the influence of the substrate, the a_p and c_p of the NN-*x*BT films must become larger than those of the bare NN. However, the a_p values of the NN-*x*BT thin films do not change despite BT addition to NN.

Table 1. Relative Densities and Chemical Composition Ratios of NN-*x*BT Targets

Target	Relative density (%)	(Na + Ba)/(Nb + Ti)	Ba/(Na + Ba)
NN-0.05BT	87.1	1.11	0.06
NN-0.10BT	94.2	1.08	0.11
NN-0.15BT	92.5	1.06	0.16

Fig. 2. X-ray diffraction patterns: (a) NN-0.05BT and (b) NN-0.10BT thin films deposited on SRO/(001)STO substrates (00*X* diffraction of the NN-*x*BT thin films are expressed by “●” and the other diffractions of the NN-*x*BT thin films are expressed by “■”).

Fig. 3. Rocking curves of 002 diffraction: (a) NN-0.05BT and (b) NN-0.10BT thin films deposited on SRO/(001)STO substrates.

Therefore, the a_p values of the NN- x BT thin films are restricted to the STO substrate. On the other hand, the c_p values of the NN- x BT thin films are enlarged in proportion to the BT concentration. From the above results, we propose the following growth

mechanism of NN- x BT films. The SRO/STO substrate strongly affects the NN- x BT layer. Therefore, the NN- x BT thin film has an in-plane lattice constant of *ca.* 0.3907 nm, whose value agrees with the lattice constant of STO, 0.3905 nm. Since this lattice constant is smaller than that of NN- x BT ceramics, the NN- x BT thin film grows in the out-plane direction with a large c_p value to keep the volume of unit cell. Therefore, the increase in the lattice parameter with the BT concentration for NN- x BT ceramics affects only the c_p value of the NN- x BT thin film.

3.3 Surface and cross-sectional profiles of NN- x BT thin films

Figure 5 shows the SEM surface images of the NN-0.05BT and NN-0.10BT thin films. The SEM surface image of the NN-0.05BT thin film showed that the surface has several asperities with an elongate shape on the smooth surface. On the other hand, the surface of the NN-0.10BT thin film has many irregular asperities. We also performed AFM measurement to investigate the surface morphologies. The obtained AFM images of these thin films resemble the SEM surface images of these films, as shown in **Fig. 6**. The root mean square (RMS) roughness of the NN-0.05BT and NN-0.10BT thin films in the area of $10\ \mu\text{m} \times 10\ \mu\text{m}$ are 33 and 53 nm, respectively. The RMS roughness hardly changes with BT concentration. We previously reported that the NN thin film deposited on SRO/(001)STO substrate by PLD has a RMS roughness of 4.0 nm.²⁰⁾ Therefore, the surface smoothness of the thin film degrades by BT doping.

Figure 7 shows the SEM cross-sectional images of the NN-0.05BT and NN-0.10BT thin films deposited on the SRO/(001)STO substrates. The thicknesses of the NN-0.05BT and NN-0.10BT layers were 2.6 and 3.5 μm , respectively. Additionally, the TEM cross-sectional image of the NN-0.10BT thin film deposited on the SRO/(001)STO is shown in **Fig. 8**. The thick-

Fig. 4. X-ray diffraction reciprocal space maps: (a) NN-0.05BT and (b) NN-0.10BT thin films near STO substrate 103 reciprocal lattice point. Diffraction of SRO layer cannot be observed because it is very thin and overlaps with STO substrate.

Fig. 6. AFM images: (a) NN-0.05BT and (b) NN-0.10BT thin films deposited on SRO/(001)STO substrates.

Fig. 5. SEM surface images: (a) NN-0.05BT and (b) NN-0.10BT thin films.

Fig. 7. SEM cross-sectional images: (a) NN-0.05BT and (b) NN-0.10BT thin films deposited on SRO/(001)STO substrates.

Fig. 8. TEM cross-sectional image of NN-0.10BT thin film deposited on SRO/(001)STO substrate.

ness of the SRO layer was 130 nm. The NN-0.10BT layer has crystalline disorder, in which is especially concentrated near the substrate. This crystalline disorder reflects the in-plane stress of the NN-0.10BT thin film. **Figure 9** shows the TED pattern of the NN-0.10BT thin film at the bright circle in Fig. 8. Weak superlattice spots in the perpendicular direction to the substrate and strong pseudo-tetragonal basic spots can be clearly shown. These superlattice peaks cannot be detected by conventional XRD. The NN-0.10BT has a perovskite structure that resembles NN. Perovskite NN has an orthorhombic unit cell and lattice constants of $c = 1.552 \text{ nm}$ ($4 \times c_p$). This TED pattern indicates that the c -axis of the NN-0.10BT layer is vertical for the SRO/(001)STO substrate. The crystal system of the NN-0.10BT is regarded as a tetragonal system with $a = a_p$ and $c = 4 \times c_p$. The NN-0.10BT thin film epitaxially grows on SRO/(001)STO substrate with a crystallographic relationship between NN-0.10BT and STO with $[001]_{\text{NN-0.10BT}} \parallel [001]_{\text{STO}}$. This result accompanies that of the bare NN thin film.²¹⁾

3.4 Dielectric and ferroelectric properties of NN- x BT thin films

Table 2 shows relative dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of NN-0.05BT and NN-0.10BT thin films with the previously reported NN thin film data.²⁰⁾ These values were determined at 1 kHz. Additionally, the ϵ_r and the $\tan\delta$ values of NN, NN-0.05BT, and NN-0.10BT ceramics are also listed for reference. The ϵ_r and the $\tan\delta$ values of the NN-0.05BT thin film were 556 and 0.02, and those of the NN-0.10BT thin film were 1220 and 0.02, respectively. Compared with the values of the NN thin film ($\epsilon_r = 252$ and $\tan\delta = 0.03$), the value of ϵ_r increased with

Fig. 9. Transmission electron diffraction pattern of NN-0.10BT thin film surrounded by bright circle shown in Fig. 8.

an increase in BT concentration. On the other hand, the value of $\tan\delta$ varied only slightly with BT concentration. Additionally, we compared the dielectric properties of the thin films with those of ceramics. Although the NN, NN-0.05BT, and NN-0.10BT thin films had slightly larger ϵ_r values than ceramics, the ϵ_r behavior of the BT concentration in the thin films is similar to that in the ceramics. Therefore, the NN- x BT thin films are expected to exhibit similar ferroelectric properties to NN- x BT ceramics.

Figure 10 shows the P - E hysteresis loops of the NN-0.05BT and NN-0.10BT thin films with the previously reported loop of the NN thin film.²⁰⁾ The P - E hysteresis loops were recorded at room temperature at 1 kHz. The obtained P_r and E_c values of these thin films are summarized in Table 2, and the P_r and the E_c values of NN, NN-0.05BT, and NN-0.10BT ceramics are also listed in Table 2 for reference. The P_r value decreased with an increase in BT concentration. On the other hand, the NN-0.05BT thin film had the largest E_c value of 53 kV/cm, and the E_c value decreased with an increase in BT concentration. The P_r and E_c behaviors of these thin films for BT concentration accord with those of ceramics. Therefore, we concluded that the fabricated NN- x BT thin films show the ferroelectricity as well as the NN- x BT ceramics. Zeng et al. reported that NN-0.10BT ceramics shows the largest piezoelectric constant value ($d_{33} = 147 \text{ pC/N}$) in the NN- x BT ceramics system while the remnant polarization decreases and the dielectric constant increases with an

Table 2. Dielectric and Ferroelectric Properties of NN-*x*BT thin Films. ϵ_r , $\tan\delta$, P_r , and E_c Values of NN, NN-0.05BT, and NN-0.10BT Ceramics are also Listed for Reference

Sample	Thin film				Ceramics			
	ϵ_r	$\tan\delta$	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	ϵ_r	$\tan\delta$	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
NN	252 ²⁰⁾	0.03 ²⁰⁾	6.4 ²⁰⁾	40 ²⁰⁾	172 ²³⁾	0.04 ²³⁾	28 ²³⁾	16 ²³⁾
NN-0.05BT	556*	0.02*	5.1*	53*	300 ¹⁴⁾	0.027 ¹⁴⁾	23 ¹⁴⁾	25 ¹⁴⁾
NN-0.10BT	1220*	0.02*	3.1*	22*	1000 ¹⁴⁾	0.015 ¹⁴⁾	16 ¹⁴⁾	21 ¹⁴⁾

* this work

Fig. 10. P - E hysteresis of NN (line), NN-0.05BT (solid), and NN-0.10BT (●) thin films deposited on SRO/(001)STO substrates.

increase in BT contained amount.²³⁾ Thus, the NN-0.10BT thin film is expected to exhibit large piezoelectric properties because the behaviors of the dielectric and ferroelectric properties for BT concentration in the NN-*x*BT thin films correspond with those in the NN-*x*BT ceramics.

4. Conclusion

NN-0.05BT and NN-0.10BT thin films with good quality in crystallinity were fabricated on SRO/(001)STO substrate by PLD and the crystal structure and the dielectric and ferroelectric properties were studied. Rocking curve analysis showed that NN-0.10BT thin film has the best crystallinity in the NN-*x*BT thin films. An X-ray diffraction reciprocal space map exhibited that the a_p of the NN-0.05BT and the NN-0.10BT layers correspond to that of the STO substrate and that c_p increases with an increase in BT concentration. Therefore, the increase in the lattice parameter with BT concentration in the NN-*x*BT ceramics only affects the c_p value of the NN-*x*BT thin film. Additionally, a TED pattern showed that NN-0.10BT thin film was epitaxially grown on the SRO/(001)STO substrate with a crystallographic relationship of $[001]_{\text{NN-}x\text{BT}} \parallel [001]_{\text{STO}}$. The fabricated NN-0.05BT and NN-0.10BT thin films showed ferroelectric properties and the dielectric and ferroelectric property behaviors for BT concentration in the NN-*x*BT thin film system accord with those in the NN-*x*BT ceramics system. Therefore, it is expected that NN-0.10BT thin film, which has the best crystallinity in these thin films, will exhibit large piezoelectric properties.

Acknowledgments This work was supported in part by a grant from the High-Tech Research Center Program for private universities

from the Japan Ministry of Education, Culture, Sports, Science and Technology, and by Ryukoku University Science and Technology fund. The authors are grateful to Dr. Y. Matsuo for useful discussion.

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