Boosting energy storage performance of low-temperature sputtered $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin film capacitors via rapid thermal annealing

Jing YAN^{a,b,c}, Yanling WANG^d, Chun-Ming WANG^e, Jun OUYANG^{b,*}

^aKey Laboratory for Liquid–Solid Structural Evolution and Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan 250061, China

^bInstitute of Advanced Energy Materials and Chemistry, School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Molecular Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China

^cCollege of Physics and Electronic Engineering, Qilu Normal University, Jinan 250013, China

^dAmperex Technology Limited, Ningde 352100, China

^eSchool of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

Received: September 28, 2020; Revised: January 9, 2021; Accepted: January 26, 2021

© The Author(s) 2021.

Abstract: $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin film capacitors were fabricated on SrRuO_3 -buffered Pt(111)/Ti/Si(100) substrates by adopting a two-step fabrication process. This process combines a low-temperature sputtering deposition with a rapid thermal annealing (RTA) to inhibit the grain growth, for the purposes of delaying the polarization saturation and reducing the ferroelectric hysteresis. By using this method, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films with uniformly distributed nanograins were obtained, which display a large recyclable energy density $W_{\text{rec}} \approx 69 \text{ J/cm}^3$ and a high energy efficiency $\eta \approx 82.4\%$. A superior fatigue-resistance (negligible energy performance degradation after 10^9 charge–discharge cycles) and a good thermal stability (from -170 to 150°C) have also been achieved. This two-step method can be used to prepare other bismuth layer-structured ferroelectric film capacitors with enhanced energy storage performances.

Keywords: bismuth layer-structured ferroelectrics (BLSFs); calcium bismuth niobate ($\text{CaBi}_2\text{Nb}_2\text{O}_9$); nanograin films; rapid thermal annealing (RTA); energy storage; fatigue-resistance

1 Introduction

Ferroelectric (FE) ceramic capacitors have been investigated intensively for applications in electric power systems and advanced pulsed-discharge devices, because of their fast charge/discharge rate, good thermal stability as well as a remarkable fatigue resistance [1–7].

Compared with bulk ceramics, ferroelectric (FE) film capacitors exhibit a better energy-storage performance due to a much higher maximum applicable electric field/breakdown strength [8,9]. Generally, the recyclable energy storage density (W_{rec}) and energy efficiency (η) are the two critical parameters to evaluate the energy storage performance of a film capacitor. With a measured polarization–electric field (P – E) hysteresis loop, W_{rec} and η of an FE capacitor can be calculated using the equations:

* Corresponding author.

E-mail: ouyangjun@qlu.edu.cn

$$W_{\text{rec}} = \int_{P_r}^{P_m} E dP$$

$$W_c = \int_0^{P_m} E dP$$

$$\eta = \frac{W_{\text{rec}}}{W_c}$$

where P_m and P_r are the maximum polarization and remnant polarization respectively, and W_c is the stored energy density. Based on these equations, FE film capacitors with a slim P – E loop, featuring a large P_m , a small P_r , and a high maximum applicable/breakdown electric field, are desirable for capacitive energy storage applications. Recently, various methods have been proposed and investigated to improve the energy storage performance of FE film capacitors, such as domain engineering, interface engineering, chemical doping, and so on [2,6,10–12]. In this work, we adopt a two-step process to fabricate nanocrystalline bismuth layer-structured ferroelectric (BLSF) $\text{CaBi}_2\text{Nb}_2\text{O}_9$ film capacitors, which display an excellent energy storage performance with a high energy density ($W_{\text{rec}} \approx 69 \text{ J/cm}^3$) and charge–discharge efficiency ($\eta \approx 82.4\%$).

Compared to pseudo-equiaxial ($a \approx b \approx c$) perovskite ferroelectrics, such as BiFeO_3 and $\text{Pb}(\text{Zr,Ti})\text{O}_3$, the BLSFs have a highly anisotropic lattice ($c \gg a \approx b$). Except for a few rare cases of epitaxial c -axis or a/b -axis oriented BLSF films including $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [13,14] and $\text{CaBi}_2\text{Nb}_2\text{O}_9$ [15,16], most of the BLSF films were polycrystalline with (1, 1, $2n+1$)-type textured grains which tilt a large angle from the c - or a/b -polar axis [17–20]. Therefore, compared with a perovskite FE film, it is more difficult to fully align the ferroelectric polarization in a BLSF film using an external electric field, leading to a relatively small remnant/saturated polarization [15,21]. On the other hand, with a large dielectric constant ($\epsilon_r \approx 480$) recently revealed in {1 1 $2n+1$ } textured BLSF-type $\text{CaBi}_2\text{Nb}_2\text{O}_9$ films [20], it is possible to create a large maximum polarization, i.e., a large total electric displacement including both ferroelectric and linear dielectric parts, under a sizable electric field [22]. This will lead to a desirable energy storage performance (high W_{rec} and η).

As a bismuth layer-structured ferroelectric, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO) has attracted a lot of research interests due to its high Curie temperature ($\sim 943^\circ\text{C}$), large ferroelectric polarization ($P_s \approx 24.4 \text{ }\mu\text{C/cm}^2$), and a remarkable fatigue resistance [15,20,23–25]. Our previous investigations achieved $W_{\text{rec}} \approx 21.5 \text{ J/cm}^3$ and $\eta \approx 50\%$ in CBNO

films on SRO-buffered MgO substrates [15], and $W_{\text{rec}} \approx 28 \text{ J/cm}^3$ and $\eta \approx 62\%$ in those grown on SRO-buffered Pt/Ti/Si substrates [20]. In this work, we aim at further improving the energy storage performance of the CBNO film by significantly reducing its grain size. This is achieved by using a two-step process combining a low-temperature sputtering growth with a rapid thermal annealing (RTA) process. Firstly, CBNO films were grown by using a radio frequency magnetron sputtering process on SrRuO_3 -buffered Pt(111)/Ti/Si(100) substrates at 350°C (denoted as “CBNO_{A350}”). Such a low-temperature deposition process facilitates nucleation of the (115) grains, which have a low activation energy and a high dielectric constant [20,27]. Then the samples were annealed in a rapid thermal annealing furnace at 700°C for 15 min, which promotes a limited growth of the (115) grains and improves the overall crystalline quality of the as-grown film [25,26,28]. Compared with a single-step, high-temperature sputtering growth at 700°C , this two-step process not only reduces the thermal budget, but also decreases the average grain size. The latter is critical in improving the energy storage performance of the CBNO films. The resulted CBNO films (denoted as “CBNO_{350-RTA}”) showed a large P_m ($\sim 51 \text{ microcoulombs/cm}^2$), a small P_r ($\sim 3.4 \text{ microcoulombs/cm}^2$), and a small coercive field E_c ($\sim 0.16 \text{ MV/cm}$) under a maximum applicable external field of 3.55 MV/cm . Such a slim P – E hysteresis loop corresponds to a large energy density ($W_{\text{rec}} \approx 69 \text{ J/cm}^3$) and a high energy efficiency ($\eta \approx 82.4\%$), which are much higher than those that we obtained earlier. Additionally, these films exhibited a remarkable fatigue resistance (fatigue-free after 10^9 charge–discharge cycles) and thermal stability (stable performance from -170 to 150°C).

2 Experimental procedure

$\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films were sputtered onto Pt(111)/Ti/Si(100) substrates using a radio-frequency magnetron sputtering process at a substrate temperature of 350°C . A SrRuO_3 thin film of $\sim 100 \text{ nm}$ thick was used as a buffer layer due to its chemical and thermal stabilities as well as a good lattice matching with CBNO [20,24]. A commercially available ceramic target of SrRuO_3 and an in-house prepared $\text{CaBi}_2\text{Nb}_2\text{O}_9$ ceramic target were used for the sputtering deposition. A base pressure of $2.0 \times 10^{-4} \text{ Pa}$ was achieved in a multi-target sputtering

chamber prior to the deposition of the SrRuO₃ layer. The detailed deposition parameters were summarized in Table 1. After the sputtering deposition, the samples were cooled down to room temperature at a cooling rate of 6–8 °C/min in a pure O₂ atmosphere with a pressure of 7.5 Pa. Then the samples were annealed in a rapid thermal annealing furnace (RTP-400, Beijing East Star Applied Physics Research Institute) at 700 °C in an ambient atmosphere for 15 min. CaBi₂Nb₂O₉ thin films sputter-deposited at 700 °C without RTA, denoted as “CBNO_{A700}”, were prepared and characterized at the same time for the purpose of comparison. Its deposition parameters were the same as those of the CBNO_{A350} films (Table 1) except for the deposition temperature.

Crystallographic characteristics of the CBNO films were analyzed by using standard X-ray diffraction (XRD) 2 θ -scans in a Rigaku Dmax-2500PC equipped with a Ni-filtered Cu K α radiation source. Cross-sectional and surface morphologies were obtained using a high-resolution thermal field emission scanning electron microscope (SEM, Hitachi, SU-70). Circular Au electrode pads with a diameter of 200 μ m were sputtered on the film surface for electrical measurements using a shadow mask. A standard ferroelectric tester (Precision Premium II, Radiant Technology, USA) was used to measure the ferroelectric properties. The room-temperature relative dielectric constant (ϵ_r) and dielectric loss tangent ($\tan\delta$) were determined using an LCR meter (7600plus, QuadTech, USA) in the frequency range between 1 kHz and 1 MHz, using a small AC signal of 1 V p-p.

3 Results and discussion

The XRD 2 θ -scan patterns and the surface and cross-sectional SEM images of the CBNO films are displayed in Fig. 1. The CBNO_{A350} films were poorly crystallized,

Table 1 Deposition parameters of the CBNO_{A350} films sputtered on Si(100) substrates

Parameter	Ti	Pt	SRO	CBNO
Base pressure (Pa)			2.0 $\times$ 10 ⁴	
Target-substrate distance (mm)			60	
Substrate temperature (°C)	300 $\pm$ 5			350 $\pm$ 5
Sputtering pressure (Pa)	0.3	0.3	0.3	1.4
Sputtering power (W)	55	55	70	130
Sputtering atmosphere	Ar	Ar	Ar/O ~ 4:1	Ar/O ~ 4:1
Deposition time	5 min	20 min	15 min	2 h

close to an amorphous state. After the RTA process, the overall crystalline quality of the as-grown film has been improved, mostly from growth of the (1, 1, 2 n +1) grains driven by an interface energy [25,26,28]. Compared with those of the perovskite Pb(Zr,Ti)O₃ thin films [28], recrystallization and grain growth of the CBNO film during an RTA process are much more limited because of its strong anisotropic lattice. The CBNO_{350-RTA} film showed a preferred (115)-orientation, which is about 56° tilted away from the [100]/[010] polar axis (with a theoretical $P_s \approx 24.4 \mu\text{C}/\text{cm}^2$) [23]. Therefore, a reduced ferroelectric polarization and an enhanced dielectric constant can be expected [20,24]. After RTA, the film's average grain size increased to ~22 nm (from analysis of Fig. 1(d)). Note that this number (“local average”) was consistent with the result obtained by using the Scherrer formula (“global average”, ~20 nm), suggesting a well-controlled grain size via the RTA process. For comparison, the XRD pattern and SEM images of the CBNO_{A700} film are shown in Fig. 1(a) and Fig. 1(c), respectively. The CBNO_{A700} film exhibited a wide range of grain size from ~28 to ~228 nm (from analysis of 50 grains in Fig. 1(c)). The difference between the global average grain size via Scherrer formula (~75 nm) and the local one via SEM analysis (~99 nm) can be partially attributed to the grain size nonuniformity. Figure 1(c) clearly reveals such a nonuniform and large-grain microstructure in the CBNO_{A700} film, which can be ascribed to an inhomogeneous nucleation and grain-growth at a high deposition temperature [27]. From Figs. 1(b) and 1(d), a smooth surface and a dense film morphology, as well as a nanograin structure, can be observed in both the CBNO_{A350} and CBNO_{350-RTA} films. The uniform and small grain size of the CBNO_{350-RTA} film is a natural consequence of the RTA process, which promotes a limited grain growth dictated by minimization of the interface energy [25,28]. A slim P – E hysteresis, a high breakdown field, and a low leakage current are expected for the CBNO_{350-RTA} film from its dense and nanograin microstructure.

Figures 2(a) and 2(b) are the polarization–electric field (P – E) curves measured at 1 kHz. A slightly nonlinear P – E curve with a P_r less than 1 $\mu\text{C}/\text{cm}^2$ was observed for the CBNO_{A350} film. After the RTA process, a slim ferroelectric P – E hysteresis loop with a $P_r \approx 3.4 \mu\text{C}/\text{cm}^2$ was displayed by the CBNO_{350-RTA} film. For the CBNO_{A350} film, its slightly nonlinear P – E curve with a sizable slope/ ϵ_r yet lacking of a saturating trend/concave

Fig. 1 (a) XRD 2θ -scan patterns for $\text{CBNO}_{\text{A350}}$, $\text{CBNO}_{\text{A700}}$, and $\text{CBNO}_{350\text{-RTA}}$ thin films, and the surface and cross-sectional SEM images of (b) $\text{CBNO}_{\text{A350}}$, (c) $\text{CBNO}_{\text{A700}}$, and (d) $\text{CBNO}_{350\text{-RTA}}$ films.

Fig. 2 Room-temperature polarization–electric field (P – E) curves for the (a) $\text{CBNO}_{\text{A350}}$ and (b) $\text{CBNO}_{350\text{-RTA}}$ thin films, and (c, d) their corresponding energy storage performances. The red dashed-line curve in (b) is a representative P – E loop of the $\text{CBNO}_{\text{A700}}$ film at its maximum applicable electric field (~ 1 MV/cm).

curvature, plus a very small grain size, indicate the likelihood of a room temperature superparaelectric (SPE) state [29,30]. In such a state, the thermal energy of a nanograin is higher than the energy needed for its polarization switching, resulting in the absence of a long-range polar order, i.e., $P_r \rightarrow 0$. The critical grain size $2R_c$ for the SPE state can be estimated by using the relation:

$$\frac{V_c P_r^2}{2\epsilon_0 \epsilon_r} = k_B T$$

where k_B , T , P_r , ϵ_0 , ϵ_r , V_c ($4\pi R_c^3/3$) are the Boltzmann constant, the absolute temperature (K), the remnant polarization, the vacuum dielectric constant, the relative dielectric constant, and the correlation volume, respectively. With the known material parameters taken from the literature [23], the critical size $2R_c$ for the appearance of an SPE state in a CBNO film was estimated to be between ~ 3.4 and ~ 4 nm, and our estimated grain size for the $\text{CBNO}_{\text{A350}}$ film ($2R_{\text{avg}} < 10$ nm) is in the same order as the $2R_c$, suggesting that it may exist in the SPE state. Compared with the

ferroelectric P – E loop of the $\text{CBNO}_{350\text{-RTA}}$ film in Fig. 2(b), the $\text{CBNO}_{\text{A}350}$ film showed about ~65%–75% of the polarization at a given electric field E , indicating an effective dielectric constant smaller yet on the same order as that of the latter. This is indicative of a strong local polar structure in the $\text{CBNO}_{\text{A}350}$ film [30]. On the other hand, both the $\text{CBNO}_{350\text{-RTA}}$ and $\text{CBNO}_{\text{A}700}$ films showed ferroelectric characteristics in their P – E curves (Fig. 2(b)), including a small yet non-zero P_r and a concave curvature indicative of polarization saturation. Their differences, however, lie on the shape of the P – E loops they present. The $\text{CBNO}_{\text{A}700}$ film showed an earlier saturation at ~1 MV/cm, as well as a larger P_r (~7.6 microcoulombs/cm²) compared with those of the $\text{CBNO}_{350\text{-RTA}}$ film. Meanwhile, the $\text{CBNO}_{350\text{-RTA}}$ film showed an extended ($E_{\text{max}} \approx 3.55$ MV/cm) and slim P – E hysteresis loop, featuring a large maximum polarization P_m (~51 microcoulombs/cm²) and a small P_r (~3.4 microcoulombs/cm²). These differences can be attributed to those in their crystalline characteristics. As shown in Figs. 1(a), 1(c), and 1(d), the $\text{CBNO}_{350\text{-RTA}}$ film has a narrowly-distributed nanograin structure ($2R_{\text{avg}} \approx 20$ nm) with a {115} texture, while the $\text{CBNO}_{\text{A}700}$ film consists of nonuniform large grains (~28–228 nm) with random crystalline orientations. Compared with the dominant {115}-oriented grains in the $\text{CBNO}_{350\text{-RTA}}$ film, the rich collection of ferroelectric domains with different orientations in the $\text{CBNO}_{\text{A}700}$ film helps ease the polarization alignment under an external electric field, leading to an early polarization saturation and hence a poor energy performance. Specifically, under the same electric field of 1 MV/cm, the energy performance of the $\text{CBNO}_{350\text{-RTA}}$ film ($W_{\text{rec}} \approx 10.4$ J/cm³ and $\eta \approx 93\%$) was much better than that of the $\text{CBNO}_{\text{A}700}$ ($W_{\text{rec}} \approx 6.4$ J/cm³ and $\eta \approx 50.4\%$). In addition, a longer exposure to the high processing temperature of 700 °C helped generate more defects in the $\text{CBNO}_{\text{A}700}$ film [28,31], leading to its lower breakdown strength/maximum applicable field, and hence contributes to a lower energy storage capability. The higher breakdown field of the $\text{CBNO}_{350\text{-RTA}}$ film, as compared to that of $\text{CBNO}_{\text{A}350}$, is most likely due to the rapid thermal annealing process, which helped improve crystallinity of the film as well as reduce the number and volume ratio of poorly crystallized grain boundaries with many associated defects [32,33]. This has led to a delayed saturation of the overall electric polarization, and an

improved energy storage capability.

From the P – E curves, the energy densities W_c , W_{rec} , and efficiency η were computed for the $\text{CBNO}_{\text{A}350}$ and $\text{CBNO}_{350\text{-RTA}}$ films, as shown in Figs. 2(c) and 2(d), respectively. Both W_{rec} and W_c increase with the applied electric field, due to the linear dielectric response (for both films), as well as an increasing ferroelectric polarization (only for the FE film of $\text{CBNO}_{350\text{-RTA}}$). As E increases from ~1.5 to 2.76 MV/cm, energy efficiency η of the $\text{CBNO}_{\text{A}350}$ film only slightly decreases (from ~92.2% to ~90.7%). A reduction in η (from ~92.1% to ~87.8%) was observed for the $\text{CBNO}_{350\text{-RTA}}$ film under a similar field change, which can be attributed to a gradual polarization saturation in the FE film, i.e., the value of $P_m - P_r$ increased at a slower pace with an increasing electric field E . In addition, a slightly increased electrical conduction at a higher E also contributes to the reduced energy efficiency. On the energy density aspect, a sizable W_{rec} (~34.8 J/cm³) was achieved in the $\text{CBNO}_{\text{A}350}$ film under its maximum applicable field of 2.76 MV/cm, while for the $\text{CBNO}_{350\text{-RTA}}$ film, a much higher W_{rec} (~47.7 J/cm³) was achieved at the same electric field, which can be attributed to a larger dielectric constant and a contribution from reversible domain switching. It is noted that, a much higher W_{rec} (~69 J/cm³) with a decent energy efficiency η (~82.4%) were achieved in the $\text{CBNO}_{350\text{-RTA}}$ film at its maximum applicable electric field of 3.55 MV/cm. These numbers are much higher than those of the CBNO film sputtered on SRO-buffered MgO substrate at 600 °C ($W_{\text{rec}} \approx 21.5$ J/cm³ and $\eta \approx 50\%$) [15], and the CBNO film sputtered on SRO-buffered Pt/Ti/Si substrate at 500 °C ($W_{\text{rec}} \approx 28$ J/cm³ and $\eta \approx 62\%$) [20].

To further understand the energy storage performance of these thin film capacitors, the switching current–electric field ($I_{\text{sw}}-E$) loops were measured for the $\text{CBNO}_{\text{A}350}$ and $\text{CBNO}_{350\text{-RTA}}$ films, as shown in Figs. 3(a) and 3(b), respectively. It has been reported that the total accumulated charges of an FE film capacitor, as well as its contributions from the linear dielectric displacement, the electric conductivity, and the ferroelectric domain switching, can be quantitatively evaluated by analyzing the $I_{\text{sw}}-E$ loop [34–36]. In the present work, the corresponding contributions were schematically illustrated in Figs. 3(a) and 3(b), for the $\text{CBNO}_{\text{A}350}$ and the $\text{CBNO}_{350\text{-RTA}}$ films under the same applied electric field (2.76 MV/cm), respectively. In both cases, the central pseudo-trapezoid area in the

Fig. 3 Room temperature (RT) switching current–electric field curves for (a) CBNO_{A350} and (b) CBNO_{350-RTA} films under an applied electric field of ~ 2.76 MV/cm. (c) Schematic illustration of the linear dielectric (W_{in}) and domain backswitching (W_{bs}) contributions to the recyclable energy density W_{rec} of the CBNO_{350-RTA} thin film. (d) Contributions from W_{in} and W_{bs} to W_{rec} as functions of the applied electric field (at RT).

I_{sw} – E loop corresponds to the dominant contribution to the power density (energy density/time) of the film capacitor from the dielectric displacement, while the upper triangular area corresponds to the power density dissipated due to electrical conduction. For the CBNO_{350-RTA} film, there is another sizable contribution to its capacitive power coming from the ferroelectric domain switching (the top light blue, pseudo-triangular area in its I_{sw} – E loop, Fig. 3(b)), which can be attributed to the size-driven transition to the ferroelectric state endowed by the RTA. The linear dielectric contribution to the recyclable energy density W_{rec} can be obtained from the I_{sw} – E loop, using the formula

$$W_{in} = \Delta J \cdot E \cdot t$$

where W_{in} is the energy density from the contribution of the linear dielectric displacement, $\Delta J \cdot E$ is the green shaded area in the J – E diagram with J being the switching current density and E the applied electric field, and t is the duration time. The schematic illustrations of W_{in} and W_{bs} for the CBNO_{350-RTA} film are also shown in Fig. 3(c). The W_{in} resulted from Fig. 3(b) is consistent with that obtained from the P – E loop in Fig. 3(c) (at the same applied field of 2.76 MV/cm). Moreover, as shown in Fig. 3(d), W_{in} consistently played a dominant role in W_{rec} under an increasing electric field, indicating a major contribution to the capacitive energy of the CBNO_{350-RTA} film from its

intrinsic linear dielectric response [22]. Furthermore, the ratio of W_{bs}/W_{rec} gradually increased with the electric field, which can be attributed to an enhanced domain backswitching in the fine-grained CBNO_{350-RTA} film at the removal of a higher electric field [37,38]. Overall, the nanometer-sized, uniformly distributed grains formed after the RTA process, not only endow the CBNO_{350-RTA} film an enhanced breakdown field, but also reduce its remnant polarization. Both features help improve the film's energy storage performance.

As important parameters to evaluate the energy storage performance of dielectric capacitors, the room temperature dielectric constant, loss tangent, and leakage current density were measured for the CBNO_{A350}, CBNO_{350-RTA}, and CBNO_{A700} films, and the results are displayed in Figs. 4(a)–4(d). From Fig. 4(a), we can see that both ϵ_r and $\tan\delta$ exhibited a weak frequency dependence for the CBNO_{A350} and CBNO_{350-RTA} films. With an increasing frequency, ϵ_r slightly decreased from 208.2 (at 1 kHz) to 203.8 (at 1 MHz) for the CBNO_{350-RTA} film, together with a frequency-insensitive low dielectric loss (≤ 0.016). However, for the CBNO_{A700} film, its ϵ_r decreased from 151 (at 1 kHz) to 97 (at 1 MHz) and dielectric loss jumped from ~ 0.11 (at 1 kHz) to ~ 0.23 (at 1 MHz). The high dielectric loss indicates a leaky dielectric while its further increase with the measuring frequency in the 100 kHz–1 MHz range can be attributed to bulk dielectric relaxation

Fig. 4 (a) Frequency-dependent dielectric constant (ϵ') and loss tangent ($\tan\delta$). The leakage current density of the (b) $\text{CBNO}_{\text{A350}}$, (c) $\text{CBNO}_{350\text{-RTA}}$, and (d) $\text{CBNO}_{\text{A700}}$ film as functions of electric fields at various temperatures. (e) Recyclable energy storage density and energy efficiency as functions of charge–discharge cycles (at RT) for the $\text{CBNO}_{350\text{-RTA}}$ film, and the corresponding P – E hysteresis loops and performance stabilities ($W_{\text{rec}}/W_{\text{rec-1st circle}}$, $\eta/\eta_{1\text{st circle}}$) at different stages of the cycling test. (f) Thermal stabilities (W/W_{RT} , η/η_{RT}) of W_{c} , W_{rec} , and η for the $\text{CBNO}_{350\text{-RTA}}$ film.

processes, which are induced by its large amount of defects generated under a long exposure to a high processing temperature [38]. The dielectric constant is affected by many factors, including structural defects, phase composition, domain structure, crystallographic orientation, and grain size [39]. In this work, the higher dielectric constant of the $\text{CBNO}_{350\text{-RTA}}$ film compared to that of $\text{CBNO}_{\text{A350}}$, can be attributed to its preferred (115)-orientation [20,24], as well as its improved crystallinity via RTA. While the lower dielectric constant in the $\text{CBNO}_{\text{A700}}$ film than $\text{CBNO}_{350\text{-RTA}}$ can be ascribed to its random crystallographic orientation.

The temperature dependent leakage current densities of the $\text{CBNO}_{\text{A350}}$, $\text{CBNO}_{350\text{-RTA}}$, and $\text{CBNO}_{\text{A700}}$ films were shown in Figs. 4(b), 4(c), and 4(d), respectively. It can be seen that, the leakage current densities of $\text{CBNO}_{\text{A350}}$ and $\text{CBNO}_{350\text{-RTA}}$ increased monotonically

with an increasing temperature, and they were about $\sim 1 \times 10^{-5}$ A/cm² and $\sim 1 \times 10^{-4}$ A/cm² respectively under 1 MV/cm at the highest testing temperature of 120 °C. For the $\text{CBNO}_{\text{A700}}$ film, all the leakage currents are very high, and the temperature dependence is rather weak except for an electric breakdown at 100 °C. This is likely due to its large amount of existing defects which can be readily driven by an external electric field. Based on the above discussion, it can be deduced that both the dielectric and leakage characteristics of the $\text{CBNO}_{350\text{-RTA}}$ film are desirable for energy storage applications.

Fatigue-resistance of the $\text{CBNO}_{350\text{-RTA}}$ film was analyzed through a charge–discharge cycling test (Fig. 4(e)). No noticeable losses can be observed for W_{rec} and η after 10^9 charge–discharge cycles under an applied electric field of 2.37 MV/cm ($\sim 2/3$ of its

maximum applicable field), indicating an excellent cycling stability ($W_{\text{rec}}/W_{\text{rec-1st circle}}$, $\eta/\eta_{\text{1st circle}}$)/fatigue-resistance. Lastly, W_c , W_{rec} , and η were measured in the temperature range of (-170) – 150 °C, and the results are shown in Fig. 4(f). Very small fluctuations were observed for these three parameters ($\sim 3.2\%$ for W_c , $\sim 6.9\%$ for W_{rec} , and $\sim 9\%$ for η) in this broad temperature range. The decreases in W_{rec} and η near $T = 150$ °C can be attributed to an enhanced electrical conduction, which is associated with the thermally-induced movement of charged defects [5,40].

4 Conclusions

In a summary, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO) thin film capacitors with an enhanced energy storage performance were successfully prepared on SRO-buffered Pt(111)/Ti/Si(100) substrates by adopting a two-step fabrication process. A low temperature sputter-deposition leads to a small grain size and lowers the electrical conduction, enhancing the breakdown field as well as reducing the remnant polarization P_r . On the other hand, the RTA process can improve the crystalline quality of the as-grown film without overgrowing the grains, thus increasing the maximum polarization P_m and recyclable energy density W_{rec} . The resulting dense and nanograined ferroelectric film not only shows an enhanced breakdown field, but also a much-reduced P_r and a delayed polarization saturation, leading to a significantly improved energy storage performance ($W_{\text{rec}} \approx 69 \text{ J/cm}^3$, $\eta \approx 82.4\%$ at 3.55 MV/cm). The linear dielectric contribution plays a dominant role in the total recyclable energy density. Excellent fatigue-resistance and thermal stability were observed in these CBNO films. This work reveals a novel processing route to produce high performance BLSF FE film capacitors for energy storage applications.

Acknowledgements

We acknowledge the financial support of the National Natural Science Foundation of China (Grant Nos. 51772175 and 51872166), and the Nano Projects of Suzhou City (Grant No. ZXG201445). J. Ouyang would also like to acknowledge the support from the Seed Funding for Top Talents in Qilu University of Technology (Shandong Academy of Sciences), the International Cooperation Research Project of Qilu University of

Technology (Grant No. QLUTGJHZ2018003), and the Independent Innovation Foundation of Shandong University (Grant Nos. 2018JC045 and 2017ZD008).

References

- [1] Chu B, Zhou X, Ren K, *et al.* A dielectric polymer with high electric energy density and fast discharge speed. *Science* 2006, **313**: 334–336.
- [2] Cheng H, Ouyang J, Zhang YX, *et al.* Demonstration of ultra-high recyclable energy densities in domain-engineered ferroelectric films. *Nat Commun* 2017, **8**: 1999.
- [3] Yao K, Chen ST, Rahimabady M, *et al.* Nonlinear dielectric thin films for high-power electric storage with energy density comparable with electrochemical supercapacitors. *IEEE Trans Ultrason Ferroelectr Freq Control* 2011, **58**: 1968–1974.
- [4] Pan ZB, Wang P, Hou X, *et al.* Fatigue-free aurivillius phase ferroelectric thin films with ultrahigh energy storage performance. *Adv Energy Mater* 2020, **10**: 2001536.
- [5] Yang BB, Guo MY, Tang XW, *et al.* Lead-free $\text{A}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ thin film capacitors ($\text{A} = \text{Ba}$ and Sr) with large energy storage density, high efficiency, and excellent thermal stability. *J Mater Chem C* 2019, **7**: 1888–1895.
- [6] Pan H, Ma J, Ma J, *et al.* Giant energy density and high efficiency achieved in bismuth ferrite-based film capacitors via domain engineering. *Nat Commun* 2018, **9**: 1813.
- [7] Tong S, Ma BH, Narayanan M, *et al.* Lead lanthanum zirconate titanate ceramic thin films for energy storage. *ACS Appl Mater Interfaces* 2013, **5**: 1474–1480.
- [8] Sun ZX, Wang Z, Tian Y, *et al.* Progress, outlook, and challenges in lead-free energy-storage ferroelectrics. *Adv Electron Mater* 2020, **6**: 1900698.
- [9] Palneedi H, Peddigari M, Hwang GT, *et al.* High-performance dielectric ceramic films for energy storage capacitors: Progress and outlook. *Adv Funct Mater* 2018, **28**: 1803665.
- [10] Lv P, Yang CH, Qian J, *et al.* Flexible lead-free perovskite oxide multilayer film capacitor based on $(\text{Na}_{0.8}\text{K}_{0.2})_{0.5}\text{Bi}_{0.5}\text{TiO}_3/\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Ti}_{0.97}\text{Mn}_{0.03})\text{O}_3$ for high-performance dielectric energy storage. *Adv Energy Mater* 2020, **10**: 1904229.
- [11] Fan QL, Ma CR, Li Y, *et al.* Realization of high energy density in an ultra-wide temperature range through engineering of ferroelectric sandwich structures. *Nano Energy* 2019, **62**: 725–733.
- [12] Sun ZX, Ma CR, Liu M, *et al.* Ultrahigh energy storage performance of lead-free oxide multilayer film capacitors via interface engineering. *Adv Mater* 2017, **29**: 1604427.
- [13] Lee HN, Hesse D, Zakharov N, *et al.* Ferroelectric $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ films of uniform a -axis orientation on silicon substrates. *Science* 2002, **296**: 2006–2009.
- [14] Watanabe T, Funakubo H, Saito K, *et al.* Preparation and characterization of a - and b -axis-oriented epitaxially grown $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -based thin films with long-range lattice matching.

- Appl Phys Lett* 2002, **81**: 1660–1662.
- [15] Zhang YX, Ouyang J, Zhang JC, *et al.* Strain engineered $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films with enhanced electrical properties. *ACS Appl Mater Interfaces* 2016, **8**: 16744–16751.
- [16] Ramesh R, Schlom DG. Orienting ferroelectric films. *Science* 2002, **296**: 1975–1976.
- [17] Park BH, Kang BS, Bu SD, *et al.* Lanthanum-substituted bismuth titanate for use in non-volatile memories. *Nature* 1999, **401**: 682–684.
- [18] De Araujo CAP, Cuchiari JD, McMillan LD, *et al.* Fatigue-free ferroelectric capacitors with platinum electrodes. *Nature* 1995, **374**: 627–629.
- [19] Maiwa H, Iizawa N, Togawa D, *et al.* Electromechanical properties of Nd-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films: A candidate for lead-free thin-film piezoelectrics. *Appl Phys Lett* 2003, **82**: 1760–1762.
- [20] Wang YL, Wang YY, Zhang YX, *et al.* Orienting high Curie point $\text{CaBi}_2\text{Nb}_2\text{O}_9$ ferroelectric films on Si at 500 °C. *Ceram Int* 2019, **45**: 20818–20823.
- [21] Hu GD, Fan SH, Cheng X. Anisotropy of ferroelectric and piezoelectric properties of $\text{Bi}_{3.15}\text{Pr}_{0.85}\text{Ti}_3\text{O}_{12}$ thin films on Pt(100)/Ti/SiO₂/Si substrates. *J Appl Phys* 2007, **101**: 054111.
- [22] Peng B, Xie ZK, Yue ZX, *et al.* Improvement of the recoverable energy storage density and efficiency by utilizing the linear dielectric response in ferroelectric capacitors. *Appl Phys Lett* 2014, **105**: 052904.
- [23] Yan H, Zhang H, Uvic R, *et al.* A lead-free high-curie-point ferroelectric ceramic, $\text{CaBi}_2\text{Nb}_2\text{O}_9$. *Adv Mater* 2005, **17**: 1261–1265.
- [24] Zhang YX, Wang CM, Li Y, *et al.* Enhancing electromechanical properties of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films grown on Si. *Ceram Int* 2016, **42**: 17928–17931.
- [25] Meng XJ, Cheng JG, Sun JL, *et al.* Growth of (100)-oriented LaNiO_3 thin films directly on Si substrates by a simple metalorganic decomposition technique for the highly oriented PZT thin films. *J Cryst Growth* 2000, **220**: 100–104.
- [26] Bennett LH, Della Torre E. Analysis of wasp-waist hysteresis loops. *J Appl Phys* 2005, **97**: 10E502.
- [27] Yan J, Hu GD, Liu ZM, *et al.* Enhanced ferroelectric properties of predominantly (100)-oriented $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ thin films on Pt/Ti/SiO₂/Si substrates. *J Appl Phys* 2008, **103**: 056109.
- [28] Wang YY, Cheng HB, Yan J, *et al.* Large piezoelectricity on Si from highly (001)-oriented PZT thick films via a CMOS-compatible sputtering/RTP process. *Materialia* 2019, **5**: 100228.
- [29] Rüdiger A, Schneller T, Roelofs A, *et al.* Nanosize ferroelectric oxides - tracking down the superparaelectric limit. *Appl Phys A* 2005, **80**: 1247–1255.
- [30] Wang K, Ouyang J, Wuttig M, *et al.* Superparaelectric $(\text{Ba}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ultracapacitors. *Adv Energy Mater* 2020, **10**: 2001778.
- [31] Yuan ML, Zhang W, Wang XY, *et al.* In situ preparation of high dielectric constant, low-loss ferroelectric BaTiO_3 films on Si at 500 °C. *Appl Surf Sci* 2013, **270**: 319–323.
- [32] Lee JS, Joo SK. Analysis of grain-boundary effects on the electrical properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films. *Appl Phys Lett* 2002, **81**: 2602–2604.
- [33] Voigt JA, Tuttle BA, Headley TJ, *et al.* The pyrochlore-to-perovskite transformation in solution-derived lead zirconate titanate thin films. *MRS Proc* 1994, **361**: 395–402.
- [34] Yan HX, Inam F, Viola G, *et al.* The contribution of electrical conductivity, dielectric permittivity and domain switching in ferroelectric hysteresis loops. *J Adv Dielect* 2011, **1**: 107–118.
- [35] Brown E, Ma CR, Acharya J, *et al.* Controlling dielectric and relaxor-ferroelectric properties for energy storage by tuning $\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ film thickness. *ACS Appl Mater Interfaces* 2014, **6**: 22417–22422.
- [36] Liang ZS, Ma CR, Shen L, *et al.* Flexible lead-free oxide film capacitors with ultrahigh energy storage performances in extremely wide operating temperature. *Nano Energy* 2019, **57**: 519–527.
- [37] Ren X. Large electric-field-induced strain in ferroelectric crystals by point-defect-mediated reversible domain switching. *Nat Mater* 2004, **3**: 91–94.
- [38] Zhang W, Hu FR, Zhang H, *et al.* Investigation of the electrical properties of RF sputtered BaTiO_3 films grown on various substrates. *Mater Res Bull* 2017, **95**: 23–29.
- [39] Damjanovic D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. *Rep Prog Phys* 1998, **61**: 1267–1324.
- [40] Pan H, Zeng Y, Shen Y, *et al.* BiFeO_3 - SrTiO_3 thin film as a new lead-free relaxor-ferroelectric capacitor with ultrahigh energy storage performance. *J Mater Chem A* 2017, **5**: 5920–5926.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.