Ferroelectric properties of neodymium-doped Bi$_4$Ti$_3$O$_{12}$ thin films crystallized in different environments

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Abstract

Neodymium (Nd)-doped Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ (BNT) ferroelectric films have been deposited on Pt/Ti/SiO$_2$/Si substrates by a sol–gel process and crystallized in nitrogen, air and oxygen environments, respectively. The crystallization environment was found to be important in determining the crystallization and ferroelectric properties of the BNT films. The film crystallized in nitrogen at a relatively low temperature of 650 °C, and exhibits excellent crystallinity and ferroelectricity with a remanent polarization of $2P_r = 63.6$ μC/cm$^2$, a coercive field of 130 kV/cm and a fatigue-free characteristic. While the films annealed in air and oxygen, they did not show good crystallinity and ferroelectricity until they were annealed at 710 and 730 °C, respectively. A correlation between the remanent polarization and dielectric constants of the BNT films has been observed.

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1. Introduction

Recently, rare-earth lanthanides doped Bi$_4$Ti$_3$O$_{12}$ (BIT) with Bi-layered perovskite structure has been studied intensively for potential applications in ferroelectric random access memories (FeRAM) due to its relatively low crystallization temperature, good fatigue endurance and larger spontaneous polarization compared to SrBi$_2$Ta$_2$O$_9$ (SBT)-based films [1–5]. However, in order to replace the conventional lead-based materials, which are the most widely used material today for FeRAMs, a lower-processing temperature, large remanent polarization and inherent high-fatigue endurance are required.

A chemical solution deposition (CSD) method has been proven effective to produce high-quality rare-earth lanthanides doped Bi$_4$Ti$_3$O$_{12}$ (BIT) films. As reported by others, the bismuth-based perovskite films prepared by CSD method are crystallized either in air or in oxygen environment, and the crystallization temperature is generally near 700 °C in order to get high-quality films [2–4,6–10]. A high-temperature oxygen ambient in the crystallization process may cause oxidation and expansion of diffusion barrier for films deposited on Pt/Ti/SiO$_2$/Si substrates [11]. An oxygen-free ambient can prevent these phenomena. Ogata and Nagata [11] have reported that SBT films can be crystallized in a N$_2$ ambient, and the electric properties of SBT films are comparable to those annealed in oxygen. Cho et al. [12] reported that, at relatively low temperature (650 °C), BIT thin film annealed in N$_2$ ambient almost completely crystallized, while the film annealed in air showed partial crystallization and was amorphous after annealed in O$_2$. These studies indicated that BIT films could be crystallized in N$_2$ atmosphere at lower temperature than in air or O$_2$. However, there have been few reports up to now about the effect of annealing environment on the structure and ferroelectric properties of rare-earth-cation-doped BIT films. In this paper, we reported the environmental effect for the Nd-doped BIT (BNT) system, which exhibits excellent ferroelectric properties among the rare-earth lanthanides doped Bi$_4$Ti$_3$O$_{12}$ (BIT) [6–9].

2. Experimental details

In our studies, the Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ films were prepared on Pt/Ti/SiO$_2$/Si substrates using a sol–gel method.
The precursor solution for the coating was prepared by first dissolving appropriate amount of bismuth nitrate \([\text{Bi(NO}_3\text{)}_3\cdot 5\text{H}_2\text{O}]\) and neodymium nitrate \([\text{Nd(NO}_3\text{)}_3]_3\) in acetic acid at room temperature in air. A stoichiometric amount of titanium isopropoxide \({\text{Ti(\{CH}_3\text{)}_2\text{CHO}}\text{_4}}\) was slowly added to the mixed precursor solution. Then, acetylacetone was added to the solution as a stabilizing agent. Finally, 2-methoxyethanol was added to adjust the concentration to obtain clear purple sol with a molar concentration of 0.08 mol/dm\(^3\) was obtained. A 15 mol\% excess amount of bismuth nitrate was used to compensate Bi evaporation during annealing. The wet films were dried in air at 350 °C for 1 min, and then preannealed at 500 °C for 10 min in air. This coating process was referred to as one deposition and all the films were fabricated using six depositions. Finally, the as-deposited films were crystallized in N\(_2\), air and O\(_2\) environments for 30 min at different temperatures. The films were about 300 nm in thickness.

For electrical measurements, Pt was sputtered on the surface of the films using a mask to produce the top electrode with an area of 5 × 10\(^{-4}\) cm\(^2\). X-ray diffraction (XRD) was performed for phase identification using a Rigaku-D/MAX3C diffractometer with Cu–K\(\alpha\) radiation at 40 kV. Film thickness was measured by an ET350 Talyurf profilometer (Kosaka Laboratory). Dielectric properties were measured using an HP4294 impedance analyzer at room temperature. Hysteresis loops and fatigue characteristics of the films were recorded at room temperature using a Radiant RT6000S type ferroelectric tester in the virtual ground mode. Current−voltage (\(I−V\)) data were acquired using a Keithley 6517A electrometer as a voltage source and a picocammere meter. The microstructure of the films was investigated using a Hitachi S-5750 scanning electron microscopy (SEM).

3. Results and discussion

The films were first crystallized at 650 °C in N\(_2\), air and O\(_2\). The corresponding XRD patterns are presented in Fig. 1a,b and c, respectively. All the diffraction peaks were identified and indexed using the standard XRD data of BNT powder. Fig. 1a shows strong and sharp BNT (00l)-identified and indexed using the standard XRD data of 1a,b and c, respectively. All the diffraction peaks were annealed in N\(_2\) atmosphere has typical bismuth-based lay-

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\begin{align*}
\text{Intensity/arb. units} \\
\text{2-theta(deg)}
\end{align*}
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Fig. 1. XRD patterns of BNT films deposited on Pt/Ti/SiO\(_2\)/Si substrates under various annealing conditions: (a) N\(_2\), 650 °C; (b) air, 650 °C; (c) O\(_2\), 650 °C; (d) air, 710 °C; and (e) O\(_2\), 730 °C, respectively.

by a CSD method generally crystallized in O\(_2\) or air at temperature between 700−750 °C. It is therefore, no sur-

prise that the BNT films annealed in air and O\(_2\) at 650 °C did not crystallize well. In order to check this point, our BNT films were crystallized at a higher temperature in air or O\(_2\) atmosphere. Fig. 1d and e show the XRD patterns for the films annealed in air at 710 °C and in O\(_2\) at 730 °C, respectively. Marked improvement of the crystallization was found in these films. The intensity of diffractions increases, with small full width at half maximum. These results indicated that the crystallization temperature is lowered significantly when the BNT films were annealed in N\(_2\), compared with those annealed in air or O\(_2\).

The surface morphology of the samples annealed in N\(_2\), air, O\(_2\) at 650 °C is shown in Fig. 2a,b and c, respectively. It can be found that all the films show smooth and dense microstructures. Fig. 2d shows the surface microstructure of the sample annealed in O\(_2\) at 730 °C. Compared with Fig. 2c, it can be noted that the average grain size of the films annealed in O\(_2\) increases as the annealing temperature increases, which indicates better crystallinity and is consist-

ent with the above XRD results. From Fig. 2, we can find that the BNT film annealed in N\(_2\) environment has plate-

like grains, while the film annealed in O\(_2\) has rod-like grains. It has been reported that, for La-doped BIT films, the rod-like grains are presented in (117) preferentially oriented films, while the plate-like grains may correspond to the c-axis preferred orientation [8,16,17]. Thus, the present SEM surface microstructures are consistent with the XRD results shown in Fig. 1, where different preferen-
tially orientations have been observed for the corresponding samples shown in Fig. 2.
Fig. 3 shows the $P$–$E$ hysteresis loops of the corresponding film samples in Fig. 1a to e. The remanent polarization ($2P_r$) values of the samples measured from the hysteresis loops (a) to (e) under a maximum applied field of 330 kV/cm were 63.6, 21.5, 7.2, 60.8 and 37.2 $\mu$C/cm$^2$, and corresponding coercive field ($E_c$) were 130, 127, 119, 128 and 136 kV/cm, respectively. The film annealed at 650 °C in N$_2$ had the highest $2P_r$ value compared with the films annealed at 650 °C in air and O$_2$. This fact is consistent with the XRD results showing that the film annealed in N$_2$ have better crystallinity than other samples. The high $2P_r$ value (near 64 $\mu$C/cm$^2$) and the coercive value of 130 kV/cm of the BNT film crystallized in N$_2$ at 650 °C are comparable to those reported by Kojima et al. [7] and Uchida et al. [8], when the films were crystallized in air or O$_2$ at temperatures above 700 °C. In this study, we also found that the remanent polarization increases with the increase of annealing temperature when the sample was annealed in air or O$_2$, as shown in Fig. 2d and e. This is again consistent with the XRD results where the improvement of crystallinity was observed as the annealing temperature increased in air and O$_2$ atmosphere.

In order to investigate the dependence of the $2P_r$ value on the annealing temperature, the BNT films were annealed at different temperatures in N$_2$, air and O$_2$. Because the quality of the films is also related to the dielectric properties, the dielectric constants have been plotted together with the $2P_r$ values. The $2P_r$ values and the corresponding dielectric constants measured at 10 kHz of BNT films are presented.
in Fig. 4 as a function of the crystallization temperature. As shown in Fig. 4a, the $2P_r$ values and dielectric constants of the BNT films annealed in N$_2$ atmosphere reach their maximum at 650 °C. Fig. 4b and c showed that the $2P_r$ values and the dielectric constants of the BNT films annealed in air and O$_2$ reach their maximum values at 710 and 730 °C, respectively. A correlation between the remnant polarization and dielectric constant can be established, which is similar to that reported in La-doped BIT films [3,13]. Generally, the crystallinity of the films will be improved as the annealing temperature increases, leading to the increase of the $2P_r$ value. However, in the present study, the remnant polarizations of the BNT films crystallized in N$_2$, O$_2$ and air environment, respectively, will decrease as the annealing temperature increases after an optimal crystalline temperature reaches for each case. There are two possible reasons for this phenomena. One is that the element of bismuth in the film is evaporative, especially at higher annealing temperature. Another may be due to that the relative intensity of the (007) and (00l) in the films will change with the crystalline temperature, leading to the changing of the ferroelectric and dielectric properties [3].

The fatigue-resistance characteristics of the BNT films crystallized in N$_2$ at 650 °C, in air at 710 °C and in O$_2$ at 730 °C, respectively, are summarized in Fig. 5, where the normalized difference between the switched and non-switched polarization ($P_{sw} - P_{ns}$) was plotted as a function of switching cycles. All the BNT capacitors showed little change in the normalized polarization up to $3 \times 10^9$ switching cycles using a frequency of 1 MHz with fatigue voltage of ±5 V and measuring voltage of 10 V. It suggests that all BNT films are fatigue-free. The $P−E$ curves of the BNT film annealed in N$_2$ at 650 °C before and after $3 \times 10^9$ cycles of polarization switching were shown in the insert of Fig. 5. There was no significant change in the shape of $P−E$ curves, suggesting excellent fatigue-free property.

We also investigated the $I−V$ characteristics of the samples crystallized in different atmosphere at 650 °C, as presented in Fig. 6. At 80 kV/cm, the leakage current densities of the films crystallized in N$_2$, air and O$_2$ at 650 °C are $1.8 \times 10^{-8}$, $2.5 \times 10^{-8}$, and $8.1 \times 10^{-8}$ A/cm$^2$, respectively. However, it is obvious that the voltage endurance is
best for the film annealed in O2 and worst for the one annealed in N2. The results are again consistent with that observed in BIT films [12].

During the crystallization process, many perovskite thin films prepared by CSD method are amorphous as-deposited, and the amorphous phase transforms first to a metastable pyrochlore-phase at lower annealing temperature which will then further crystallize to become stable perovskite at a higher temperature [14]. It was reported [15] that annealing in oxygen favors the pyrochlore structure to such an extent that it may remain upon annealing at a high temperature (700 °C, such as for PZT), while annealing in reducing atmosphere, such as Ar or N2, favors the formation of the perovskite phase. Our experimental results showed that the situation is also true for the BNT films prepared by the CSD method. Thus, the films annealed in N2 crystallize into layered-perovskite phase at much lower temperature than those annealed in air or O2. However, more oxygen vacancies will form when the films were crystallized in N2 due to the reducing atmosphere, which may cause the low breakdown voltage.

4. Conclusions

In summary, the effect of crystallization environment on crystal structure and ferroelectric properties of the sol–gel derived BNT films have been investigated. The film crystallized in nitrogen at a relatively low temperature of 650 °C exhibited excellent crystallinity and ferroelectricity with a remanent polarization ($2P_r$) of 63.6 μC/cm², a coercive field of 130 kV/cm and a fatigue-free characteristic. On the other hand, BNT films annealed in air and oxygen did not show good crystallinity and ferroelectricity until they were annealed at 710 and 730 °C, respectively. A correlation between the remanent polarization and dielectric constants has also been observed. In addition, the fatigue resistance and the $I–V$ characteristics have also been studied.

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