AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **100**, 074110 (2006); doi: 10.1063/1.2357419
View online: http://dx.doi.org/10.1063/1.2357419
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/100/7?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **100**, 074110 (2006)

High Curie point $CaBi_2Nb_2O_9$ thin films: A potential candidate for lead-free thin-film piezoelectrics

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(Received 29 March 2006; accepted 23 July 2006; published online 12 October 2006)

$CaBi_2Nb_2O_9$ (CBNO) thin films deposited on platinum coated silicon substrates by the polymeric precursor method exhibited good structural, dielectric, and piezoelectric characteristics. Capacitance-voltage measurements indicated good ferroelectric polarization switching characteristics. Remanent polarization and drive voltage values were 4.2 $\mu C/cm^2$ and 1.7 V for a maximum applied voltage of 10 V. The film has a piezoelectric coefficient d_{33} equal to 60 pm/V, current density of 0.7 $\mu A/cm^2$, and Curie temperature of 940 °C. The polar-axis-oriented CBNO is a promising candidate for use in lead-free high Curie point in ferroelectric and piezoelectric devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357419]

I. INTRODUCTION

High-temperature sensing technology is of major importance for chemical and material processing, as well as automotive, aerospace, and power generating industries. Electromechanical transducer materials are required to sense strains, vibrations, and noise under several thermal conditions. Among the different types of acoustic and strain sensors, piezoelectric ones are the best candidates considering sensitivity, cost, and design.[1]

When an operating temperature of 400 °C or greater is required, the choice of materials for high-temperature piezoelectric transducers is limited. Modified bismuth titanate compositions are interesting for sensor applications up to 500 °C.[2] When an operating temperature of up to 750 °C is required, there is no suitable commercial ceramic available. $CaBi_2Nb_2O_9$ (CBNO) is a member of Bi-based layer-structured perovskite compounds[3] such as $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2TaNb_2O_9$ (SBTN) for which there has been a huge amount of research on nonvolatile random access memory applications.[4] Compared with SBT and SBNT thin films, there has been little reported on electrical properties of CBNO thin films. CBNO is a layered perovskite ferroelectric oxide, whose lattice constants are a=50.5435 nm, b=50.546 58 nm, and c=52.4970 nm.[5] The spontaneous polarization P_s for CBNO is along the a-axis direction. Therefore, thin films with a-axis orientation are preferred for use in many kinds of devices, such as ferroelectric random access memories, piezoelectric microactuators, and resonators. The crystallinity and orientation of the Pt bottom electrodes were found to affect the phase transition of paraelectric to ferroelectric in bismuth layered compounds.[6]

Among various methods such as metal-organic chemical vapor deposition, pulsed laser deposition, and sol gel, the polymeric precursor method has its advantages over the other production techniques including its low cost, good compositional homogeneity, relatively low processing temperatures, and the ability to coat large substrate areas.[7,8]

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However, there is no publication on CBNO thin films deposited on (100) $Pt/Ti/SiO_2/Si$ bottom electrodes by the polymeric precursor method. In this article, we report the oriented lead-free high Curie point (T_C) ferroelectric thin film through a polymeric precursor method, CBNO, which has the highest known T_C (943 °C) of the Aurivillius-phase structure materials.

II. EXPERIMENTAL PROCEDURE

Calcium citrate (Synth), niobium oxide (Aldrich), and bismuth oxide (Aldrich) were used as raw materials. The precursor solutions of calcium, bismuth, and niobium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of Ca, Bi, and Nb solutions were mixed and homogenized by stirring at 90 °C. The molar ratio of metal:citric acid:ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 12 cP by controlling the water content using a Brookfield viscosimeter. The CBNO thin films were spin coated on $Pt/Ti/SiO_2/Si$ substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). In this work, an excess of 5% by weight of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as was reported in literature.[9] The thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness value of about 320 nm for CBNO, reached by repeating the spin coating and heating treatment cycles. The thickness of the annealed films was studied using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case backscattering electrons were used. Phase analysis of the films was performed at room temperature by x-ray diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 2000) and Cu $K\alpha$ radiation. The morphology of the thin films was examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) by using a silicium nitride tip in the contact

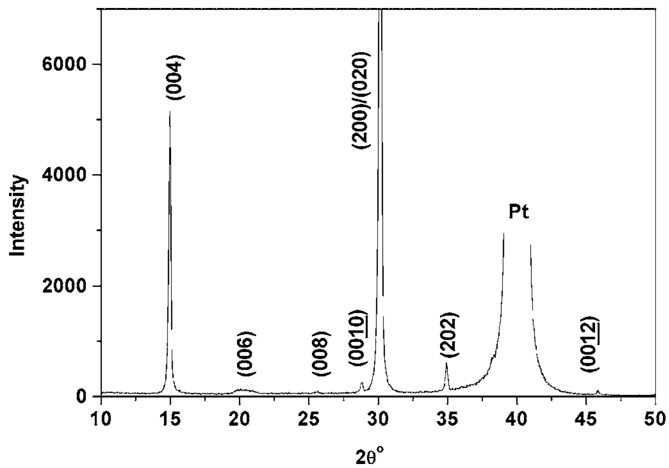

FIG. 1. X-ray diffraction for CBNO thin film annealed at 700 °C for 2 h.

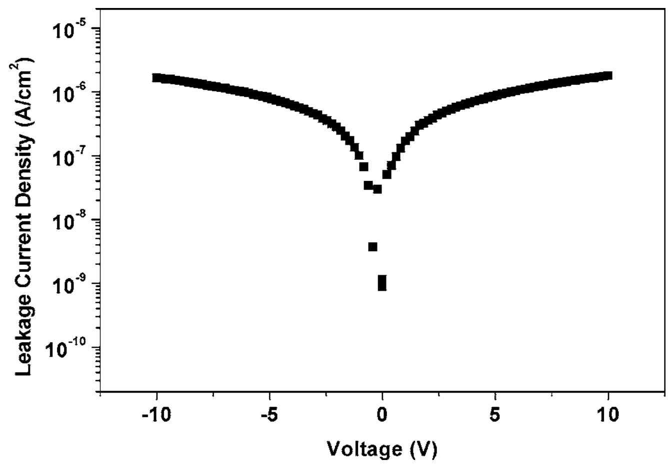

FIG. 2. Leakage current density in dependence of voltage for CBNO thin film annealed at 700 °C for 2 h.

mode. AFM was used to obtain a three-dimensional image reconstruction of the sample's surface. These images allow for an accurate analysis of the sample's surface and the quantification of very important parameters such as roughness and grain size. The scan area was $1 \times 1\ \mu m^2$ in the *x-y* plane. For electrical measurements, a 0.5 mm diameter top Au electrode was deposited by evaporation through a shadow mask at room temperature. The electric properties were measured by a Au/CBNO/Pt/Ti/SiO_2/Si (100) capacitor structure. The capacitance-voltage (*C-V*) characteristic was measured in the metal-ferroelectric-metal (MFM) configuration using a small alternate current (ac) signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the direct current (dc) was swept from positive to negative bias. The relative dielectric constant ε_r was measured versus frequency using an impedance analyzer (model 4192 A, Hewlett Packard). *J-E* characteristics of the films were measured using a Radiant Technology RT6000 A in a virtual ground mode at room temperature. A contact with probe electrodes was made with a wire-bonding method. Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology RT6000 A). The dielectric characterization was accomplished in an impedance analyzer, model 4192 of HP, and measurements of the capacitance as a function of the temperature for the frequency of 100 kHz were performed. The Curie temperature of the material is obtained from the capacitance dependent temperature curves.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of CBNO thin film annealed at 700 °C for 2 h. CBNO films on the platinum coated silicon substrates showed a high intensity of the (200)/(020) diffraction line compared to the other lines, although the (200) and (020) diffraction lines could not be distinguished from each other. The characteristic orientation is considered to be due to good matching of atomic arrangements in CBNO (100)/(010) and underlying Pt planes. The annealed thin film was a single phase of a layer-structured perovskite with orthorhombic crystallographic structure. The diffraction peaks are matched and indexed based on CBNO crystal-structure parameters.[10]

Low leakage current density is another important parameter for memory device applications. Here the measured logarithmic current density (log *J*) versus the voltage (*V*) is shown (Fig. 2). The CBNO thin films exhibited good leakage current characteristics. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an Ohmic conduction. This Ohmic behavior occurs in insulating film as long as the film is almost neutral, that is, as long as the bulk generated current in the film exceeds the current due to injected free carriers from the electrode. This current would be due to the hopping conduction mechanism in a low electric field, because thermal excitation of trapped electrons from one trap site to another dominates the transport in the films. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole-Frenkel emission mechanism. The leakage current density at 1.0 V is equal to 10^{-7} A/cm^2 up to an applied electric field of 30 kV/cm, establishing good insulating characteristics. A symmetric *J-V* characteristic for both voltage polarities was noted, indicating that the bulk controls the properties once we have used different top and bottom electrodes and different processing conditions. Therefore, the low leakage current can be an effect of a small grain size and roughness, which implies several grain boundaries along the current flow acting as potential barriers. Since the conductivity is strongly affected by the characteristics of the film-electrode interface, the surface morphology of CBNO thin films is one of the major factors determining the leakage current in capacitors.

Because the CBNO thin film showed ferroelectric nature, hysteresis curve was examined at room temperature (Fig. 3). Ferroelectricity of the calcium bismuth niobate was observed with remanent polarization (P_r) and a drive voltage V_c of 4.2 μC/cm^2 and 1.7 V. The P_r and E_c values were improved compared with the values obtained for polycrystalline CBNO thin films.[11] The higher P_r value suggests that the

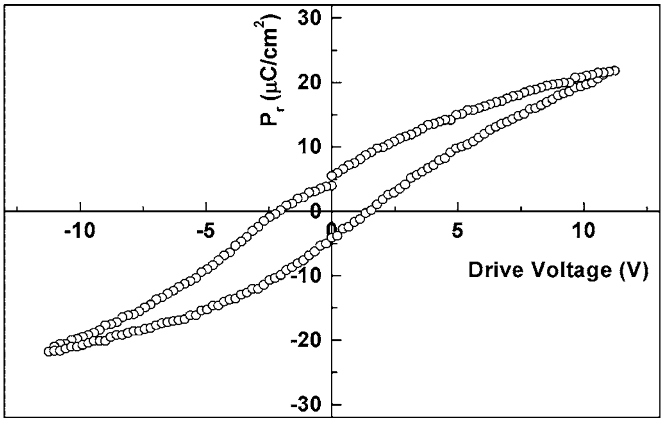

FIG. 3. *C-V* curve for CBNO thin film annealed at 700 °C for 2 h.

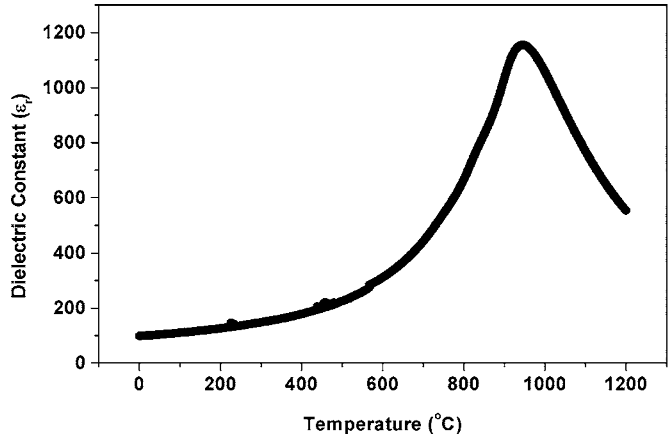

FIG. 5. Temperature dependence of dielectric constant in CBNO thin film annealed at 700 °C for 2 h.

(100) orientation is preferred rather than the (010) orientation with respect to the present CBNO film. The reason for this improvement is that the ferroelectric polarization switching occurs in the *a-b* plane in CBNO.

Figure 4 illustrates the *C-V* curve for CBNO films obtained at 100 kHz and dc sweep voltage from +8 to −8 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The *C-V* curve for the film annealed at 700 °C for 2 h also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The symmetry around the zero bias axis indicates that the films contain few movable ions or charge accumulation at the film-electrode interface. The dielectric constant of the CBNO thin films calculated from C_{max} was 1000. The dissipation factor was 0.053 at 100 kHz.

Figure 5 shows the temperature dependence of the dielectric constant of CBNO thin film at 100 kHz. The Curie point of CBNO was (944±2) °C. This value of the Curie point is much higher than that reported by Ismailzade for CBNO.[12] The fact that the Curie point of our CBNO thin films is higher suggests that Ismailzade's result for T_C may be an error because it was obtained under the assumption that it coincided with a phase transformation observed by XRD.

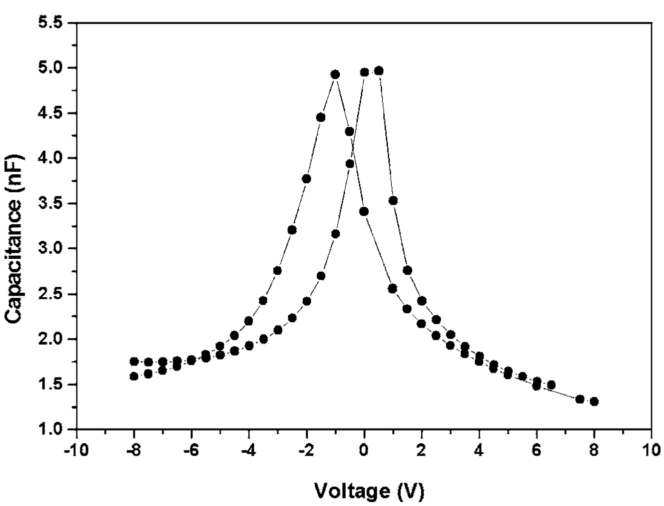

FIG. 4. *P-V* hysteresis loop for CBNO thin film annealed at 700 °C for 2 h.

In spite of their relatively larger P_s, the piezoelectric activity of bismuth layer-structured ferroelectrics (BLSFs) is limited because of two-dimensional orientation restriction of the rotation of their spontaneous polarization and their higher coercive field E_c. Orientation of films is an effective method to improve piezoelectric activity of BLSFs because of the anisotropy of their microstructure and properties. Figures 6 and 7 show the out-of-plane (OP) and in-plane (IP) piezoresponse images of the as-grown films after applying a bias of −12 V on an area of $2\times 2\ \mu m^2$, and then an opposite bias of +12 V in the central $1\times 1\ \mu m^2$ area. To obtain the domain images of the CBNO films, a high voltage that exceeds the coercive field was applied during scanning. The contrast in these images is associated with the direction of the polarization.[13] The white regions in the out-of-plane piezoresponse force microscopy (PFM) images correspond to domains with the polarization vector oriented toward the bottom electrode hereafter referred to as downpolarization (Fig.

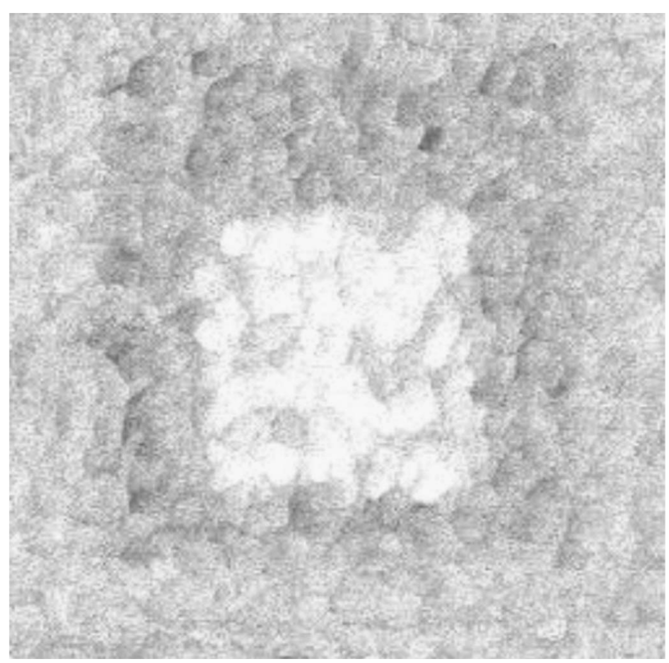

FIG. 6. Out-of-plane (OP) PFM image of CBNO thin film deposited on (100) $Pt/Ti/SiO_2/Si$ substrate at 700 °C for 2 h.

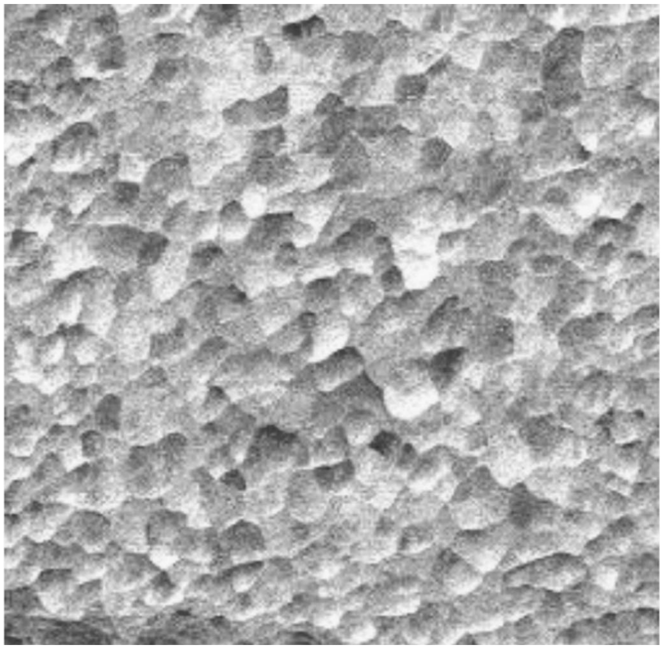

FIG. 7. In-plane (IP) PFM image of CBNO thin film deposited on (100) $Pt/Ti/SiO_2/Si$ substrate at 700 °C for 2 h.

6), while the dark regions correspond to domains oriented upward referred to as up-polarization. Grains which exhibit no contrast change are associated with zero out-of-plane polarization. After a negative bias was applied, a polarization pointing predominantly out of plane was observed. A similar situation was observed when a positive bias was applied to the film. We noticed that some of the grains exhibit a white contrast associated with a component of the polarization pointing toward the bottom electrode. On the other hand, in the in-plane PFM images (Fig. 7) the contrast changes were associated with changes of the in-plane polarization components. In this case, the white contrast indicates polarization, e.g., in the positive direction of the y axis, while dark contrast are given by in-plane polarization components pointing to the negative part of the y axis. The $d_{33}(V)$ hysteresis loop is shown in Fig. 8. The maximum d_{33} value, ~58 pm/V, is higher than the textured ceramics grown by plasma spark sintering.[14] The enhancement of polarization could be caused by the a/b-axis orientation of the ferroelectric films due to the preferred orientation of Pt substrate. Considering the oriented growth of our films the effective piezoelectric coefficient depends on grain orientation. Therefore, as expected the piezoelectric response is rather larger due to the a/b-axis orientation of the ferroelectric films. As can be seen, the hysteresis loop shows an offset in the vertical direction which can be probably caused by clamping effect due to the substrate and the existence of an ultrathin air gap between the tip and the sample which might lower the actual voltage drop in the film.[15] The presented values reported for our CBNO films suggest that this material can be considered as a viable alternative for lead-free piezoferroelectric devices. This value is much higher compared to that of single phase CBNO ceramics (piezoelectric coefficient d_{33} equal to 7 and 20 pm/V) derived from ordinary firing (OF) and Spark plasma sintering (SPS), respectively.[14]

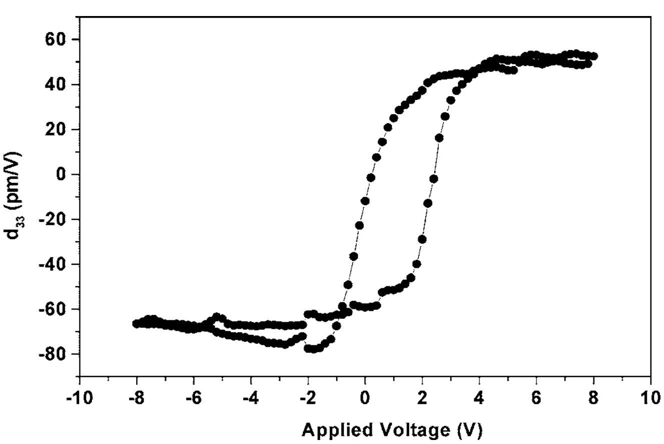

FIG. 8. Piezoresponse loop of CBNO thin film deposited on (100) $Pt/Ti/SiO_2/Si$ substrate at 700 °C for 2 h.

IV. CONCLUSION

Highly polar-axis-oriented $CaBi_2Nb_2O_9$ (CBNO) thin films were deposited on platinum coated silicon substrates by the polymeric precursor method. The a/b-axis orientation of the ferroelectric films is considered to associate with the preferred orientation of Pt substrate. The leakage current density was around 10^{-7} A/cm^2 at an applied electric field of 30 kV/cm. The film showed improved ferro- and piezoelectric properties. The P_r, E_c, ε, and d_{33} values were enhanced compared to those of the CBNO ceramics with random orientation. The polar-axis-oriented CBNO films would open up possibilities for devices as Pb-free piezoelectric materials.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq, and CAPES.

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