Fabrication of (100)c-oriented Mn-doped bismuth ferrite films on silicon and stainless steel substrates using calcium niobate nanosheets

Kohei NAGASAKA, Naoya OSHIMA,* Jin Woong KIM,** Hiromi SHIMA,** Akihiro AKAMA,*** Takanori KIGUCHI,*** Ken NISHIDA**
Toyohiko J. KONNO, Hiroshi FUNAKUBO† and Hiroshi UCHIDA†

Department of Materials and Life Sciences, Sophia University, Tokyo 102–8554, Japan
*Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama 226–8503, Japan
**Department of Communications Engineering, National Defense Academy of Japan, Yokosuka 239–8686, Japan
***Institute for Material Research, Tohoku University, Sendai 980–8577, Japan

One-axis-oriented BiFeO₃ (BFO)-based films were fabricated on platinized silicon and SUS 316L substrates using nanosheets of calcium niobate (ns-CN) with pseudo-perovskite crystal structure. Ca₂Nb₃O₁₀ nanosheets (ns-CN) were supported on the substrates by dip coating, followed by chemical solution deposition (CSD) of Mn-doped BFO (Mn-BFO) films. Preferential crystal growth of (100)-oriented BFO films was achieved on both ns-CN/(111)Pt/TiO₂/(100)Si and ns-CN/(111)Pt/SUS316L substrates. The out-of-plane lattice parameters of the BFO films on ns-CN/(111)Pt/SUS316L were larger than the parameter reported for BFO bulk because of elastic deformation caused by thermal stress between the BFO films and SUS316L substrate, whereas those of the films on ns-CN/(111)Pt/TiO₂/(100)Si were smaller than the reported value. The remanent polarization of the Mn-BFO films was enhanced to approximately 30 µC/cm² on ns-CN/(111)Pt/SUS316L because of the compressive thermal stress that causes elastic elongation of Mn-BFO crystals to align or change the tilt angle of their polar axes for the substrate surface.

Key-words: Ferroelectrics, Thin film, Bismuth ferrite, Calcium niobate, Chemical solution deposition (CSD), Nanosheets, Crystal orientation, Thermal stress

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1. Introduction

Bismuth ferrite (BiFeO₃; BFO) is a lead-free ferroelectric material with perovskite-type crystal structure. The excellent polarization property of BFO-based materials has earned them recognition as a potential candidate for replacing Pb-based ferroelectrics that include toxic Pb components, such as lead zirconate titanates [Pb(Zr,Ti)O₃; PZT] and Pb(Mg₁/₃Nb₂/₃)O₃–PbTiO₃.¹⁻³ We especially note that epitaxial BFO thin films deposited on single crystal substrates with perovskite structure, such as (100)SrRuO₃/(100) SrTiO₃ heterostructure and (100) La-doped SrTiO₃ monolith, exhibited enhanced ferroelectricity with remanent polarization (Pᵣ) above 50 µC/cm² as well as strong piezoelectric response of about 70 pm/V, which is significantly larger than those of bulk and polycrystalline films of BFO. This is owing to preferential crystal orientation of BFO unit cells (mainly along out-of-plane) and favorable lattice strain caused by in-plane lattice mismatch and/or thermal stress between BFO and substrate crystals.⁴,⁵ These properties are significantly superior to those of other Bi-based ferroelectrics and comparable to those of PZT, which makes epitaxial BFO thin films potentially useful for constructing actual ferroelectric/piezoelectric devices (e.g., nonvolatile memories, MEMS actuators, piezosensors, energy harvesters)⁶,⁷ without toxic Pb components under environmental restrictions.

One large disadvantage for adopting the epitaxial BFO//substrate heterostructure into actual devices lies in the substrate specificities, i.e., expensive costs, poor workability (cutting, polishing, machining, etc.), and mechanical stiffness of the substrate crystals. Most of these problems could be solved by using ubiquitous substrates (such as silicon wafer, glass, or metal substrates) with relatively low cost, superior workability and elastic behavior. However, BFO films with preferential crystal orientation can hardly be grown on these substrates because there is no epitaxial relationship between the BFO unit cell and the substrate surface. Therefore, there is a strong need for suitable techniques for controlling the crystal orientation of BFO films on ubiquitous substrates in order to adopt the BFO//substrate heterostructure.

Some researchers (including those in our group) have reported the preferential crystal growth of BFO films on platinized silicon wafers using a self-aligned (100)LaNiO₃ interface layer.⁹⁻¹⁰ This resulted in (100)c-oriented BFO films with enhanced crystallinity owing to favorable lattice matching [lattice parameter: a = 0.394 (BFO) and 0.386 nm (LaNiO₃)], as well as moderate remanent polarization of approximately 30 µC/cm². However, this process also includes a technical problem in that the deposition of a (100)-oriented LaNiO₃ layer can only be accomplished by using a sol–gel process with high-temperature annealing (above 700°C) or plasma sputtering,¹¹ which can degrade ubiquitous substrates as a result of thermal oxidation or plasma damage. Any other process with milder conditions would be preferable for these substrates.

† Corresponding author: H. Uchida; E-mail: uchidah@sophia.ac.jp
‡ Preface for this article: DOI http://dx.doi.org/10.2109/jcersj.123.PS-1

DOI http://dx.doi.org/10.2109/jcersj.123.322
In the work reported in this paper, a metal oxide nanosheet with pseudo-perovskite structure, Ca$_2$Nb$_3$O$_{10}$, was selected as an interface layer between BFO and ubiquitous substrates for controlling the crystal orientation of overlaid BFO films. The Ca$_2$Nb$_3$O$_{10}$ nanosheets (ns-CNs) consist of an ultrathin single crystal (lattice parameter: $a = 0.395$ nm, $b = 0.397$ nm) with thickness of $\sim 1.45$ nm, whose (001) plane is oriented to the sheet surface; the lateral sizes of ns-CNs ranged from several hundred nanometers to several ten micrometers. They can be prepared by using a simple soft solution process and then coated on versatile substrates by dip coating (Langmuir–Blodgett manner, etc.)

Furthermore, our group has reported that the ns-CN layer aligned the crystal orientation of PZT (simple perovskite) and SrBi$_4$Ti$_4$O$_{15}$ (layered perovskite) on platinized silicon and stainless steel substrates. We expected the ns-CN layer would also align the crystal orientation of the BFO- and related materials because the unit size of BFO is significantly close to that of ns-CN. Therefore, we attempted to fabricate BFO-based films with preferential crystal orientation on two types of ubiquitous substrates, i.e., platinized silicon and stainless steel, using an ns-CN interface layer.

2. Experimental

Four kinds of substrates were prepared for the experiment we conducted, i.e., substrates of platinized silicon [(111)Pt/TiO$_2$/(100)Si], platinized SUS316L stainless steel [(111)Pt/LaNiO$_3$ heterostructures], and two ns-CN-supported ones [(001)ns-CN/(111)Pt/TiO$_2$/(100)Si and (001)ns-CN/(111)Pt/SUS316L]. An aqueous ns-CN dispersion was prepared by ion exchange and chemical exfoliation of a layered metal oxide precursor, KCa$_2$Nb$_3$O$_{10}$. The ns-CN-supported substrates were prepared by dip-coating using the ns-CN dispersion. Details of the ns-CN preparation and dip-coating processes are described elsewhere.

In this experiment, Mn-doped BFO [Bi$_{1.00}$Fe$_{0.97}$Mn$_{0.03}$O$_3$; Mn-BFO] was selected as a constituent material of BFO-based films, in order to ensure the resistivity of the ferroelectric layer and then to confirm intrinsic polarization behavior without leakage current conduction. Thin films of Mn-BFO were fabricated using a chemical solution deposition (CSD) technique. Bismuth tri-terti-amylxide, iron(III) acetylacetonate, and manganese(II) acetate tetrahydrate were used as starting materials. A precursor solution for Mn-BFO film with a chemical composition of Bi$_2$Fe$_3$Mn$_{1.00}$O$_{10.07}$:0.03 [in molar ratio, Bi$_{1.00}$Fe$_{0.97}$Mn$_{0.03}$O$_3$], concentration: 0.100 mol/dm$^3$] was prepared by dissolving the starting materials in 2-methoxyethanol solvent. The solution was spin-coated on the substrates at a rotation rate of 3000 rpm for 50 s, followed by a drying process at 150$^\circ$C for 1 min and a pyrolysis process at 400$^\circ$C for 1 min using a hot plate. The pyrolized films were crystallized by rapid thermal annealing (RTA) at 500–650$^\circ$C for 5 min in nitrogen atmosphere with respect to each of three coatings. The coating processes were repeated to obtain the resulting films with thicknesses of approximately 300 nm. After the film coating, gold (Au) top electrodes with 200$\mu$m diameter were deposited on the film surface by vacuum evaporation.

The constituent phase, crystal orientation, and lattice parameter of the films were confirmed by X-ray diffraction (XRD) using a Rigaku RINT2000 diffractometer. To simplify the notation of crystal orientation, the pseudocubic Miller index of the crystal, designated in brackets as $(hkl)_p$, was used for Mn-BFO. The thicknesses of the films were determined by scanning electron microscope (SEM) observation on a fractured surface using a Hitachi SU8000 electron microscope. The dielectric property was evaluated using an Agilent technology 4294A impedance analyzer with an oscillation voltage of 1 V. The ferroelectric property was evaluated using a Toyo Technica FCE-3 ferroelectric test system with a frequency of 10kHz.

3. Results and discussion

3.1 Mn-BFO films fabricated on Si-based substrates

Figure 1 shows wide-range XRD patterns of Mn-BFO films on (a) (111)Pt/TiO$_2$/(100)Si and (b) (001)ns-CN/(111)Pt/TiO$_2$/(100)Si substrates, fabricated at the crystallization of 500–650$^\circ$C. Other than XRD peaks from the substrate, we confirmed there were peaks indexed by perovskite (001), (110), (200), and (210), planes for the resulting films on (111)Pt/TiO$_2$/Si substrates. However, additional peaks derived from a Bi$_2$Fe$_3$O$_9$ second phase also appeared in these peaks. The peak intensities of the perovskite (i.e., Mn-BFO) and Bi$_2$Fe$_3$O$_9$ phase increased as the crystallization temperature increased to 650$^\circ$C. The Bi$_2$Fe$_3$O$_9$ phase was formed by the thermal evaporation and/or interfacial diffusion (into bottom Pt electrode) of Bi components from the BFO-based phase due to excessive heating at higher temperature. On the other hand, the XRD pattern for the films fabricated on (001)ns-CN/(111)Pt/TiO$_2$/(100)Si indicated intensive peaks indexed by perovskite (100), and (200), planes, together with minor perks derived from perovskite (110), and Bi$_2$Fe$_3$O$_9$, at the crystallization temperature of 500–550$^\circ$C. These results indicate that (100)-oriented Mn-BFO films were successfully grown by applying the ns-CN layer.
supported on (111)Pt/TiO₂/(100)Si, as we had expected in the Introduction section we reported.

Narrow-range XRD patterns for the (100)c-oriented Mn-BFO films on (001)ns-CN/(111)Pt/TiO₂/(100)Si [2θ = 44.4–47.4°, perovskite (200) peak] are shown in Fig. 2. The peak position of the resulting films was slightly higher than that reported in the literature (2θ = 45.814°).²²) The peak derived from perovskite (200)c was shifted to a higher diffraction angle as the crystalization temperature increased, meaning that the out-of-plane lattice parameter of Mn-BFO decreased as a consequence of the heating at higher crystallization temperature. The XRD patterns exhibited a single diffraction peak of perovskite (h00)c planes normal to the substrate surface without a shoulder peak. These results suggest that the crystal system of the film is one of tetragonal or strained-rhombohedral symmetry with one-axis orientation.

Figure 3 shows the relative dielectric constant, εᵣ, and the dielectric loss, tan δ, of Mn-BFO films on (a) (111)Pt/TiO₂/(100)Si and (b) (001)ns-CN/(111)Pt/TiO₂/(100)Si fabricated at 500–650°C. The εᵣ values of the resulting films ranged from approximately 100 to 120 in the frequency range above 10⁴ Hz, independent of substrate species and the crystallization temperature. The tan δ values of the films were below 0.1 in the frequency range above 10⁴ Hz, although larger values were confirmed in the range of less than 10⁴ Hz owing to leakage current conduction. No obvious dependence of the εᵣ and tan δ values on the crystal orientation or crystallization temperature was confirmed from these data.

Figure 4 shows polarization vs. electric field, P–E, hysteresis loops of Mn-BFO films on (a) (111)Pt/TiO₂/(100)Si and (b) (001)ns-CN/(111)Pt/TiO₂/(100)Si fabricated at 500–650°C. Saturated P–E loops were measured for all the films successfully. The coercive field (Ec) values of the resulting films were around 420 kV/cm and were independent of the processing conditions. The change in the Ec value with the processing conditions will be discussed comprehensively in the following section 3.3.

3.2 Mn-BFO films fabricated on SUS-based substrates

Figure 5 shows wide-range XRD patterns of Mn-BFO films on (a) (111)Pt/SUS316L and (b) (001)ns-CN/(111)Pt/SUS316L, fabricated at the crystallization temperature of 500–650°C. It was confirmed there were peaks indexed by perovskite (100)c, (110)c, (200)c, and (210)c planes on the XRD patterns for the films on (111)Pt/SUS316L. They were similar to those on (111)Pt/TiO₂/(100)Si, which also indicates random crystal orientation Mn-doped BFO crystals. Trace amounts of Bi₂Fe₄O₉ were found only
in the film on (111)Pt/SUS316L fabricated at 650°C. The Mn-BFO films fabricated on (001)ns-CN/(111)Pt/SUS316L, on the other hand, exhibited only intensive perovskite (100) peaks, which indicates the preferential crystal orientation of the perovskite (100) plane, similarly to the films on (001)ns-CN/(111)Pt/TiO2/(100)Si [in Fig. 1(b)]. Additionally, we found no Bi2Fe4O9 phase in the films on (001)ns-CN/(111)Pt/SUS316L (even when they were fabricated at 650°C), and a trace of randomly-oriented perovskite phase indexed by (110). These results indicated that the (100)ns-CN layer on (111)Pt/SUS316L promoted the preferential crystal growth of (100)Mn-BFO normal to the substrate surface, as well as suppressing the secondary Bi2Fe4O9 phase.

Narrow-range XRD patterns for the (100)c-oriented Mn-BFO films on (001)ns-CN/(111)Pt/SUS316L are shown in Fig. 6. The only diffraction peaks of perovskite (h00)c planes were detected for normal to the substrate surface of all the films, similar to the results obtained for (001)ns-CN/(111)Pt/TiO2/(100)Si (in Fig. 2). However, the peak position of the resulting film was significantly lower than that reported in the literature. Furthermore, the diffraction peak was shifted to a lower angle as the crystallization temperature increased, meaning that the out-of-plane lattice parameter of Mn-BFO was increased by heating at higher temperature. This contrasts with the results in Fig. 2. The crystal system of these films is assumed to be tetragonal or strained-rhombohedral symmetry, but it differs from that of (001)ns-CN/(111)Pt/TiO2/(100)Si with respect to the in-plane/out-of-plane aspect ratio.

Figure 7 shows $\varepsilon_r$ and $\tan\delta$ values of Mn-BFO films on (a) (111)Pt/SUS316L and (b) (001)ns-CN/(111)Pt/SUS316L fabricated at 500–650°C. The $\varepsilon_r$ values (around 90–100) measured for these films were lower than those on (111)Pt/TiO2/(100)Si and (001)ns-CN/(111)Pt/TiO2/(100)Si, except for the film on (111)Pt/SUS316L fabricated at 650°C which exhibited dielectric degradation with excessive dielectric loss. The dielectric degradation was caused by the presence of the Bi2Fe4O9 phase, which also caused the decrement of the Mn-BFO phase [in Fig. 5(a)].

Figure 8 shows P–E hysteresis loops of Mn-BFO films on (a) (111)Pt/SUS316L and (b) (001)ns-CN/(111)Pt/SUS316L fabricated at 500–650°C. Saturated P–E loops were measured for these films, except for the film on (111)Pt/SUS316L fabricated at 650°C where the loops were not saturated due to dielectric breakdown occurring at a lower applied field. The $E_c$ values of the films, around 330 kV/cm independent of the processing conditions, were slightly larger than those measured on Si-based substrates (in Fig. 4).
the literature data for BFO lattices.\textsuperscript{23} The lattice parameters of Mn-BFO varied significantly depending on the substrate species. The parameters for (001)\textit{ns}-CN/(111)Pt/TiO\textsubscript{2}/(100)Si were smaller than the literature data; conversely, those for (001)\textit{ns}-CN/(111)Pt/SUS316L were larger. Furthermore, the parameters for (001)\textit{ns}-CN/(111)Pt/TiO\textsubscript{2}/(100)Si decreased as the crystallization temperature increased, whereas those for (001)\textit{ns}-CN/(111)Pt/SUS316L increased. The continuous change in the parameters with increased crystallization temperature can be explained by in-plane thermal stress, which is generated due to differences in thermal expansion (or shrinkage) behavior during the cooling-down step in the CSD process. The thermal stress, $\sigma$, is expressed by

$$
\frac{E_v}{1 - v} (\alpha_t - \alpha_s) (T_f - T_0)
$$

where $E_v$, $\alpha_t$, $\alpha_s$, $T_f$, and $T_0$ are Young’s modulus, Poisson ratio, linear thermal expansion coefficients of the film and the substrate, crystallization temperature, and room temperature, respectively. This Eq. (1) suggests that the difference in thermal expansion coefficient, $\alpha_t - \alpha_s$, mainly determines the thermal stress mode (i.e., whether tensile or compressive). As the thermal expansion coefficient of BFO varied in the range of approximately $11-14 \times 10^{-6}$ K\textsuperscript{-1},\textsuperscript{24} the value of $(\alpha_t - \alpha_s)$ was positive for the films on (001)\textit{ns}-CN/(111)Pt/TiO\textsubscript{2}/(100)Si (Si: $\alpha_s = 2.6 \times 10^{-6}$ K\textsuperscript{-1}) and negative for those on (001)\textit{ns}-CN/(111)Pt/SUS316L (SUS316L: $\alpha_s = 20.5 \times 10^{-6}$ K\textsuperscript{-1}).\textsuperscript{25} Also, the amplitude of the thermal stress varies with $T_f$ because the $\sigma$ value is directly proportional to the difference between crystallization temperature and room temperature, $(T_f - T_0)$. That is, the absolute $\sigma$ value increased as the crystallization temperature increased. As a consequence of elastic deformation, in-plane tensile stress lowers the out-of-plane lattice parameter of Mn-BFO and in-plane compressive stress raises it, as shown in Fig. 9. The $P_f$ values of Mn-BFO films on Si-based and SUS-based substrates, measured from the $P-E$ loops in Figs. 4 and 8, are summarized in Figs. 10 and 11, respectively. The general tendency observed was that applying the \textit{ns}-CN layer lowered the $P_f$ value for the films on (111)Pt/TiO\textsubscript{2}/(100)Si and enhanced it for the films on (111)Pt/SUS316L. These results are evidently related to the change in the out-of-plane lattice parameters (as shown in Fig. 9).

That is, the (100),-oriented Mn-BFO films on (001)\textit{ns}-CN/(111)Pt/SUS316L receive compressive thermal stress that causes elastic elongation of Mn-BFO crystals to align their polar axis along the substrate surface. Conversely, the same films on (001)\textit{ns}-CN/(111)Pt/(111)Pt/TiO\textsubscript{2}/(100)Si receive tensile thermal stress that resulted in the shrinkage of the Mn-BFO crystal lattices and consequent suppression of their polarization behavior. The authors assume that the change in the remanent polarization induced from the thermal stress is caused by the change in the tilting angle of the polar axes in strained-rhombohedral BFO crystals, rather than by the complete $a$-/$c$-axis orientation switching of tetragonal BFO. The latter may be accompanied by a significant increment/decrement of the spontaneous polarization, because the $P_s$ values of the films on (001)\textit{ns}-CN/(111)Pt/TiO\textsubscript{2}/(100)Si (approximately 35; see Figs. 4 and 8) were not particularly small. The gradual decrement of the $P_f$ value with increasing crystallization temperature in the films on (001)\textit{ns}-CN/(111)Pt/SUS316L can be explained by the formation of the Bi$_2$Fe$_2$O$_{12}$ second phase. Further enhancement in the $P_f$ value can be expected for the (100)-oriented Mn-BFO film on a \textit{ns}-CN layer by using certain substrates with larger thermal expansion coefficients.
The $\varepsilon_r$ values of Mn-BFO films on (001)ns-CN/(111)Pt/SUS316L [60–81 at 1 kHz in Fig. 7(a)] were relatively smaller than those on (111)Pt/SUS316L [75–94 in Fig. 7(b)], while the Mn-BFO films on (001)ns-CN/(111)Pt/TiO$_2$/(100)Si exhibited $\varepsilon_r$ values [85–123 in Fig. 3(a)] slightly larger than those on (111)Pt/ TiO$_2$/(100)Si [87–103 at 1 kHz in Fig. 3(b)]. The ns-CN itself does not directly contribute to the change of $\varepsilon_r$ value because of its constant value of dielectric permittivity (Ca$_2$Nb$_3$O$_{10}$: ~200)$^{30}$ irrespective of the substrate species. These tendencies are inversely coincident with the tendency observed for remanent polarization, which can be explained by experimental evidence that perovskite crystals generally exhibit relatively lower dielectric permittivity along the polar axis.$^{20-28}$

4. Conclusion

In conclusion, (100)$_z$-oriented Mn-doped BiFeO$_3$ (Mn-BFO) films were successfully fabricated on a (001)ns-CN layer applied to (111)Pt/TiO$_2$/(100)Si and (111)Pt/SUS316L substrates. The out-of-plane lattice parameters of the films on (001)ns-CN/(111)Pt/SUS316L were enhanced while those of the films on (001)ns-CN/(111)Pt/TiO$_2$/(100)Si were lowered, as a consequence of thermal stress generated during the cooling-down step in the chemical solution deposition (CSD) process. Applying the (001)ns-CN layer enhanced the remanent polarization ($P_r$) values for the films on (111)Pt/SUS316L; conversely, it decreased them for the films on (111)Pt/TiO$_2$/(100)Si substrates. The contrasting results for the $P_r$ values are strongly related to the change in the out-of-plane lattice parameters.

Acknowledgment This research was supported by the Center for Integrated Nanotechnology Center at Tohoku University and also by Nanotechnology Network Project of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of the Japanese Government.

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