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Ferroelectric properties of lead-free polycrystalline CaBi₂Nb₂O₉ thin films on glass substrates

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CaBi₂Nb₂O₉ (CBNO) thin film, a lead-free ferroelectric material, was prepared on a Pt/Ta/glass substrate via pulsed laser deposition. The Ta film was deposited on the glass substrate for a buffer layer. A (115) preferred orientation of the polycrystalline CBNO thin film was verified via X-ray diffraction measurements. The CBNO thin film on a glass substrate exhibited good ferroelectric properties with a remnant polarization of 4.8 μ C/cm² (2*P_r* ~9.6 μ C/cm²), although it had lower polarization than the epitaxially *c*-oriented CBNO thin film reported previously. A mosaic-like ferroelectric domain structure was observed via piezoresponse force microscopy. Significantly, the polycrystalline CBNO thin film showed much faster switching behavior within about 100 ns than that of the epitaxially *c*-oriented CBNO thin film. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4944956]

I. INTRODUCTION

Ferroelectric materials are widely used for various applications such as actuators, sensors, power generators, and non-volatile random access memories.^{1–6} Among these ferroelectric materials, Pb(Zr, Ti)O₃ (PZT) systems have been studied with a great deal of interest due to their high ferroelectric polarizations and piezoelectric coefficients. However, lead components in PZT systems have harmful effects on human health and the environment; creating a need for alternative, environment-friendly materials. A great deal of effort has been devoted to lead-free ferroelectric materials, but most current materials in use have relatively low ferroelectric and piezoelectric properties as compared to PZT systems.^{7,8} SrBi₂Ta₂O₉ (SBT) thin films, known as Bi-layered ferroelectrics with an Aurivillius structure, have been intensively studied and are used in memory devices due to their high spontaneous polarizations and fatigue-free property.^{9,10} CaBi₂Nb₂O₉ (CBNO) compounds have also attracted attention over the years;^{11,12} however, few studies have been reported on thin-film-type materials.^{13–15} Because the CBNO compounds show high Curie temperatures as Bi-layered ferroelectrics,¹¹ they show great potential for high-temperature device applications. Characteristically, CBNO shows spontaneous polarization along the *a*-axis orientation at room temperature with an orthorhombic crystal structure ($A2_1am$).^{11,16}

It is possible to deposit ferroelectric thin films on ideal single crystalline substrates for device applications. For example, oxide single crystalline substrates such as SrTiO₃ and MgO are suitable for the deposition of well-crystallized ferroelectric thin films because they have a perovskite structure; however, they are not likely to be chosen for industrial applications owing to their high cost and limited substrate size. In contrast, Si single crystalline substrates are ill suited for ferroelectric thin films because of the relative difference between their lattice constants, as well as several



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problems related to interdiffusion and interfacial defects.¹⁷ For these reasons, glass is considered an applicable substitute for single crystal substrates even though it is necessary to employ buffer layers consisting of materials such as layered yttria-stabilized zirconia (YSZ) and Ta.^{18,19} In this work, we investigate the ferroelectric properties of CBNO thin film grown on Pt/Ta/glass substrates via pulsed laser deposition (PLD). The polycrystalline CBNO thin film shows good ferroelectric properties with a remnant polarization of 4.8 μ C/cm². We further demonstrate the switching and conduction current behavior of the polycrystalline CBNO thin film for device applications.

II. EXPERIMENTAL DETAILS

CBNO thin film was grown on Pt/Ta/fused silica glass substrates via PLD. As an adhesion layer, a Ta film with a thickness of 5 nm was deposited on glass under 10 mTorr Ar gas at 500 °C using radiofrequency (RF) magnetron sputtering at 100 W RF power. A Pt electrode film with a thickness of 50 nm was then deposited on the Ta/glass substrate under 10 mTorr Ar gas at 600 °C using RF magnetron sputtering at 50 W RF power. A KrF eximer laser with a wavelength of 248 nm and energy density of 0.5 J/cm² was focused on the CBNO target. The distance between the target and substrate was ~4 cm. After the base pressure reached ~ 5×10^{-7} Torr, the substrate temperature was set at 850 °C with an oxygen partial pressure of 100 mTorr. After deposition, the CBNO thin film was immediately cooled to room temperature in oxygen ambient at 300 Torr. The structure of the CBNO thin film was investigated using x-ray diffraction techniques (XRD, Cu Ka1 radiation 1.542 Å). The surface morphology and roughness of the CBNO thin film were evaluated via atomic force microscopy (AFM) and its ferroelectric domain structure was investigated using piezoresponse force microscopy (PFM). RF magnetron sputtering was also used to fabricate the Pt top electrode (with a diameter of 100 µm and thickness of 100 nm) on the CBNO thin film. The Pt top electrode was annealed at 450 °C for 30 min prior to obtaining the ferroelectric hysteresis loop, which was measured using the RT66A test system (Radiant Technologies, Inc.).

III. RESULTS AND DISCUSSION

Fig. 1(a) shows a schematic drawing of a 100-nm thick CBNO thin film grown on a Pt/Ta/glass substrate. We first checked the crystal structure of the CBNO thin film on the substrates; the θ -2 θ XRD pattern is shown in Fig. 1(b). In an out-of-plane XRD measurement, a peak of (115) was observed in the CBNO thin film. There are no peaks in the in-plane XRD measurement, indicating a polycrystalline nature. As expected, the (115) preferred orientation growth of the CBNO thin film was associated with a (111) orientation growth of the Pt bottom electrode. No polar-axis-oriented peaks of CBNO were observed; however, the position of the (115) peak is consistent with the index XRD patterns of the CBNO reported previously.¹¹ A rocking curve measurement was also employed to evaluate the degree of preferred orientation for the (115) peak. This result confirms that



FIG. 1. (a) A schematic drawing of the CBNO thin film on a Pt/Ta/glass substrate. (b) X-ray diffraction pattern of the CBNO thin film grown on the Pt/Ta/glass substrate.



FIG. 2. (a) Ferroelectric hysteresis loops of the polycrystalline (CBNO1) and epitaxial (CBNO2) CBNO thin films. The remnant polarization of the polycrystalline CBNO thin film is approximately 4.8 μ C/cm². (b) Switching current curves as a function of time under switching bias of 5V.

the full width at half maximum (FWHM) of the (115) peak is approximately 1.5 degree, indicating poor crystallinity.

To investigate the ferroelectric properties of the polycrystalline CBNO thin film, we observed hysteresis loops of the polycrystalline and epitaxial CBNO thin film at a measurement frequency of 1kHz. The ferroelectric polarizations were compared under an applied electric filed, as shown in Fig. 2(a). The Pt/CBNO/Nb-doped SrTiO₃ capacitor (CBNO1, epitaxially *c*-oriented CBNO thin film) fabricated in our previous work exhibited good ferroelectric property with a high remnant polarization of 10.6 μ C/cm² (2*P_r* ~21.2 μ C/cm²) and coercive electric field of approximately 170 kV/cm.²⁰ In contrast, the Pt/CBNO/Pt/Ta/glass capacitor (CBNO2, polycrystalline CBNO thin film) in the present study exhibited a low remnant polarization of 4.8 μ C/cm² (2*P_r* ~9.6 μ C/cm²) and coercive electric field of 147 kV/cm. This result suggests that the poor crystallinity of the polycrystalline CBNO thin film on the Pt/Ta/glass substrate gives rise to the observed polarization value which is lower values found with epitaxially *c*-oriented CBNO thin film.

The switching speed of ferroelectric polarization in the ferroelectric capacitor is directly related to the performance of ferroelectric memory devices. Thus, it is necessary to speed up the switching speed of the ferroelectric polarization to enhance the performance of the ferroelectric memory devices. To check switching speed of a ferroelectric polarization, we measured the switching current curves as a function of time for the CBNO1 and CBNO2 capacitors. Here, switching current was actually recorded by the response difference of two consecutive (switching and non-switching) pulses train which consisted of square pulses with an input width of 1 μ s and arising time of about 1ns.²¹ For the positive and negative pulses, we applied + 5 and - 5 V as switching bias. The pure



FIG. 3. (a) AFM image of the CBNO thin film showing round-shaped grains. (b) PFM image of the CBNO thin film showing a mosaiclike domain structure.



FIG. 4. Leakage current density of the CBNO thin film as a function of applied field (J-E curve).

(net) switching current curve was obtained as shown in Fig. 2(b). The switching time of the CBNO1 was measured to be about 175 ns. On the other hand, the CBNO2 exhibited much faster switching behavior within about 100 ns despite its low remnant polarization.

The surface morphology of the CBNO thin film on glass substrate was observed via AFM. Fig. 3(a) shows round grains on the CBNO thin film surface, which indicates that the growth of the polycrystalline CBNO thin film has been governed by the island growth mode due to the influence of the polycrystalline Pt bottom electrode. The root-mean-square (RMS) roughness of the CBNO thin film was evaluated to be approximately 1.7 nm. The ferroelectric domain structure was also observed via PFM using an Rh-coated tip ($f_0 \sim 25$ kHz, $k \sim 3$ N/m) and a 10 kHz applied voltage. Fig. 3(b) shows mosaic-like domain structures with clear color contrast according to the polarization direction.

For practical applications such as memory devices, we need to consider the conduction current in the dielectric thin film. Fig. 4 presents a leakage current density versus applied electric field (J-E) curve of the CBNO thin film on a Pt/Ta/glass substrate. The J-E curve was plotted on the *log-log* scale at positive bias. In low applied electric field (under approximately 250 kV/cm, I region), the leakage current of the CBNO thin film exhibits Ohmic conduction behavior. As shown in Fig. 4, there exists a linear relationship between the current density and electric field, and its slope was determined to be exactly 1. Since Ohmic conduction is a typical behavior, it is observed at low electric field in the dielectric thin films. We also found that the current density showed a sudden change with a steep slope (n=4) in the higher electric field range (over approximately 250 kV/cm, II region). This behavior is likely caused by space charge carriers, which is generally in agreement with the space-charge-limited current (SCLC) and leads to the leakage current in dielectric thin films. At the Ohmic contact, the SCLC is induced via the injection of electrons with increasing applied electric field.²²

IV. CONCLUSION

We deposited lead-free polycrystalline CaBi₂Nb₂O₉ (CBNO) thin films on Pt/Ta/glass substrates using pulsed laser deposition. X-ray diffraction measurements revealed that the CBNO thin film was preferentially oriented along the (115) direction. The CBNO thin film exhibited good ferroelectric properties with a remnant polarization of 4.8 μ C/cm², although at a lower value than that of the epitaxially *c*-oriented CBNO thin film. In particular, the CBNO thin film showed much faster switching behavior within about 100 ns than that of the epitaxially *c*-oriented CBNO thin film. A space-charge-limited current (SCLC) was observed at a higher electric field of 250 kV/cm. 035123-5 Ahn, Jang, and Son

Our results provide options for the possible fabrication of ferroelectric capacitors consisting of lead-free CBNO thin films on glass substrates.

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