Energy Storage Performance of Sandwich Structured Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$/BaZr$_{0.2}$Ti$_{0.8}$O$_3$/Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$ Films

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Abstract: We reported a sandwich structured Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$/BaZr$_{0.2}$Ti$_{0.8}$O$_3$/Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$ (PZT/BZT/PZT) film fabricated by using the sol–gel method, which was dense and uniform with a unique perovskite structure. The PZT/BZT/PZT films displayed high dielectric constants up to 1722.45 at the frequency of 10 kHz. Additionally, the enhanced energy storage density of 39.27 J cm$^{-3}$ was achieved at room temperature and 2.00 MV/cm, which was higher than that of the individual BaZr$_{0.2}$Ti$_{0.8}$O$_3$ film (21.28 J cm$^{-3}$). Furthermore, the energy storage density and efficiency of PZT/BZT/PZT film increased slightly with the increasing temperature from $-140$ °C to 200 °C. This work proves the feasibility and effectiveness of a sandwich structure in improving dielectric, leakage, and energy storage performances, providing a new paradigm for high-energy–density dielectrics applications.

Keywords: sandwich structure; thin films; energy storage; dielectric properties

1. Introduction

Development of high-power and large energy–density capacitors are main requisites for fast growing compact and commercially viable electronic devices [1–4]. Barium zirconate–titane with a perovskite structure is one of the well-known lead free relaxor ferroelectric materials, which has attracted great attention for its potential applications for microwave technology, due to its high dielectric constant, low dielectric loss, and large tunability [5–9]. Liang et al. prepared a BaZr$_{0.35}$Ti$_{0.65}$O$_3$ thin film with ultrahigh energy storage density on (100) Nb:SrTiO$_3$ (NSTO) substrates by using a high-pressure radio-frequency sputtering system [10]. The energy storage density of the thin film exceeded that of most BaTiO$_3$ (BT) based materials, and it could reach the value of 78.7 J cm$^{-3}$, and the efficiency was 80.5% under a large electric strength of 4.0 MV cm$^{-1}$ at room temperature. In addition, BaZr$_{0.2}$Ti$_{0.8}$O$_3$ epitaxial thin films with a large energy storage density of 30.4 J cm$^{-3}$ and high energy efficiency of 81.7% at 3 MV cm$^{-1}$ and RT were prepared by using a radio-frequency magnetron sputtering system [11].

To further improve the figures of merit, much attention has been paid to heterogeneous multilayer films, which have successive layers of different materials, due to their artificially improved dielectric, ferroelectric, and pyroelectric performances [6,9]. It has been shown that multilayered dielectric films such as PbZr$_{0.4}$Ti$_{0.6}$O$_3$/PbZr$_{0.2}$Ti$_{0.8}$O$_3$, Crystals 2019, 9, 575; doi:10.3390/cryst9110575 www.mdpi.com/journal/crystals
Impedance analyzer (Ametek, London, UK).

The process of the film preparation was repeated to obtain the sandwich structured films of which could enhance the energy storage density of the BaZr
Adrich, Pittsburgh, PA, USA), lead acetate trihydrate (Pb(CH
Technologies Premier II ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM, USA).

In a previous work, Bao and co-workers designed BLT/PZT/BLT multilayered structure films by using a chemical solution deposition method [15]. This kind of sandwich structured film could combine the individual advantages of PZT and BLT thin films, the fatigue-free characters of BLT thin films, and the good ferroelectric characters of PZT films. At last, good fatigue and retention properties were obtained for the film with a sandwich structure. Besides, lead zirconate titanate ferroelectric materials have a great maximum polarization ($P_{max}$) even under a low electric field [17,18].

In this work, we prepared a novel PZT/BZT/PZT sandwich structure film by the sol–gel method, which could enhance the energy storage density of the BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT) film via Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$ layer structure modulation. Furthermore, the structure, dielectric, leakage current, ferroelectric, and energy storage properties of the sandwich structured films were thoroughly investigated, which is critical for future materials engineering and energy applications.

2. Experiment

Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$/BaZr$_{0.2}$Ti$_{0.8}$O$_3$/Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$ (PZT/BZT/PZT) sandwich structured films were fabricated via the sol–gel method on Pt(111)/Ti/SiO$_2$/Si substrates. Barium acetate (Ba(CH$_3$COO)$_2$,
Adrich, Pittsburgh, PA, USA), lead acetate trihydrate (Pb(CH$_3$COO)$_2$·3H$_2$O, Beijing Yili Fine Chemicals Co., Ltd., Beijing, China), zirconium iso-propoxide (Zr(OCH$_3$)$_4$,
Adrich, Pittsburgh, PA, USA), and tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$,
Adrich, Pittsburgh, PA, USA) were chosen as starting materials for the BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT) and Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$ (PZT) precursor solutions. Acetic acid (Beijing Yili Fine Chemicals Co., Ltd., Beijing, China) and ethylene glycol monomethyl ether (Beijing Yili Fine Chemicals Co., Ltd., Beijing, China) were solvents for 0.4 mol/L BZT solutions. For the preparation of PZT solutions, ethylene glycol monomethyl ether was the solvent and 20 mol% excess lead acetate trihydrate was put into the PZT solution to compensate for the loss of the lead [19]. After aging 24 h, the BZT solutions and PZT solutions were deposited on the Pt(111)/Ti/SiO$_2$/Si substrates by spin-coated process according PZT/BZT/PZT from the substrates. Each layer was spin-coated at 3000 rpm for 20 s, then heated on the hot plate at 450 $^\circ$C for 3 min and finally annealed at 850 $^\circ$C for 10 min. The process of the film preparation was repeated to obtain the sandwich structured films of desired thickness. Besides, for the electrical performance testing of the thin films, a top electrode with a diameter of 0.2 mm was prepared on the surface by using Pt to form the capacitor structure of the top electrode/ferroelectric thin film/bottom electrode.

The crystal structure of the sandwich films was characterized at small incident angle by X-ray diffraction (XRD, X’ Pert, Philips, Amsterdam, The Netherlands). A scanning electron microscope (SEM, HITACHI S-4800, Hitachi, Tokyo, Japan) was used to confirm the micro-topography and the thickness of the films. Dielectric properties for the BZT and PZT/BZT/PZT thin films were measured by a Solartron 1260 impedance analyzer (Ametek, London, UK). P–E loops were systematically studied by Radiant Technologies Premier II ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM, USA).

3. Results and Discussion

XRD patterns of the BZT and PZT/BZT/PZT thin films are shown in Figure 1. The BZT and PZT/BZT/PZT films showed a well-developed perovskite structure and could be characterized by the appearance of (100), (110), (111), (200), (210), and (211) peaks. No obvious second phases or impurity peaks were observed in the BZT and PZT/BZT/PZT films. As shown in Figure 1, the intensity of the (111) peak of the PZT/BZT/PZT film was much higher than that of BZT films, which indicated that the compatibility between the PZT and Pt layer was better in the sandwich structured film, owing to the
reason that the Pb near the surface of the PZT films could react with the Pt electrodes, generating a new phase Pb$_x$Pt$_{1-x}$, and then the Pb$_x$Pt$_{1-x}$ intermetallic phase could induce the growth of PZT films in the (111) orientation [20,21].

The surfaces of the films were observed by SEM, as illustrated in Figure 2. The BZT and PZT/BZT/PZT films showed similar smooth and uniform surface morphologies, and the overall thickness was about 400 nm for BZT and PZT/BZT/PZT films in the cross-sectional micrographs. Although the unclear interface between the BZT layer and PZT layer made it difficult to observe the thickness of the PZT layer directly, a PZT single film in the sandwich structured film could be estimated, which was about 50 nm.
The temperature dependent dielectric constant ($\varepsilon_r$) and loss ($\tan\delta$) of the PZT/BZT/PZT film measured at $-90^\circ$C to $90^\circ$C were plotted in Figure 3a. Dielectric constant showed the maximum value at $T_s$ in Figure 3a. $T_s$ is about $25^\circ$C in BZT films, and the Curie temperature of the PZT/BZT/PZT film is about $40^\circ$C; there is a slight rise in the Curie temperature. The materials were suitable for working near the room temperature. Figure 3b shows the frequency-dependent $\varepsilon_r$ and dielectric tan$\delta$, which were measured at room temperature from 1 kHz to 1000 kHz. As the frequency increased, the dielectric constant decreased for each sample. While the dielectric loss increased with the frequency increasing at the frequency up to 100 kHz, it may have been due to the polarization value of the thin films not being able to keep up with the change of electric field, and the relaxation loss increased with the higher frequency. At low frequencies, all the polarizations responded easily to the electric field, but as the frequency increased, different polarization contributions were ignored [22]. As last, the net polarization of the films decreased, leading to the decrease of $\varepsilon_r$. The dielectric constant of the PZT/BZT/PZT film reached the maximum 1722.45 and the loss decreased to 0.010 when the frequency was 10 kHz. The $\varepsilon_r$ of the PZT/BZT/PZT film greatly improved compared with that of pure BZT film of 737.59, while the tan $\delta$ of PZT/BZT/PZT film was similar to that of the pure BZT film (0.006) at 10 kHz, indicating a high quality sandwich structured film.

![Figure 3](image.png)

**Figure 3.** (a) Temperature, (b) frequency, and (c) voltage dependence of dielectric constant $\varepsilon$ (upper curves) and loss tan$\delta$ (lower curves).

The DC bias dependence of dielectric constant and loss at room temperature were tested at a DC bias of $-10$ V to 10 V to evaluate the tunability of the PZT/BZT/PZT film, as shown in Figure 3c. The tunability is defined as $(\varepsilon_{\text{max}}-\varepsilon_{\text{min}})/\varepsilon_{\text{max}}$, where $\varepsilon_{\text{max}}$ and $\varepsilon_{\text{min}}$ are the maximum and minimum dielectric constant [9]. The BZT film showed the maximum dielectric constant of 743.91, while the $\varepsilon_r$ of PZT/BZT/PZT film could be up to 1255.12 at 100 kHz. Additionally, the tunability of the sandwich structured film and the BZT thin film were 25.68% and 15.34%, respectively. The dielectric loss of the multilayer (0.017) was a little higher than that of BZT films (0.011). Obviously, the leading PZT layer could increase the dielectric tunability.

For practical application, the leakage current should be as low as possible. Figure 4 shows the leakage current densities of the PZT/BZT/PZT film measured at $-10$ V DC bias to 10 V DC bias under 10 kHz and the temperature of 30 $^\circ$C and 50 $^\circ$C. The leakage current densities of both samples gradually rose with increases in voltage. In the sandwich structured films, the upper and lower PZT buffer layers suppressed the increase of the leakage current, their leakage current densities became smaller in contrast of the single structured BZT films, and were less than $5 \times 10^{-6}$ J (A·cm$^{-2}$)$^{-1}$. It was believed that the PZT/BZT/PZT sandwich structured film had stable interfaces and uniform structure. In addition, thermal stability is an important factor to evaluate the applicability of the films. The leakage current densities of both thin films at 30 $^\circ$C and 50 $^\circ$C were tested. Changes of temperature from 30 $^\circ$C and 50 $^\circ$C were found to have little effect on the leakage current densities of both thin films as shown in Figure 4a,b. Both samples had relative thermodynamic stability with the change of temperature.
Figure 4. Leakage current densities for BZT and PZT/BZT/PZT films under different temperatures. (a) 30 °C and (b) 50 °C.

Figure 5a shows the $P–E$ loops of the BZT and PZT/BZT/PZT films tested at 10 kHz and 30 °C. All samples showed double slim loops, exhibiting typical soft ferroelectric behaviors. Increasing the intensity of the electric field improved $P_{\text{max}}$ of both thin films, as shown in Figure 5b. At 2.0 MV·cm$^{-1}$, the measured $P_{\text{max}}$ was 67.78 μC·cm$^{-2}$ and 29.05 μC·cm$^{-2}$, and $P_{r}$ was 8.61 μC·cm$^{-2}$ and 2.61 μC·cm$^{-2}$ for the BZT/PZT/BZT films and the BZT films, respectively. The $P_{\text{max}}$ of the sandwich structured film was much higher than that of the BZT thin film due to the introduction of the PZT film with a larger polarization value. PZT films, as the longitudinal symmetry buffer layer structure of the PZT/BZT/PZT thin films, can increase the polarization value of the PZT/BZT/PZT films by adding the number of bound electrons. As seen in Figure 5c, the $P_{\text{max}}$ varied little with the change of the temperature from −140 °C to 200 °C. It was noted that $P_{\text{max}}$ decreased slowly with the increase of temperature for both samples, indicating that the PZT/BZT/PZT and BZT thin films had good relaxor features and good thermal stability.

The values of energy storage can be described by the $P–E$ loop, according to the following formulas [16,23–25]:

$$J_s = \int_0^{P_{\text{max}}} EdP$$

(1)

$$J_{\text{rev}} = \int_{P_{r}}^{P_{\text{max}}} EdP$$

(2)
were also compared with other reports summarized from previous literatures, as shown in Table 1.

At approximately the same electric field intensity, the energy storage properties of the PZT crystals were greater than those of some other materials published already: 0.88 BaTiO$_3$–0.12 Bi(Mg,Ti)O$_3$ film, (Ba$_{0.95}$Ca$_{0.05}$)(Zr$_{0.17}$Ti$_{0.83}$)O$_3$ film, and BiFeO$_3$/BaTiO$_3$/BiFeO$_3$ [26–29]. Thermal stability was considered as one key factor to assess the performance of the samples. Figure 6b depicts the temperature dependent energy storage properties. Both the samples were tested in a range of −140 °C to 200 °C under 2 MV·cm$^{-1}$. The $J_{rec}$ and η for the PZT/BZT/PZT and BZT thin films were 36.80 J·cm$^{-3}$ and 20.80 J·cm$^{-3}$ and 76.38% and 89.37% at −140 °C, respectively. Additionally, under the temperature of 200 °C, the energy storage densities and efficiencies were 35.69 J·cm$^{-3}$ and 18.77 J·cm$^{-3}$ and 72.07% and 84.24% for sandwich structured film and the unique thin film, respectively. The nearly unchanged $J_{rec}$ and η indicated the optimistic thermal stability of the PZT/BZT/PZT and BZT thin films.

$$\eta = \frac{J_{rec}}{J_s} = \frac{J_{rec}}{J_{rec} + J_{loss}} \times 100\%$$ (3)

where $P_{max}$ is the maximum polarization value, $E_{max}$ is the maximum electric field, $J_s$ is the stored energy storage density, $J_{rec}$ is the recoverable energy storage density, $J_{loss}$ represents the energy loss, and η is the energy efficiency. To consider the feasibility of applications in practice, the energy storage performances of both samples were investigated as a function of applied electric field and temperature. As shown in Figure 6a, the $J_{rec}$ increased with increases in the electric field, while the η had the opposite trend, because of the large leakage conduction losses under the high electric field [17]. The maximum $J_{rec}$ of BZT thin films was 21.28 J·cm$^{-3}$ and η was 83.51% at 2.00 MV·cm$^{-1}$. However, in PZT/BZT/PZT thin films, the largest $J_{rec}$ could reach 39.27 J·cm$^{-3}$ with a relatively high energy efficiency of 78.71% under the same conditions, owing to the introduction of the PZT layer on the basis of the BZT thin film. The energy storage properties were also compared with other reports summarized from previous literatures, as shown in Table 1.

At approximately the same electric field intensity, the energy storage properties of the PZT/BZT/PZT films were greater than those of some other materials published already: 0.88 BaTiO$_3$–0.12 Bi(Mg,Ti)O$_3$ film, (Ba$_{0.95}$Ca$_{0.05}$)(Zr$_{0.17}$Ti$_{0.83}$)O$_3$ film, and BiFeO$_3$/BaTiO$_3$/BiFeO$_3$ [26–29]. Thermal stability was considered as one key factor to assess the performance of the samples. Figure 6b depicts the temperature dependent energy storage properties. Both the samples were tested in a range of −140 °C to 200 °C under 2 MV·cm$^{-1}$. The $J_{rec}$ and η for the PZT/BZT/PZT and BZT thin films were 36.80 J·cm$^{-3}$ and 20.80 J·cm$^{-3}$ and 76.38% and 89.37% at −140 °C, respectively. Additionally, under the temperature of 200 °C, the energy storage densities and efficiencies were 35.69 J·cm$^{-3}$ and 18.77 J·cm$^{-3}$ and 72.07% and 84.24% for sandwich structured film and the unique thin film, respectively. The nearly unchanged $J_{rec}$ and η indicated the optimistic thermal stability of the PZT/BZT/PZT and BZT thin films.

Figure 6. Energy storage properties of the BZT and PZT/BZT/PZT thin films under (a) different electric fields and (b) different temperatures.

Table 1. Energy storage properties and electric field strength of this work and the related BaTiO$_3$(BT) based materials in previous researches.

<table>
<thead>
<tr>
<th>Material</th>
<th>$J_{rec}$ (J·cm$^{-3}$)</th>
<th>η (%)</th>
<th>Electric Strength (MV·cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ba(Zn$<em>{0.2}$Ti$</em>{0.8}$)O$<em>3$)$</em>{0.85}$((Ba$<em>{0.7}$Ca$</em>{0.3}$)TiO$<em>3$)$</em>{0.15}$ ceramic</td>
<td>0.94</td>
<td>72</td>
<td>0.17</td>
<td>[1]</td>
</tr>
<tr>
<td>Ba$<em>{0.95}$Zn$</em>{0.05}$TiO$_3$ ceramic</td>
<td>0.71</td>
<td>-</td>
<td>0.15</td>
<td>[26]</td>
</tr>
<tr>
<td>BaZn$<em>{0.35}$Ti$</em>{0.65}$O$_3$ film</td>
<td>78.7</td>
<td>80.5</td>
<td>4.0</td>
<td>[10]</td>
</tr>
<tr>
<td>BaZn$<em>{0.35}$Ti$</em>{0.65}$O$_3$ film</td>
<td>30.4</td>
<td>81.7</td>
<td>3.00</td>
<td>[11]</td>
</tr>
<tr>
<td>0.88 BaTiO$_3$–0.12 Bi(Mg,Ti)O$_3$ film</td>
<td>37</td>
<td>-</td>
<td>1.90</td>
<td>[27]</td>
</tr>
<tr>
<td>(Ba$<em>{0.95}$Ca$</em>{0.05}$)(Zr$<em>{0.17}$Ti$</em>{0.83}$)O$_3$ film</td>
<td>39.1</td>
<td>50</td>
<td>2.08</td>
<td>[28]</td>
</tr>
<tr>
<td>Ba$<em>{0.4}$Sr$</em>{0.6}$TiO$<em>3$/BaTiO$<em>3$/Ba$</em>{0.4}$Sr$</em>{0.6}$TiO$_3$ film</td>
<td>14.69</td>
<td>33.9</td>
<td>1.44</td>
<td>[16]</td>
</tr>
<tr>
<td>BiFeO$_3$/BaTiO$_3$/BiFeO$_3$ film</td>
<td>18.5</td>
<td>82.3</td>
<td>2.32</td>
<td>[29]</td>
</tr>
<tr>
<td>PVDF/CFO@BZT–BCT NFs-PVDF/PVDF film</td>
<td>11.3</td>
<td>55.5</td>
<td>0.35</td>
<td>[30]</td>
</tr>
<tr>
<td>BaZn$<em>{0.35}$Ti$</em>{0.65}$O$_3$ film</td>
<td>21.28</td>
<td>83.51</td>
<td>2.00</td>
<td>This work</td>
</tr>
<tr>
<td>Pb(Zn$<em>{0.4}$Ti$</em>{0.6}$)O$<em>3$/BaZn$</em>{0.35}$Ti$<em>{0.65}$/Pb(Zn$</em>{0.4}$Ti$_{0.6}$)O$_3$ film</td>
<td>39.27</td>
<td>78.71</td>
<td>2.00</td>
<td>This work</td>
</tr>
</tbody>
</table>
4. Conclusions

Sandwich structured PZT/BZT/PZT films were fabricated by the sol–gel method. It is demonstrated that the dielectric and energy storage properties of the BZT based film could be improved by the introduction of PZT layers. The large recoverable energy storage density of 39.27 J cm$^{-3}$ with a relatively high efficiency of 78.71% was obtained in the sandwich structured films at 2.00 MV cm$^{-1}$. Moreover, the PZT/BZT/PZT and BZT films exhibited great thermal stability in the temperature range of $-140$ °C to 200 °C at 2.00 MV cm$^{-1}$. All of those excellent performances indicate that introducing PZT layers is an alternative way to optimize the energy storage properties of the BZT films, and the sandwich structured PZT/BZT/PZT films have a promising application in high energy storage capacitors.

Author Contributions: Q.S. and X.C. designed the experiments; J.G., P.Q. and Y.T. performed the experiments; J.G., P.Q., D.W., and Y.T. analyzed the data; Q.S., Y.S., and D.W. contributed analysis tools; J.G. and Q.S. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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