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Ferroelectric properties of Nd-substituted bismuth titanate thin films processed at low temperature

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ABSTRACT Nd-substituted bismuth titanate $Bi_{3.54}Nd_{0.46}Ti_3O_{12}$ (BNT) thin films were prepared on $(111)Pt/Ti/SiO_2/Si$ substrates by a sol–gel method. The BNT thin films processed at a low annealing temperature of ~ 600 °C showed good ferroelectric properties. The randomly oriented BNT single phases and the improved ferroelectric properties were confirmed by X-ray diffraction and polarization–electric field hysteresis loops, respectively. The remanent polarization of the BNT thin films is $64\,\mu C/cm^2$, which is larger than that of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films. After 10^{10} read/write switching cycles, the effective non-volatile charges showed no polarization fatigue. Regardless of the low annealing temperature of 600 °C, the BNT thin films had good ferroelectric properties with high remanent polarizations and strong fatigue resistances.

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1 Introduction

For optics, electro-optics and non-volatile ferroelectric random access memory (FeRAM) device applications, much attention has been paid to ferroelectrics [1]. $Pb(Zr_xTi_{1-x})O_3$ (PZT)-, $SrBi_2Ta_2O_9$ (SBT)- and $Bi_4Ti_3O_{12}$ (BIT)-based ferroelectric materials are the most promising candidates for FeRAM applications [2–9]. PZT has advantages because of its high remanent polarization and low processing temperature; however, PZT suffers from severe polarization fatigue at the Pt electrode after read/write switching cycles. Although SBT has a good fatigue resistance, high processing temperatures above 750 °C are an obstacle to practical applications. Recently, the ferroelectric and electrical properties of BIT-based ferroelectric thin films have been widely studied for FeRAM applications.

In the general formula of the Bi-layered perovskite structure $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$ ($x = 3$), A and B sites of BIT were occupied by Bi and Ti ions, respectively. Thus the BIT consists of three perovskite-like units $(Bi_2Ti_3O_{10})^{2-}$, sandwiched between bismuth oxide $(Bi_2O_2)^{2+}$ layers. The ferroelectric properties are known to arise from the perovskite block, $(Bi_2Ti_3O_{10})^{2-}$. BIT materials have a high leakage current and domain pinning due to defects, which prevent their FeRAM application. To improve the ferroelectric properties and fatigue resistance, effects of ion doping of BIT thin films substituted by lanthanide ions such as La^{3+}, Nd^{3+}, Sm^{3+} and Gd^{3+} ions for the Bi^{3+} ion were studied [10–15]. Currently, much attention has been paid to Nd-substituted BIT (BNT) thin films due to their highly enhanced remanent polarization.

However, it has been reported that BIT-based ferroelectric thin films can be obtained at the high annealing temperatures of 650–750 °C [3, 5–8, 10–14]. For practical applications in FeRAMs, it is necessary to have a low annealing temperature. In this work, the BNT thin films prepared by a sol–gel method were annealed at low temperatures. Then, the ferroelectric properties were investigated by P–E hysteresis loops and polarization fatigue measurements.

2 Experimental procedures

$Bi_{3.54}Nd_{0.46}Ti_3O_{12}$ (BNT) thin films were deposited on a $Pt(111)/Ti/SiO_2/Si$ substrate by a sol–gel spin-coating process. Bismuth nitrate $[Bi(NO_3)_3 \cdot 5H_2O]$, neodymium nitrate hydrate $[Nd(NO_3)_3 \cdot 6H_2O]$ and titanium isopropoxide $[Ti[OCH(CH_3)_2]_4]$ were used as starting materials for Bi, Nd and Ti, respectively. Bismuth nitrate (15 mol. % excess) and neodymium nitrate were dissolved at 40 °C in 2-methoxyethanol $[CH_3OCH_2CH_2OH]$. Separately, titanium isopropoxide was dissolved in 2-methoxyethanol in a glove box, and acetylacetone $[CH_3COCH_2COCH_3]$ was used as a chelating agent. The titanium solution had been added to the bismuth–neodymium solution by continuous stirring and the final mixture was stirred for an additional 2 h. The concentration of BNT in the final solution was adjusted to approximately 0.1 M for an optimum deposition. For preparing the films, the $Pt(111)/Ti/SiO_2/Si$ substrate was spin coated with the prepared solution at a speed of 3500 rpm for 20 s. After drying at room temperature for 5 min, the wet film was preheated over a hotplate at 150 °C for 5 min and 350 °C for 5 min. The coating and preheating process was repeated several times to obtain the desired film thickness. Then, the film was heated by a rapid thermal annealing (RTA) process at 500 °C for 3 min. Finally, the BNT films were annealed by a RTA process at 580–600 °C. The crystal structures and grain

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morphologies of BNT single phases were investigated by X-ray diffraction (XRD, Philips, APD system) and scanning electron microscopy (SEM, Hitachi, S-2400), respectively. For the electrical measurements, Au top electrodes with an area of 7.85×10^{-5} cm^2 were deposited by thermal evaporation to form metal–ferroelectric–metal capacitors. The ferroelectric hysteresis loops and switching polarization fatigue were investigated by a ferroelectric tester (Radiant, RT66A).

3 Results and discussion

Figure 1 shows the XRD patterns of the BNT thin films annealed at 600 °C for 3, 5 and 10 min each. To compare the phases between random grain orientation and partial *c*-axis orientation, the powder XRD pattern with randomly oriented phase was investigated, which shows various (*hkl*) peaks as well as weak (00*l*) peaks. The XRD peaks were indexed according to the standard powder XRD data of the BIT. XRD peaks such as (00*l*) and (117) agree with previous results [3, 5, 6, 8–10], which indicated that well-crystallized BNT thin films with bismuth-layered perovskite structure were obtained. There are differences in the intensity ratio between the (006) peak and the (117) peak. As the annealing time increased from 3 to 10 min, the (00*l*) peaks became stronger, which suggests that the grains of BNT thin films tend to the *c*-axis orientation. Then, the degree of *c*-axis orientation is calculated to be 20% for 3 min, 33% for 5 min and 43% for 10 min by the reference $I(006)/(I(006) + I(117))$ formula [16, 17] involving the XRD peak intensities. This means that for short annealing times the randomly oriented BNT phase was the dominant phase due to the low degree of *c*-axis orientation.

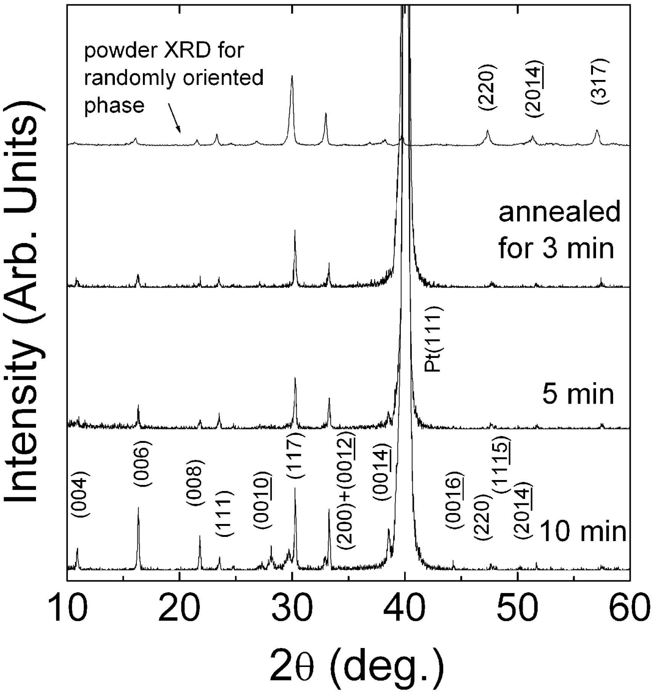

FIGURE 1 XRD patterns of the $Bi_{3.54}Nd_{0.46}Ti_3O_{12}$ thin films annealed at 600 °C for 3, 5 and 10 min and powder XRD pattern with randomly oriented phase

Figure 2 shows the surface and cross-sectional morphologies of the BNT thin films annealed at 600 °C for 3, 5 and 10 min each. The film thicknesses were estimated to be 500 nm from the cross-sectional view, as shown in Fig. 2d. The BNT thin films were composed of platelet-like grains. As the annealing time increased, the grain size also increased. However, the surface was homogeneous and uniform due to the small grains, particularly for the short annealing time of 3 min.

The *P–E* hysteresis loops were measured at applied voltages ranging between 8 and 19 V. Figure 3a shows the *P–E* hysteresis loops of the BNT thin films annealed at 600 °C and also (inset) shows that of the BNT thin film annealed at 580 °C. The well-saturated *P–E* hysteresis loops were obtained at an annealing temperature of 580 °C, which is similar to that of the BNT thin film annealed at 600 °C. Figure 3b shows the remanent polarization ($2P_r$) and the coercive field ($2E_c$) as a function of the applied electric field. The $2P_r$ values rapidly increased with an increasing applied electric field and became saturated at ∼ 300 kV/cm, for which the $2P_r$ and the $2E_c$ values were 64 μC/cm^2 and 146 kV/cm at 250 kV/cm, respectively. The measured remanent polarization of 64 μC/cm^2 is higher than that of previously studied $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films [3, 5, 6, 8, 9] annealed at the high temperatures of 650–750 °C. According to previous reports, BIT single crystals were strongly anisotropic in nature in, for example, the polarization and the coercive field [6, 18]. The *a*-axis polarization (45–50 μC/cm^2) was larger than the *c*-axis polarization (4.5 μC/cm^2). Since the polarization along the *c* axis is very small, the higher remanent polarization of the BNT thin film can be explained by the increment of the random orientation.

Figure 4 shows the fatigue characteristics between switchable (P_{sw}) and non-switchable polarizations (P_{ns}) as a function of switching cycles. The fatigue measurement was made with an electric field of 240 kV/cm at 1-MHz frequency. The BNT thin film showed no degradation up to 10^{10} switching cycles. The value of the non-volatile charge between the switching and non-switching polarizations ($P_{sw} - P_{ns}$ or $-P_{sw} - P_{ns}$) was approximately 34 μC/cm^2, and this value remained up to 10^{10} switching cycles. Regardless of the low annealing temperature and the short annealing time, the measured non-volatile charge of 34 μC/cm^2 was the highest value. According to previous research, the switching polarization of a ferroelectric thin film was affected by the charge aggregation on the domain wall [5, 18]; then, polarization fatigue was caused by the aggregated charge screen of the electric field. Drift and aggregation of oxygen vacancies have been proposed to result in polarization fatigue. Thus, BIT thin films suffer from high leakage current and domain pinning due to defects, leading to the polarization fatigue of a small remanent polarization after read/write cycles. However, La-modified BIT has a high remanent polarization. Also, the fatigue was improved by replacing an unstable Bi ion with a La ion at the A site [3]. The role of A-site substitution was to replace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen vacancies that act as space charges. The BNT thin films processed at the low annealing temperature were considered to have high remanent polarizations and good fatigue resistances as good as those of the BLT thin film.

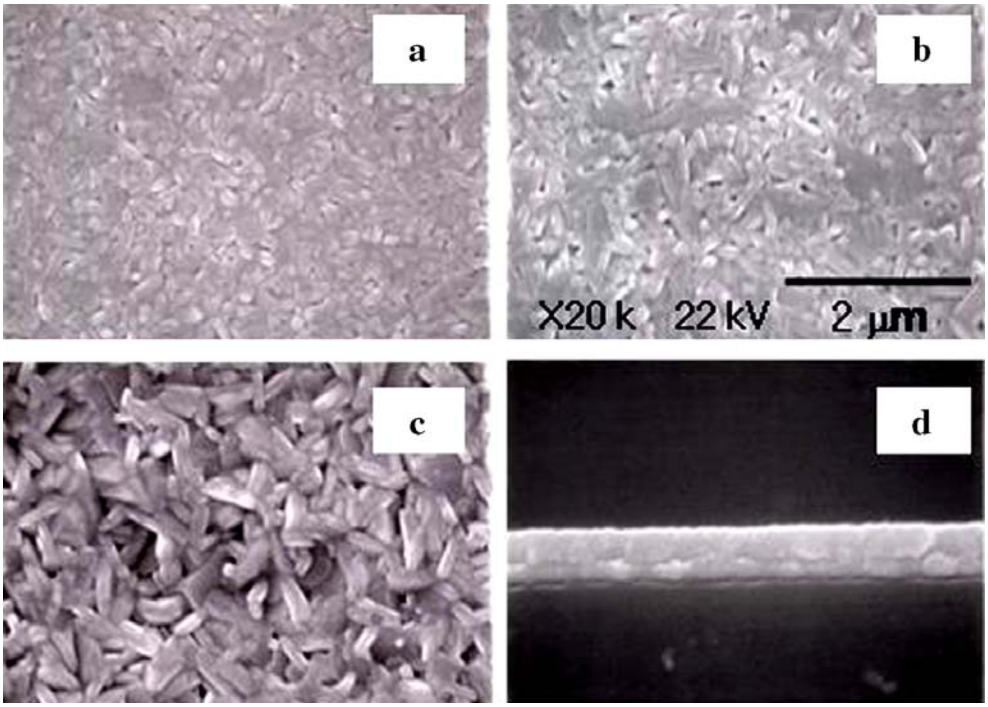

FIGURE 2 SEM images of the $Bi_{3.54}Nd_{0.46}Ti_3O_{12}$ thin films annealed at 600 °C for 3, 5 and 10 min

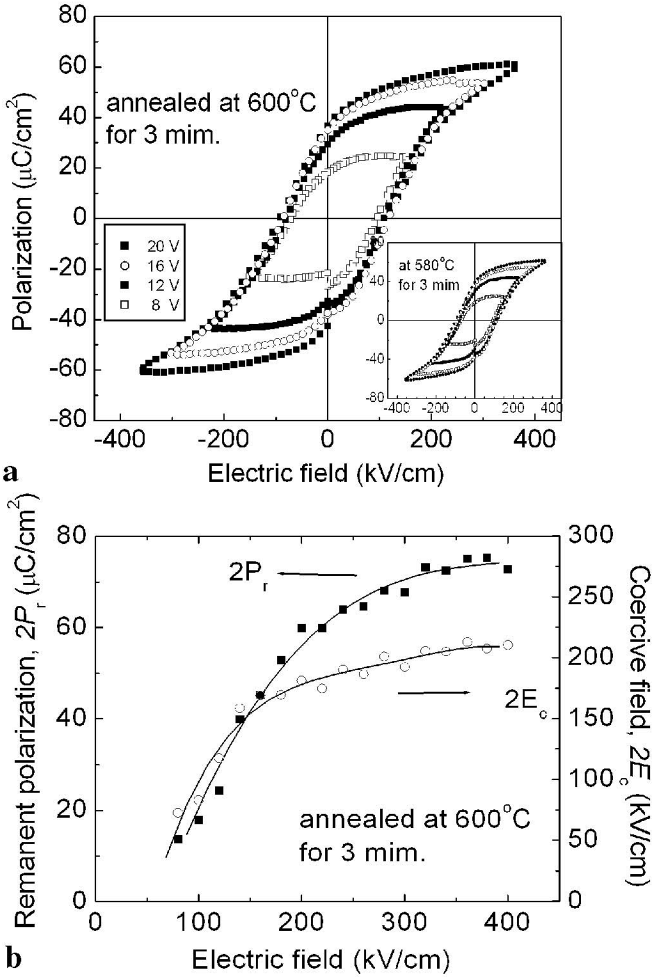

FIGURE 3 **a** P–E hysteresis loops of the $Bi_{3.54}Nd_{0.46}Ti_3O_{12}$ thin films annealed at 600 °C and **b** the remanent polarization ($2P_r$) and the coercive field ($2E_c$)

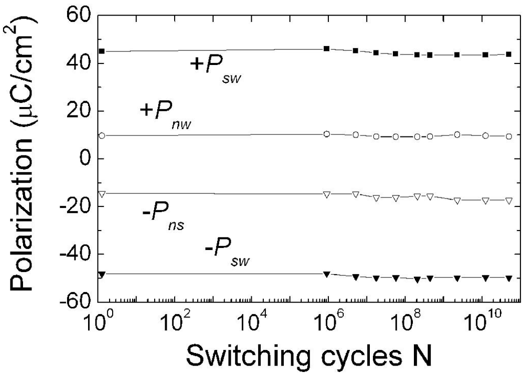

FIGURE 4 The effective polarization between switchable P_{sw} and non-switchable polarizations P_{sw} as a function of switching cycles

Thus, these results imply that there was little accumulation of vacancies at interfaces, space-charge buildup and domain pinning [6, 18].

To improve ferroelectric properties, BNT thin films were prepared by a sol–gel method, metalorganic decomposition, magnetic sputtering and pulsed-laser deposition [3, 5–7]. The BNT thin films were crystallized into Bi-layered perovskite structures at the higher temperatures of 600–750 °C. Then, the high remanent polarizations ($2P_r$) [12–14] were reported to be $\sim 100\,\mu C/cm^2$, $50\,\mu C/cm^2$ and $40\,\mu C/cm^2$, and larger than that of BLT with $24\,\mu C/cm^2$ [3]. However, the remanent polarization ($2P_r$) of BNT thin films annealed at 600 °C was reported to be $14\,\mu C/cm^2$, which was relatively low [15]. Thus, the ferroelectric properties of BNT thin films strongly depended on the annealing temperature, deposition method, substrate, Nd composition and grain orientations [10–15]. In this work, the BNT thin films prepared by the sol–gel method were annealed at the low temperature of 580–600 °C; the remanent polarization and fatigue resistance were better than those of the BLT thin film annealed at high temperatures. The improvement of the ferroelectricity can be attributed to the random *c*-axis orientation. In addition to the grain orientations, the decrease of defects such as bismuth and oxygen vacancies may have improved the ferroelectric properties by Nd doping. Regardless of the low annealing temperature of 600 °C, the BNT thin films had good ferroelectric properties with high remanent polarization and fatigue resistance.

4 Conclusions

$Bi_{3.54}Nd_{0.46}Ti_3O_{12}$ (BNT) thin films annealed at the low temperature of 580–600 °C were successfully prepared by a sol–gel method. For a short annealing time by the RTA process, BNT thin films were crystallized with random grain orientation. The remanent polarization ($2P_r$) and the coercive field ($2E_c$) were $64\ \mu C/cm^2$ and 146 kV/cm at an electric field of 250 kV/cm, respectively. The remanent polarization was highly improved by Nd substitution of BIT. The polarization fatigue showed no degradation up to 10^{10} switching cycles. The non-volatile charge of $34\ \mu C/cm^2$ remained up to 10^{10} switching cycles. The BNT thin films processed at low temperature had good ferroelectric properties for FeRAM applications.

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