Enhancing electromechanical properties of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films grown on Si

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Abstract: In this work, ferroelectric $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films were grown on Yttria-stabilized zirconia (YSZ) -buffered (100) Si substrate via radio-frequency magnetron sputtering. X-Ray diffraction analysis showed that the $\text{CaBi}_2\text{Nb}_2\text{O}_9$ films were (200/020) textured, while the commonly-observed (00 l) grains which are weakly polarizable have been eliminated. Enhanced dielectric (~ 533 @ 5 kHz) and ferroelectric properties ($P_r \sim 13 \mu\text{C}/\text{cm}^2$, $P_s \sim 55 \mu\text{C}/\text{cm}^2$ @ 1 kHz) were achieved in this high T_c piezoelectric material, leading to a significant improvement of the d_{33} piezoelectric modulus (from $\sim 15\text{--}20$ pm/V to ~ 30 pm/v). The method of strain engineering used in this work can be applied to the integration of other bismuth-layer structured ferroelectrics into Si-based microelectronics.

Keywords: Magnetron sputtering; YSZ-buffered Si; Electrical properties; Strain engineering; Bismuth-layer structured ferroelectrics

1. Introduction

$\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO), as one of the family members of bismuth layer-structured ferroelectrics (BLSFs), has attracted a lot of research interests due to its high Curie temperature ($T_c \sim 943^\circ\text{C}$) [1-3]. Such a high T_c opens up a lot of opportunities for high temperature electromechanical applications [1, 4]. Growth of high quality CBNO films on Si substrate will enable its many applications in microelectronic devices, including capacitors, integrated sensors, and piezoelectric microactuators. Cho and Desu [5, 6] are among the first groups of researchers who prepared CBNO films on Si, their films grown via pulsed laser deposition showed a remnant polarization of $\sim 3.6 \mu\text{C}/\text{cm}^2$ and a dielectric constant of ~ 76.5 , both being inferior to their counterparts in bulk materials. More recent work include those by A. Z. Simões et al. [3, 7, 8], who prepared polycrystalline CBNO films on Si by using a polymeric precursor method, and that with a strong polar-axis orientation by Y. Ahn et al. [9] via pulsed laser deposition. The reported electrical property data showed substantial yet not decisive improvements. For example, the dielectric constants were still in the range of 100~180. More importantly, the lack of a systematic study of the CBNO films on Si based on understanding of the processing-structure-property interrelationships, has cast a shadow on the continuing improvement of their electrical properties.

As a key feature of the BLSFs, the spontaneous polarization mainly exists in the

a - b plane and is quite small along the c axis. Therefore, electrical and electromechanical properties of BLSFs are highly dependent on their crystalline orientations [10]. Bulk CBNO has an orthorhombic symmetry with its polarization along the a -axis [1], which suggests that epitaxial or highly textured a -axis oriented CBNO films will have the largest polarizations among their peers. Difficulty in preparing such films has become a major challenge for the applications of CBNO as well as many other BLSFs in microelectronics. Moreover, for the applications in piezoelectric devices, a large dielectric constant is as important as a sizable remnant polarization on yielding a large piezoelectric modulus. Based on the relationship $d_{33} = 2Q_{\text{eff}}\epsilon_r\epsilon_0P_s$ [11, 12], where d_{33} is the longitudinal piezoelectric modulus, Q_{eff} is an effective electrostrictive coefficient, ϵ_r is the relative dielectric constant, ϵ_0 is the vacuum dielectric constant, P_s is the spontaneous polarization, a large product of ferroelectric polarization and dielectric constant ϵ_rP_s of a ferroelectric film is the key for the enhancement of its piezoelectric property.

Buffer layers, such as Yttria-stabilized zirconia (YSZ) [13], TiO_2 [9], Bi_2SiO_5 [14], were used to grow a -axis oriented BLSF films. YSZ (15% Y) has a cubic lattice with a lattice parameter of 5.14Å. The use of YSZ has facilitated the growth of nearly 100% a -axis oriented BLZT films [13]. However, to the authors' best knowledge, there is no reported work on using YSZ as a buffer layer to optimize the growth orientation of a CBNO film on Si substrate. As shown in Table 1, the lattice misfits and the preferred crystalline orientations of CBNO films grown on single-crystalline

YSZ and Si substrates were summarized and compared. While the weakly polarizable *c*-axis oriented grains are energetically favorable to grow on unbuffered Si substrate, strongly polarizable *a*-axis grains will dominate in CBNO films grown on YSZ. Therefore, depositing a YSZ layer in-situ prior to the growth of a CBNO film on Si will increase the amount of non *c*-axis oriented grains, leading to improved electrical properties including a larger remnant polarization and a higher dielectric constant.

2. Materials and methods

CBNO films of ~250 nm thick were deposited on (100) YSZ and YSZ-buffered (100) Si substrates by using a radio-frequency (RF) magnetron sputtering technique. The base pressure of the sputtering chamber was set at 2.0×10^{-4} Pa. SrRuO₃ (SRO), a conductive metallic oxide with a cubic perovskite structure, was chosen as the bottom electrode as it has been proven a working electrode to promote the formation of *a/b*-axis oriented BLFs films [13]. During the sputtering process, the substrate was kept at 600 °C, and a sputtering pressure of 1.2 Pa was used with a fixed Ar:O₂ flow ratio of 4:1. The sputtering power was set at 70W, and a target-substrate distance of 55 mm was used. Prior to the growth of the CBNO film, YSZ buffer layer and SRO bottom electrode were deposited under the same sputtering conditions. The finished multilayer structures were cooled down at a rate of 6-8 °C/min in the same atmosphere.

Phase structure and crystallographic orientations of the CBNO films were analyzed by using X-ray θ - 2θ scans (Rigaku Dmax-rc XRD diffractometer equipped with a

Ni-filtered Cu-K α radiation source). Dielectric properties (C - V characteristics) of the CBNO films were measured by using an impedance analyzer (HP4194A, Hewlett–Packard Ltd.), while the room-temperature ferroelectric hysteresis loops were obtained by using a Radiant Precision Premier II ferroelectric tester. The piezoelectric displacements of the samples were measured by using quantitative piezoelectric force microscopy (Scanning Probe Microscope, SPA-300HV controlled by SPI, Seiko Instruments, Inc.). Circular Au top electrodes (Φ = 200 μ m) were sputtered at room temperature via a shadow mask for the electrical measurements.

3. Results and discussion

Fig. 1 showed the XRD 2θ scan spectra of the CBNO films deposited on (100) YSZ and YSZ-buffered (100) Si substrates, respectively. The film deposited on (100) YSZ showed (200)/(020) and (117) textures with the addition of (20 10) oriented grains. On the other hand, the film deposited on YSZ-buffered (100) Si was (200/020) textured with small amount of $(112m+1)(m=2,3)$, (20 10) and (315) oriented grains. Compared with the CBNO films deposited on unbuffered (100) Si substrates [3, 20], the film deposited on YSZ-buffered (100) Si consists of grains either oriented along the strong polar axis of a - and b -, or slightly tilted away from the a -/ b -axis. This means that by using a YSZ buffer layer, the commonly-observed c -axis oriented grains have been successfully replaced by grains with higher polarizability. Therefore, a larger polarization and a higher dielectric constant can be expected in the CBNO films grown

on YSZ-buffered (100) Si.

The voltage dependent dielectric constant (ϵ_r - V) and loss tangent ($tg\delta$ - V) of the CBNO films were measured at 5 kHz and the results were shown in Fig. 2. The butterfly shape of both ϵ_r - V curves due to domain switching revealed a sound ferroelectricity of our CBNO films. The zero field dielectric constants of the CBNO films deposited on (100) YSZ and YSZ-buffered (100) Si were 443 and 533, respectively. The latter result is nearly a four-fold improvement against the best reported results of the dielectric constant for CBNO films grown on Si substrate (~ 180) [7]. This is consistent with the replacement of weakly polarizable c -grains with strongly polarizable a -grains and grains slightly tilting away from the a - b -axis. Moreover, the CBNO film showed a good figure of merit (FOM) for the dielectric tunability ($\sim 22\%$) due to its low dielectric loss. Under an applied electric field of 600kV/cm, the dielectric constant decreased to 416 with a dielectric loss tangent $tg\delta \sim 0.01$, resulting in a FOM of ~ 22 ¹.

Ferroelectricity of the CBNO films were investigated by measuring the room-temperature pseudo-static P - E hysteresis loops, which are shown in Fig. 3. The P - E hysteresis loops were both measured at 1 kHz under different maximum applied electric fields (E_{max}). As E_{max} was increased (up to breakdown fields of the films), P - E loops of both films showed the tendency of saturation, characteristic of a ferroelectric material. For the film deposited on (100) YSZ, it showed sizable polarization values in

¹ FOM = tunability/loss. In our work, FOM $\approx 0.22/0.01=22$

P_r ($12\mu\text{C}/\text{cm}^2$) and P_s ($\sim 40\mu\text{C}/\text{cm}^2$), consistent with its textured structure. Furthermore, CBNO film grown on YSZ-buffered (100) Si showed even higher polarization values due to a higher breakdown field. When E_{max} was increased to 2000 kV/cm, a saturated polarization (P_s) of $\sim 55\mu\text{C}/\text{cm}^2$, a remnant polarization (P_r) of $\sim 13\mu\text{C}/\text{cm}^2$, and a coercive field (E_c) of $\sim 320\text{kV}/\text{cm}$ were achieved in the CBNO film grown on Si. The P_r value achieved in our CBNO films on Si is about 200% higher than those grown on unbuffered Si substrates ($\sim 4.2\mu\text{C}/\text{cm}^2$) [3, 20], and $\sim 30\%$ higher as compared with the CBNO film deposited on TiO_2 -buffered Si [9]. The significantly improved P_r corresponds to an improved ferroelectricity in our CBNO films, which was a result of the increased amount of electrically active grains via the strain buffering effect provided by the YSZ layer. The enhanced P_s (i.e., electrical displacement), on the other hand, is a reflection of the improved dielectric property, not the ferroelectric one [21].

Fig. 4 gives the piezoelectric displacement (D - V) curves and the resulting d_{33} - V loops of the CBNO films. Both D - V curves showed a typical butterfly shape, signifying a piezoelectricity originated from ferroelectricity of the CBNO films. The maximum values of the piezoelectric displacements were about 2 nm and 1.2nm for the films deposited on YSZ-buffered Si (@ 75V) and YSZ (@ 55V) substrates, respectively. The coercive voltage of the film on YSZ-buffered Si was measured to be $\sim 7.8\text{V}$ from the D - V curve, which is in a good agreement with that measured from the P - V loop ($V_c \sim 8\text{V}$). The piezoelectric moduli d_{33} calculated from slopes of the D - V curves (dD/dV) are $\sim 31\text{ pm}/\text{V}$ and $\sim 22\text{ pm}/\text{V}$ for the films deposited on Si and YSZ substrates,

respectively. The d_{33} value of the film deposited on YSZ is comparable to those of the CBNO ceramics' (10~20 pm/V or pC/N) [1, 2, 22], while d_{33} of the film deposited on YSZ-buffered (100) Si showed ~ 50% improvement against the best bulk value of ~20 pm/V.

The superior piezoelectric performance of the films can be explained by their improved textures with strongly polarizable grains. Furthermore, a larger d_{33} modulus in the CBNO film grown on Si can be attributed to a stronger (200)/(020) film texture and a softer substrate. [23, 24]. While the dominant (200)/(020) grains can yield a larger longitudinal piezoelectric response at a given electric field [1], a softer substrate has a smaller clamping effect and a larger “Poisson strain” contribution [23] to the piezoelectric deformation of the film, and, therefore, effectively enhances its d_{33} piezoelectric modulus.

4. Conclusion

Non-*c*-axis oriented ferroelectric $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO) thin films have been successfully prepared on YSZ-buffered (100) Si substrates by using a radio-frequency (RF) magnetron sputtering technique. Increased amount of *a*-axis grains or grains slightly tilting away from the strong polar axis of *a*- and *b*-, has led to enhanced dielectric, ferroelectric and piezoelectric properties. A high dielectric constant (~533 @ 5kHz) and a small dielectric loss ($\tan\delta \sim 1\%$ up to an applied electric field of ~600kV/cm) were achieved in the CBNO films on Si. As compared with the results of

unbuffered CBNO films grown on Si, the remnant polarization P_r of our CBNO films ($\sim 13 \mu\text{C}/\text{cm}^2$) was improved by threefold. Lastly, a high piezoelectric modulus d_{33} ($\sim 30 \text{ pm}/\text{V}$) was achieved in the CBNO film, due to its high dielectric constant and large remnant polarization.

Acknowledgement

The authors acknowledge the financial support of the NSFC of China (Project Grant No. 91122024 and No. 50902087), the NSFC of Shandong Province of China (Project Grant No. ZR2012EMQ005 and ZR2014EMM012), the Program for New Century Excellent Talents in University (State Education Ministry), Nano Projects of Soochow City (Grant No. ZXG201445), the Fundamental Research Funds of Shandong University (Grant Nos. 2015JC034, 2015YQ009 and 2016JC036), and a foundation under the Grant No.2015JMRH0103. J.O. would also like to thank the “Qi-Lu Young Scholar Fund” of Shandong University and the support from the Material Measurement Laboratory of NIST, Gaithersburg, MD (USA).

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Table 1. Lattice constants of relevant materials and calculated/measured lattice mismatches between a CBNO film and a substrate.

Materials	CBNO ceramic	(100) Si	(100) YSZ	CBNO film on YSZ (this work)	CBNO film on YSZ buffered Si (this work)
Lattice constants (nm)	a=0.5435, b=0.54658, c=2.4970 ^[15]	a=b=c=0.5430 ^[16]	a=b=c=0.514 ^[13]	a=b=0.5555 (measured)	a=b=0.5427 (measured)
Lattice mismatch at room temperature (%)	N/A	a-axis: -0.09 b-axis: -0.66 c-axis: 8	a-axis: -5.74 b-axis: -5.95 c-axis: 2.84	a-axis: 2.21 b-axis: 1.63 (measured)	a-axis: -0.15 b-axis: -0.71 (measured)
Thermal expansion coefficients ($\times 10^{-6}/K$) between RT and growth temperature	a/b-axis: -2.5 c-axis: 12 ^[17]	2.57-3.84 ^[18]	10.3 ^[19]	a/b-axis: -2.5 c-axis: 12 ^[17]	a/b-axis: -2.5 c-axis: 12 ^[17]
Estimated lattice mismatch with substrate at growth temperature* (%)	N/A	a-axis: 0.24 b-axis: -0.33 c-axis: 7.57	a-axis: -4.97 b-axis: -5.57 c-axis: 2.74	N/A	N/A
Preferred crystalline orientation	N/A	c-axis oriented grain (a-/b- axis in-plane)	a-axis oriented grain(c-axis in-plane)	(200)/(020) and (117) textures (measured)	(200)/(020) texture (measured)

*: Extrapolated to the growth temperature.

Figure captions

Fig. 1 XRD 2θ scan spectra of the CBNO films sputtered on (a) (100) YSZ and (b) YSZ-buffered (100) Si substrates.

Fig. 2 The voltage dependent dielectric constant (ϵ_r -V) and loss tangent ($\tan\delta$ -V) of the CBNO films deposited on (100) YSZ and YSZ-buffered (100) Si (measured at 5 kHz).

Fig. 3 Ferroelectric hysteresis loops of the CBNO film deposited on (a) (100) YSZ and (b) YSZ-buffered (100) Si substrates. The measuring frequency is 1 kHz.

Fig. 4 Piezoelectric displacement versus voltage (D-V) curves of the CBNO films deposited on (a) (100) YSZ and (b) YSZ-buffered (100) Si substrates. The corresponding d_{33} -V loops were computed and plotted in the same graphs.

Fig. 1

Fig. 2

Fig. 3

(a)

(b)

Fig. 4

(a)

(b)