Energy Storage Characteristics of BiFeO₃/BaTiO₃ Bi-Layers Integrated on Si

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Abstract: BiFeO₃/BaTiO₃ bi-layer thick films (~1 µm) were deposited on Pt/Ti/SiO₂/(100) Si substrates with LaNiO₃ buffer layers at 500 °C via a rf magnetron sputtering process. X-ray diffraction (XRD) analysis revealed that both BiFeO₃ and BaTiO₃ layers have a (00l) preferred orientation. The films showed a small remnant polarization ($P_r$ ~ 7.8 µC/cm²) and a large saturated polarization ($P_s$ ~ 65 µC/cm²), resulting in a slim polarization-electric field ($P$-$E$) hysteresis loop with improved energy storage characteristics ($W_c$ = 71 J/cm³, $\eta$ = 61%). The successful “slim-down” of the $P$-$E$ loop from that of the pure BiFeO₃ film can be attributed to the competing effects of space charges and the interlayer charge coupling on charge transport of the bi-layer film. The accompanying electrical properties of the bi-layer films were measured and the results confirmed their good quality.

Keywords: ferroelectrics; lead-free; energy storage; bilayer; BiFeO₃; BaTiO₃; Si

1. Introduction

Densities of electrical energy stored in or released from a dielectric can be calculated from their characteristic dielectric displacement-electric field ($D$-$E$) curves by the formula [1]:

$$ W_c = \int_0^{D_s} EdD, \quad W_d = \int_{D_r}^{D_s} EdD \quad (1a) $$

$$ \eta = \frac{W_d}{W_c}, \quad (1b) $$

where $W_c$ is the charged (stored) energy density, $W_d$ is the discharged (released) energy density and $\eta$ the energy efficiency. $D_s$ and $D_r$ are the saturated/maximum and remnant electrical displacements, respectively. For an ideal linear dielectric with a relative dielectric constant $\varepsilon_r$, $D = \varepsilon_0\varepsilon_rE$ and $D_r = 0$, the energy densities are given by [1]:

$$ W_c = \frac{1}{2}\varepsilon_0\varepsilon_rE_{max}^2, \quad (2a) $$

$$ W_d = W_c = \frac{1}{2}\varepsilon_0\varepsilon_rE_{max}^2, \quad (2b) $$

and the efficiency $\eta$ equals 1. Here $\varepsilon_0$ is the vacuum dielectric constant, $E_{max}$ is the maximum applicable electric field which increases with the breakdown field $E_b$ ($E_{max} \approx E_b$ for an ideal dielectric). On the other hand, non-linear dielectrics like ferroelectrics usually don’t have $D \propto E$ or $D_r = 0$, hence $W_c > W_d$. 

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and $\eta < 1$. Nevertheless, Equation (2a) can still be used for the estimation of energy densities $W_c$ in non-linear dielectrics, wherein $\varepsilon_r$ is the average or effective dielectric constant.

To meet the demands in developing portable and integrable power electronics, thin film ceramic capacitors with a high energy storage density $W_c$ and a high efficiency $\eta$ have been intensively investigated [2–4]. The previous studies on thin film ceramic capacitors have been focused on lead-containing perovskite ferroelectrics, including BNZ-PT, BNT-PT and BNH-PT [5–7]. $P-E$ (*) curve of a typical ferroelectric is presented in Figure 1. In this figure, the green area represents the discharged energy density ($W_d$), the yellow area encircled by the hysteresis loop is the energy loss ($W_{loss}$), and the charged energy density is the sum of the two, $W_c = W_d + W_{loss}$. It’s obvious that the energy storage characteristics of a ferroelectric strongly depend on the shape of its $P-E$ loop.

![Figure 1. Schematic of a ferroelectric P-E loop. The green area is the discharged energy density $W_d$, while the yellow area is the energy loss of one charge-discharge cycle ($W_{loss}$).](image)

In the past decade, large energy storage densities (40 J/cm$^3$–60 J/cm$^3$) have been reported in lead-containing ferroelectric films together with good energy efficiencies (40%–60%) [6–9]. However, the growing environment concerns on lead and the usually complex compositions of the solid solutions being used are the two major drawbacks of the lead-containing ferroelectric capacitors. In order to minimize the environmental impact and promote a manufacturing-friendly preparation process, single component lead-free perovskites have been investigated by several research groups for applications in thin film dielectric capacitors [10–14]. Among them, BiFeO$_3$ and BaTiO$_3$ films are most popular candidates [13,14]. The former has a giant saturated polarization and tunable electrical properties via strain or chemical doping, while the latter has excellent dielectric properties (large $\varepsilon_r$ and high $E_b$) and hence has been broadly used in multi-layer ceramic capacitors (MLCC). However, large leakage currents and poor energy efficiencies associated with BiFeO$_3$ thin films have hindered its further development for energy storage applications. On the other hand, a small saturated polarization of BaTiO$_3$ has capped its energy densities (see Equation (1a)) and limited most of its capacitor applications in MLCC.

According to Equation 1, dielectrics with high $E_b$ and $\varepsilon_r$, a small remnant polarization and a large saturated polarization are ideal for high efficiency energy-storage applications. In this work, we demonstrate a novel approach to compensate for the lack of a single material with the above properties. We prepared ferroelectric bilayers of BiFeO$_3$/BaTiO$_3$ on Si substrates via an in-situ rf magnetron sputtering process at 500 °C. Textured growth of the bi-layer films at this moderate temperature was promoted by using a LaNiO$_3$ template layer. The resulted thin film capacitors of Au/BiFeO$_3$/BaTiO$_3$/LaNiO$_3$/Pt/Ti not only showed good dielectric properties (high $\varepsilon_r$ and low leakage current), but also a slim $P-E$ hysteresis featuring an enhanced energy storage density and efficiency, as compared with those of single layers of BiFeO$_3$ and BaTiO$_3$ on Si. The improved energy storage characteristics are interpreted based on our understanding of the charge transport process, which is dominated by the effect of space charges at low electric fields and by the interface charge coupling at high electric fields.
2. Experimental Section

BiFeO$_3$/BaTiO$_3$ bi-layer thick films were fabricated on Pt/Ti/SiO$_2$/(100)Si substrates buffered with a LaNiO$_3$ layer via a rf magnetron sputtering process. Commercially available ceramic targets of BaTiO$_3$, Bi$_{1.05}$FeO$_3$ and LaNiO$_3$ (4N purity, $\Phi = 50$ mm, $L = 5$ mm) were used in the deposition process, which was carried out in a multi-target magnetron sputtering system with a base pressure of $2.0 \times 10^{-4}$ Pa. Firstly, a 120-nm-thick Pt/Ti layer was deposited as the bottom electrode at 300 °C in a pure argon atmosphere. Then the LaNiO$_3$, BaTiO$_3$ and BiFeO$_3$ layers were sequentially sputtered at 500 °C in a mixed gas of Ar and O$_2$. The thickness of the BiFeO$_3$/BaTiO$_3$ bi-layer was about 1 μm with a 1:1 thickness ratio. Lastly, the as-deposited multi-layer thick film was cooled down at a rate of 6 °C/min–8 °C/min in pure oxygen. The deposition parameters of the sputtering process were summarized in Table 1 and the schematics of experimental procedures was shown in Figure 2. For electrical characterizations, circular Au top electrodes with a diameter of 200 μm were deposited at room temperature by using a shadow mask.

| Deposition Parameters | BFO | BTO | LNO |
|----------------------|-----|-----|-----|
| Sputtering power (W)  | 100 | 500 |     |
| Substrate temperature (°C) | 500 | 500 |     |
| Sputtering pressure (Pa) | 1.2 | 0.3 |     |
| Sputtering atmosphere | Ar + O$_2$ (4:1 flow ratio) | |        |
| Cooling atmosphere and pressure | Pure oxygen, 2.5 Pa | | |
| Pt/Ti sputtering parameters | 300 °C, 0.3 Pa, 55 W, pure Ar | | |

Figure 2. Schematics of the experimental procedures.

The phase structures and crystallographic orientations of the bilayer films were characterized by using X-ray diffraction (XRD) $\theta$-2$\theta$ scans with a Ni-filtered Cu-Ka radiation resource (Dmax-rc, Monaghan, Ireland) and pole figures (R-156 Axis Spider, SmartLab® Rigaku, Tokyo, Japan, 40 kV, 200 mA). A commercially available MicroNano D-5A Scanning Probe Microscope (SPM) (MicroNano, Shanghai, China) was used to analyze the surface morphology while the cross-sectional thin film morphology was analyzed by using a thermal field emission scanning electron microscope (SEM) (SU-70, HITACHI, Hitachi, Japan) The room temperature ferroelectric hysteresis loops ($P$-$V$) and leakage currents ($I$-$V$) were measured by using a Radiant Precision Premium II ferroelectric tester (Radiant Technology, Albuquerque, NM, USA). The dielectric properties were measured by using a high precision digital bridge (QuadTech 7600 Plus Precision LCR Meter, IET LABS, Inc., West Roxbury, MA, USA).
3. Results

3.1. Microstructures and Crystallographic Orientations

Figure 3a shows the XRD 2θ scan spectrum of the BiFeO$_3$/BaTiO$_3$ bilayer film grown on LaNiO$_3$/Pt/Ti/SiO$_2$/(100) Si, which is dominated by the preferred (00l) diffraction peaks of the bulk perovskite structures and does not show any crystalline impurities or secondary phases. A tiny amount of (110)-oriented BaTiO$_3$ grains and (100)-oriented tetragonal BiFeO$_3$ grains were detected, which can be attributed to the moderate growth temperature and the effect of residual stress [15,16]. In our previous work [17], it was revealed that a highly (00l)-oriented BaTiO$_3$ thin film can be grown on Pt/Ti/SiO$_2$/(100) Si substrate by using a LaNiO$_3$ buffer layer at 500 °C. Here it is confirmed that the presence of a (00l)-oriented LaNiO$_3$ buffer layer promoted the growth of a (00l) oriented BiFeO$_3$/BaTiO$_3$ bi-layer film.

Figure 3. (a) XRD 2θ scan spectrum (R-rhombohedral, T- tetragonal for BFO peaks, while the BTO phase is tetragonal); (b) X-ray pole figure analyses by using the (001)$_R$ BFO peak; (c) AFM surface scan image (5 µm × 5 µm); and (d) cross-sectional SEM image of the BiFeO$_3$/BaTiO$_3$ bi-layer film deposited on LaNiO$_3$/Pt/Ti/SiO$_2$/(100) Si substrate.

To further investigate the crystallographic characteristics of the bi-layer film, pole figure analysis was carried out on the (001) BiFeO$_3$ reflection (2θ = 22.56°). During collection of the XRD signals, the sample was rotated by varying the tilt angle (0° < ψ < 70°) and the azimuthal angle (0° < φ < 360°) with respect to the scattering vector. The pole figure of (001)$_{BFO}$, as shown in Figure 3b, revealed a strong diffraction peak at the center (tilt angle ψ = 0°), and a set of 4-fold diffraction peaks at ψ ≈ 46°, corresponding to the [101] BiFeO$_3$ plane. This result confirmed the preferred (00l) orientation of the BiFeO$_3$ layer, as suggested by the result of the XRD 2θ scans.

Surface morphology of the BiFeO$_3$/BaTiO$_3$ bi-layer film is displayed in Figure 3c. It can be seen that the grains of the top BiFeO$_3$ layer are densely packed with an average size of ~200–300 nm.
The dense and smooth growth of the BiFeO$_3$ films (Ra is on the order of ~10 nm or above) [18–21]. The smooth growth of the BiFeO$_3$ layer can be attributed to the good quality perovskite underlayers of LaNiO$_3$/BaTiO$_3$. In Figure 3d, the cross-sectional SEM image shows clean and sharp interfaces in the multi-layer thin film. The BiFeO$_3$ and BaTiO$_3$ layers were measured to be ~480 nm and ~500 nm, respectively.

3.2. Energy Storage Characteristics from the P-E Hysteresis Loop

The poling and depoling process of a dielectric under an external electric field simulates the charge-discharge process of a capacitor. Therefore, from the polarization–electric field (P–E) hysteresis loop, the energy storage density $W_c$ and the energy efficiency $\eta$ of the Au/BiFeO$_3$/BaTiO$_3$/LaNiO$_3$/Pt/Ti capacitors can be calculated by using Equation (1). Figure 4a displays the P–E hysteresis loop measured at a pseudo-static frequency of 1 kHz for the bi-layer film (under an applied electric field of 1940 kV/cm). A large maximum polarization ($P_m \approx 65 \mu C/cm^2$) and a small remnant polarization ($P_r \approx 7.8 \mu C/cm^2$) are simultaneously obtained, together with a reduced coercive field $E_c$ ($E_c \approx 152$ kV/cm) as compared with that of pure BiFeO$_3$ film [22]. These features of the P–E curve ensure excellent energy storage characteristics of the film. When compared with pure BaTiO$_3$ films deposited under similar conditions [23], the energy storage density $W_c$ of the bi-layer film reached 71 J/cm$^3$ ($E_{max} = 1940$ kV/cm), a 100%–110% improvement, while the energy efficiency $\eta$ stayed about the same level (~61% vs. 60%–70%). This improvement in $W_c$ can be attributed to a much improved maximum polarization and a high dielectric strength in par with that of a pure BaTiO$_3$ film.

Figure 4. (a) Room temperature ferroelectric hysteresis loop of the BiFeO$_3$/BaTiO$_3$ bi-layer film deposited on LaNiO$_3$/Pt/Ti/SiO$_2$/(100)Si substrate, the insets compare P–E loops of the pure BiFeO$_3$ and BaTiO$_3$ films with those of the bi-layer film measured under the same electric field [22,23]; (b) schematics of the ferroelectric bi-layer considered in our work; (c) the space charge effect dominant at a low electric field, $\omega$ is the depletion layer width under an electric field $E$; (d) strong interlayer charge coupling dominant at a high electric field (after the BaTiO$_3$ layer has been fully depleted).
The “slim-down” of the P-E loop can be explained by the competition between the space charge effect and interlayer charge coupling in the bi-layer film. As demonstrated in our previous study, a space charge layer in BaTiO₃ near its interface with LaNiO₃ dominates the film’s electrical characteristics at a low electric field [24]. Basically, a depletion region with width \( \omega \) forms at the BaTiO₃/LaNiO₃ interface upon the application of a small electric field. The width \( \omega \) can be computed by [24]:

\[
w = \sqrt{\frac{2\varepsilon(V + V_{bi}^*)}{qN_{eff}}},
\]

where \( V_{bi}^* \) is the modified built-in voltage, \( \varepsilon \) is the dielectric constant (\( \varepsilon = \varepsilon_0\varepsilon_r \)), \( N_{eff} \) is the space charge concentration, \( V \) is the applied electric voltage and \( q \) is the electronic charge. The voltage \( V \) will be concentrated across the depletion region and drives its expansion until the BaTiO₃ layer has been fully depleted. It has been shown that the existence and evolution of a depletion layer in a ferroelectric film will cause shrinking and tilting of its P-E loop, leading to reduced \( P_r \) and \( E_c \) [25]. On the other hand, after the BaTiO₃ layer has been completely depleted, a substantial amount of bound charges appear at the BiFeO₃/BaTiO₃ interface owing to the large difference in polarizations between the two layers. Hence the charge transport of the bi-layer film under a high electric field will be dominated by the interface charge coupling, which can be described by an added energy term \( \frac{1}{2\varepsilon_0}\alpha(1 - \alpha)(P_1 - P_2)^2 \) in the Landau-Ginzburg-Devonshire (LGD) thermodynamic potential (free energy density \( F \)) of the bilayer thick film [26]:

\[
F = (1 - \alpha) [F_1(\vec{P}_1) - \vec{E} \cdot \vec{P}_1] + \alpha [F_2(\vec{P}_2) - \vec{E} \cdot \vec{P}_2] + \frac{1}{2\varepsilon_0}\alpha(1 - \alpha)(\vec{P}_1 - \vec{P}_2)^2
\]

(4)

here \( \alpha = h_2/h \) (\( h = h_1 + h_2 \)) is the relative thickness of the second layer, \( F_i, P_i \) (\( i = 1, 2 \)) are the bulk free energy density and polarization of the \( i \)th layer, and \( \vec{E} \) is the applied electric field (see Figure 4b). The third term of the free energy density with the coefficient \( \alpha(1 - \alpha) \) expresses the energy of electrostatic interaction between the two layers, and it becomes dominant when the field is large enough to allow both layers become fully poled. In this case, the difference between the two polarizations diminishes and the film shows an “average” polarization. In our case, the polarization of the fully poled bi-layer film \( P_{bi} \) is close to that of BiFeO₃ due to the fact that \( P_{BTO} \gg P_{BFO} \). The computed \( P_{bi} \) by solving the equilibrium state of Equation (4) is close to 50 \( \mu \)C/cm² [21], fairly consistent with the observed \( P_m \) value if the linear contribution from dielectric susceptibility to the total polarization is deducted. Therefore, the enhanced energy storage capability of the BiFeO₃/BaTiO₃ bi-layer film can be attributed to a combination of space charge effect (dominant at low field, leading to small \( P_r \) and \( E_c \)) and effect of interlayer charge coupling (dominant at high field, leading to a large \( P_m \)).

Figure 5a shows the leakage current density versus electric field \( (J-E) \) curve. At an electric field of 100 kV/cm (bias voltage of 10 V), the leakage current density of the bi-layer film is \( 5.0 \times 10^{-6} \) A/cm². This is about an order of magnitude lower than those reported for single layer BiFeO₃ films grown on Si substrates [27,28]. The reduction in leakage current is in good agreement with the observed morphology change shown in AFM and SEM images, i.e., a densely and smoothly grown BiFeO₃ film was endowed with a much improved electrical resistivity [29]. In addition, an interface energy barrier \( \varphi_B \) between the BiFeO₃ (work function \( W \approx 4.7 \) eV) and BaTiO₃ \( (W \approx 4.0 \) eV) layers can also reduce the leakage current and hence allow the film to be exposed to a large electric field [30,31]. As a result, a high energy density is achieved in the BiFeO₃/BaTiO₃ bi-layer film.

Figure 5b displays frequency-dependent relative dielectric constant \( \varepsilon_r \) and loss tangent \( \tan \delta \) of the bi-layer film. It can be seen that the pseudo static \( \varepsilon_r \) is about 425 (@1 kHz), which is about 33% and 70% higher than those of the single layer BaTiO₃ and BFO films grown on Si, respectively \( (\varepsilon_r \approx 320 \) for BTO, \( \varepsilon_r \approx 250 \) for BFO) [22,32]. When the frequency increases from 1 kHz to 1 MHz, \( \varepsilon_r \) decreases from \( \approx 425 \) to \( \approx 380 \). On the other hand, \( \tan \delta \) varies between 2.4% and 8.4% in the same frequency range,
similar to that of pure BTO films grown on Si. The enhanced dielectric constant \( \varepsilon_r \) contributes to the improved maximum polarization \( P_m \), based on the relation \( P_m = D_m = P + \varepsilon_r \times E_{max} \), where \( P \) is the self-polarization and \( P \approx P_r \) for ferroelectrics.

4. Conclusions

In this study, BiFeO\(_3\)/BaTiO\(_3\) bi-layer thick films deposited on the LaNiO\(_3\) -buffered Pt/Ti/SiO\(_2\)/(100) Si substrates display an enhanced energy density and charge-discharge efficiency \( (W_c = 71 \text{ J/cm}^3, \eta = 61\%) \) as compared with those of the single layer films. This enhancement can be attributed to combined effects of space charges and the interlayer charge coupling. The bi-layer film exhibits a low leakage current density \( (5.0 \times 10^{-6} \text{ A/cm}^2 \text{ at } 100 \text{ kV/cm}) \) as a result of the dense and smooth film morphology achieved in the BFO layer, which is induced by the high quality underlayer of BaTiO\(_3\)/LaNiO\(_3\). The relative dielectric constant \( \varepsilon_r \) is about 33% higher than that of the pure BaTiO\(_3\) film and 70% higher than that of the pure BFO film. In conclusion, the BiFeO\(_3\)/BaTiO\(_3\) bi-layer film shows excellent dielectric performance and energy storage characteristics, making this structure a promising candidate for applications in microelectronics as lead-free thin film ceramic capacitors.

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Notes: For a ferroelectric, its \( P-E \) curve is close to \( D-E \) curve and the two notations \((P-E, D-E)\) are often interchangeably used for one another. Rigorously, what is measured in a polarization-electric field test \((P-E \text{ test})\) of a ferroelectric material is its \( D-E \) curve.

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