Unique nano-domain structures in self-assembled BiFeO$_3$ and Pb(Zr,Ti)O$_3$ ferroelectric nanocapacitors

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Abstract

In this work, self-assembled ferroelectric BiFeO$_3$ (BFO) and Pb(Zr,Ti)O$_3$ (PZT) nanocapacitors were fabricated by a one-step pulsed-laser deposition process. Each individual nanocapacitor consists of a SrRuO$_3$ or LaSrMnO$_3$ bottom electrode layer, an epitaxial ferroelectric middle layer and a self-assembled nanoisland of conductive Bi$_2$O$_3$ or PbO$_2$ as the top nanoelectrode. The nanoelectrodes have a lateral size of 10–100 nm depending on various deposition equivalent thickness. The as-fabricated nanocapacitors exhibit unique so-called anti-domain structures, with opposite polarization orientation to that of the naked ferroelectric films, which can be understood by the different interface built-in-voltages between their neighboring layers. They also show apparent reduced coercive fields and enhanced piezoelectricity compared to the naked films, as revealed by the switching spectroscopy piezoresponse force microscopy (SSPFM) and band-excitation mapping. Besides that, individual addressable polarization writing and erasing properties were also observed in these nanocapacitors and the written domain can maintain stability up to 12 h, which is promising for data storage devices.

Keywords: BiFeO$_3$, Pb(Zr, Ti)O$_3$, ferroelectrics, nanocapacitors, nanodomains

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent decades, ferroelectric Pb(Zr,Ti)O$_3$ (PZT) and multiferroic BiFeO$_3$ (BFO) have attracted tremendous research interest due to their large switchable polarization, superior piezoelectricity, pyroelectricity, resistive switching, magnetoelectric properties, as well as photovoltaic properties. These functionalities are indispensable for applications in electronic devices such as sensors, micro actuators, infrared detectors, microwave phase filters and ultimately non-volatile memories [1–5]. With the ever-increasing demand on ultrahigh-density data storage with low power consumption for portable consumer electronic devices, investigations on ferroelectric and multiferroic nanostructured memories have attracted more and more interest [6–8]. There have also been several efforts to develop new generation nanoferroelectric devices. For instance, Wang et al developed a crossbar structure, which demonstrates a polarization dependent photovoltaic, showing potential for an electric write and photovoltage read device [9]. Recently, a prototype ferroelectric tunneling device with nanoscale BFO ferroelectric tunneling junction (FTJ) was fabricated, which exhibits a large on/off resistance ratio of $10^4$ as well as good retention and endurance properties [10].

To achieve ultrahigh recording density, investigations into nanoscale solid state nanocapacitor cells are essential. In recent years, several groups have developed sub-micrometer
or nanometer scale solid state FTJ or capacitor structures which are able to achieve large electroresistance [11–15]. It was revealed that nanoscale top electrodes play a critical role in the electrical properties of ferroelectric nanostructures. Previously most nanoscale electric property characterizations usually relied on a conductive atomic force microscopy (AFM) probe as the top electrode, which can bring about spurious effects from mechanical contact or nonuniform electrical field distribution. But a small top electrode can help to make stable electric contact and improve electric field uniformity, which is rather useful for obtaining the true electric properties of the nanostructures [16]. Furthermore, we found that the electrode itself can also greatly change the interface band structure and electric properties, which has not been adequately addressed [16, 17]. In particular, their effects on the ferroelectric domain evolutions are largely ignored.

In this work, we studied the unique domain structure in epitaxial BFO- and PZT-based self-assembled nanocapacitor structures fabricated by a single-step pulsed-laser deposition (PLD). The nanocapacitor cell consists of a self-assembled conductive Bi$_2$O$_3$ or PbO$_2$ nanoisland as the top electrode, a ferroelectric thin film middle layer and a LaSrMnO$_3$ or SrRuO$_3$ bottom electrode layer, on single crystalline SrTiO$_3$ substrate as the bottom electrode. The PLD deposition used a laser energy density of 1.0 J cm$^{-2}$. The morphology and chemistry of the as-generated islands are very sensitive to the oxygen pressure and environmental temperature during the deposition, and well-defined Bi-rich islands were formed at an ambient pressure of 100 mTorr and a depositing temperature of 600–750 °C. In addition, epitaxial Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$(PZT) nanocapacitor cells can also be fabricated by a similar one-step self-assembly method. The PZT thin films with floating lead-rich nanoislands were deposited using PLD in an ambient pressure of 150 mTorr and ambient temperature 600 °C. Prior to the PZT film deposition, an atomic flat conducting SrRuO$_3$(SRO) layer was first epitaxially grown on the vicinal (001)-oriented SrTiO$_3$(STO) substrate as the bottom electrode layer.

The self-assembled top electrode of islands on these BFO and PZT thin films were then proved to be Bi$_2$O$_3$ and PbO$_2$ by x-ray diffraction (XRD), respectively. The small uniform nanoislands can clearly be characterized by atomic force microscopy (AFM, Cypher, Asylum Research). The piezoelectric properties and domain maps of the BFO and PZT films can be observed via piezoresponse force microscopy (PFM), band-excitation PFM (BE-PFM) and switching spectroscopy PFM (SSPFM), with a sharp conductive AFM probe (ARROW-EFM, Nanoworld) using the same AFM unit (Cypher, Asylum Research). To obtain a high-quality ferroelectric domain image, we employed the dual frequency resonance tracking PFM technique, which can apparently improve the sensitivity and resolution of the PFM images, compared to the conventional PFM imaging technique.

### 3. Results and discussion

#### 3.1. Self-assembled BFO nanocapacitors

Prior to the BFO deposition in each trial, a conducting layer of LSMO was first epitaxially grown by PLD on (100) oriented SrTiO$_3$(STO) as the bottom electrode layer.
Figure 2 shows the flat bottom LSMO electrode with a root-mean-square value of 179 pm, which is below one unit cell of 400 pm. The as-deposited BFO structure shows square nanoislands along with ∼15 nm-thick BFO thin film, as shown in figure 2(b). The XRD diffraction pattern of this BFO sample is shown in figure 2(c), which consists of a BFO phase along with some impurity phases of bismuth oxides. In our previous work, we have examined the compositional content and structures of the nanoislands, which indicates that they are close to α-Bi₂O₃ [17], similar to that reported by Alexe [18]. As the α-Bi₂O₃ nanoislands are conductive [17, 18], they can well be considered as the nanoelectrodes for the BFO films [19]. In combination with the LSMO bottom electrode and BFO film, this Bi₂O₃/BFO/LSMO sandwich structure constitutes a well-established nanoscale capacitor cell. Hereafter, we focus on this type of BFO nanocapacitor cell.

The vertical PFM measurements were performed in order to examine the ferroelectric properties of the nanocapacitor cells. Figures 3(a) and (b) show the amplitude- and phase-contrast piezoresponse micrographs for the sample shown in figure 2(b). For the phase-contrast imaging, the bright-dark contrast reflects the different polarization orientations (e.g. upward or downward). As shown in figure 3(b), the whole scanned bare area absent of any nanoislands shows the uniform dark contrast, indicating that the polarization in this area has uniform upward polarization along the vertical orientation. In contrast, the small regions covered by nanoislands exhibit clear bright contrast rather than dark, indicating the opposite vertical component of polarization (downwards), called anti-domain structures. What is more, delicate differences can be found in those nanoislands with different sizes. We can obviously identify that the regions covered by small islands often show uniform anti-domain polarization, but those regions with large size islands tend to accommodate complex multiple domains as shown in figure 3(c). In addition, we are able to identify various anti-domain structures, e.g. complex domain, even bubble domain, with the smallest detectable domain of about ∼10 nm in lateral size. Figures 3(c) and (d) further illustrate the three-dimensional topological image superimposed by amplitude/phase images, which help to locate the anti-domain regions. It also supports the fact that the anti-domains are generally located at the nanoisland site.

The piezoelectric properties can be further examined by the local d₃₃ hysteresis loops. In this measurement, the conductive PFM tip was positioned at the center of the nanoisland and naked film, with the external dc bias applied between the α-Bi₂O₃/PFM tip and the back LSMO electrode. Figure 3(e) shows the d₃₃ loops derived from the piezoresponse phase-voltage loop and butterfly-like amplitude-voltage hysteresis. A relatively higher d₃₃ and a smaller coercivity were observed on the Bi₂O₃/BFO/LSMO nanocapacitor cell, compared with that of naked BFO ultrathin film. On the other hand, there is also asymmetric behavior of the d₃₃ hysteresis loop for both the nanocapacitor cell and the
Figure 3. Amplitude (a) and piezoresponse phase (b) images for the self-assembled BFO thin film and nanocapacitors. Three-dimensional topographical images superimposed on its piezoresponse amplitude (c) and phase (d) mappings, based on the data in the rectangle region from (a) and (b) marked in the dotted red line. Local $d_{33}$ hysteresis loops (e) on both the self-assembled BFO nanocapacitor and the naked BFO thin film, respectively.

Figure 4. Topology (a), (d), piezoresponse amplitude (b), (e), and piezoresponse phase (c), (f) images for the self-assembled film-island structure for two different equivalent thicknesses: ultrathin ($\sim$3 nm) BFO film (a), (b), (c), and relatively thicker ($\sim$40 nm) BFO film (d), (e), (f).
naked films, implying some extent of preferred polarization (or imprint). There are two possible causes that may lead to preferred polarization. Firstly, different built-in fields existed between the top/bottom electrodes and BFO [20]. These built-in fields provide a tendency to polarize the domains to a certain preferred orientation, which made the two polarization states no longer in equivalence, which will be further discussed later. Secondly, oxygen vacancies adjacent to the BFO top surface may also result in the observed asymmetric polarization states through the pinning effect [21].

To study the thickness effects on the nanoislands and anti-domain structures, we fabricated another two similar BFO self-assembled structures with different equivalent thickness (∼3 nm and ∼40 nm). The topological and piezoresponse images for those two as-deposited BFO films plus nanoislands are shown in figure 4. The nanoislands on an ultrathin (∼3 nm) BFO layer in figure 4(a) show a lateral size of 10 ∼ 30 nm and a small average height of about ∼5 nm. In comparison, the nanoislands on thicker film (∼40 nm) show some rectangular-like nanoislands with a relatively large lateral size of 80 ∼150 nm and an average height of about ∼40 nm. We can clearly see that the nanoislands on the thicker film are square-shaped with well-developed crystalline faces, whereas the islands on the ultrathin film are usually a small round shape, indicating that the crystalline faces are not well-developed. To further study the anti-domain phenomena, we examined the piezoresponse images shown in figures 4(b), (c), (e) and (f). We can see apparently different anti-domain structures between these two films. The ultrathin film with small round-shaped islands shows regular single anti-domains which nearly cover the whole of the nanoislands, while the thick BFO film with large nanoislands shows irregular complex multi-domains. For the thicker film, we can also observe some complex domains outside the big islands, unlike what has been observed in thinner film (figure 3). However, if we carefully examined the area outside the big islands, it was not difficult to identify a lot of closely packed small nanoislands, which can also account for the observed complexed domain beyond the large islands. The above observation also indicates that the smaller islands tend to produce uniform single domains, while large islands prefer complex anti-domains, similar to that observed in figure 3. This can be accounted for by the competition between the domain walls’ energy which favors the single-domain structure, and the electrostatic energy from incomplete screening which prefers multi-domain structures [22]. Furthermore, we also tested the effects of islands’ sizes on the piezoresponse loops, and found that with the decrease of the lateral size of the nanoislands, a systematic reduction of the coercive field is shown. These observations indicate that both the domain structures and piezoelectric properties can be apparently affected by the size of nanoelectrodes.

From figures 3 and 4, we can clearly conclude that the naked BFO film prefers the uniform domain structure while that with bismuth oxide nanoislands favors the anti-domain structures. These can be understood from the interface built-in-voltages generated by the work function difference between the adjacent layers, as shown in figure 5(a). In the present case, the LSMO/BFO interface creates a built-in voltage of ∼0.26 V due to the work function difference (V_{built} = (\theta_{LSMO} - \theta_{BFO})/\epsilon), noting that the work function for LSMO is \theta_{LSMO} = 4.96 eV [23], and for BFO is \theta_{BFO} = 4.7 eV [24]. This small built-in voltage tends to induce the uniform polarization state (dark contrast in the piezoresponse phase image in figure 3(b)) in the naked BFO film during the film growth process. However, for the Bi$_2$O$_3$/BFO interface, due to the large work function of α-Bi$_2$O$_3$ being \theta_{BFO} = 6.23 eV, a sizable built-in voltage V_{built} = ∼1.5 V (V_{built} = (\theta_{Bi2O3} - \theta_{BFO})/\epsilon) with opposite orientation is produced on the top interface, which is opposite to the previous V_{built} from the bottom interface, and finally leads to the formation of the observed anti-domains. As straightforwardly illustrated in figures 5(b) and (c), those naked BFO thin films have uniform polarization, while those underneath the Bi$_2$O$_3$ islands have opposite polarizations due to the different built-in voltages, forming the observed anti-domain structures.

3.2. Self-assembled PZT nanocapacitors

On the other hand, we have obtained similar PZT nanocapacitors by using a single-step PLD process. The topology of the as-deposited nanoislands and PZT film structure on SRO/STO substrate are illustrated in figure 6(a). The nanoislands show a separated round shape of ∼50 nm in lateral size and ∼3 nm height. Figure 6(b) shows the XRD diffraction pattern, which indicates that the as-grown structures are PZT phase with a PbO$_2$ impurity phase. This is similar to that observed on BFO/Bi$_2$O$_3$ structures. As the nanoisland PbO$_2$ is also
conductive [25], which can serve as the nanoscale top electrode, the structure can form nanocapacitor structures of PbO2/PZT/SRO as well. Similar to the BFO nanocapacitor, we have also identified anti-domains on the regions of nanoislands.

To further study the distribution of switching fields on both islands and films, we use SSPFM mapping (48 × 48 pixels in a 300 × 300 nm region), as shown figure 7. SSPFM testing is based on acquisition of multiple piezoresponse hysteresis loops on a dense spatial grid of points, providing an avenue to explore the local distributions in polarization switching behaviors for the ferroelectric materials [26]. The SSPFM are conducted on an area with several separated nanoislands distributed on PZT film, as shown in the topographic image of figure 7(a). From the coercivity distribution, we can find that the average coercive fields ($V_c^+ + |V_c^-|)/2$ on nanoislands are much smaller than that of the naked film, as shown in figure 7(b) (the coercivity distribution mappings of $V_c^+$ and $V_c^-$ are shown in figures 7(c) and (d), respectively). If one carefully examines the loops (figure 7(e)), one can see that the piezoresponse loops in the islands are rather symmetric (with coercive fields of $V_c^-$ and $V_c^+$ exhibiting similar magnitudes but with opposite signs), while those on naked films show unsaturated loops with a strong imprint, in which both the $V_c^+$ and $V_c^-$ are larger than zero voltage. As a result, one can see that the distribution of $V_c^-$ for the naked film is

Figure 6. AFM topographic image for a self-assembled PZT-based nanocapacitor structure (a), together with its correspondent XRD diffraction pattern (b).

Figure 7. SSPFM images for the PZT film-island structure in an area of 0.3 × 0.3 μm²: topography image (a), $V_c^+$ and $V_c^-$ mappings. (e) Piezoresponse loops for the three typical locations: center of an island (location A), island edge (location B) and naked film (location C), respectively. PNB and NNB denote the positive domain switching nucleation bias field and negative domain switching nucleation bias field, respectively.
above 0 V, while that on the islands is below 0 V. It is also obviously from the field distribution that the nanoislands have greatly reduced the switching fields of the PZT films, and also make it more symmetric. This also in agreement with our previous observation from the d33 loops in figure 3(e), which shows that the BFO underneath the Bi2O3 islands have much smaller nucleation fields. This can be accounted for by the fact that the nanoelectrodes make the external field more uniformly distributed and greatly improve the symmetry of the interface barriers as well, which makes the nanocapacitor much easier to switch. In addition, it is also interesting that the coercivities at the island edge are much smaller than those inside the nanoislands and at the naked film. This implies that the polarization switching can nucleate first from the island edges which have smaller nucleation biases in both positive and negative bias range (shown in figure 7(e)).

In order to further understand the details of the piezo-electric properties, we use band-excitation piezoresponse force microscopy (BE-PFM), wherein the response is captured across a band of frequencies around the cantilever resonance [27]. Here, we analyzed the piezoresponse curve at a range of frequencies, and obtained the amplitude and phase at the resonance frequency, accurate resonant frequency and quality factors, point by point over the whole area. This method can greatly reduce the topological effect on the piezoelectric properties. One can clearly see that at the position of nanodots there is a relative larger amplitude, smaller resonant frequency, smaller quality factor and opposite polarization orientation, compared to those of the naked film, as shown in figure 8. The piezoresponse amplitude and phase are in agreement with dual PFM observation. As the piezoelectric constant can be derived from amplitude/quality factor, we can also find that the piezoelectricity is relative higher in the nanodots compared with that in the naked film area, based on the fact that a relatively larger amplitude and smaller Q-factor is observed in the nanodots. This result also agrees with our previous observation on the d33 curve for the BFO nanocapacitor shown in figure 3(e).

To test the retention and individual addressability for the nanocapacitors, certain selected capacitors were written by external field through AFM tips. Figures 9(a), (b) and (c) show the topography, piezoresponse amplitude and phase images for the PZT thin film and nanoislands’ structure. The piezoresponse phase image shows uniform dark color on the naked film and bright color on the nanoislands, indicating a similar anti-domain structure as the BFO nanoislands and the thin film structure shown in figure 3. To test the reversibility of the nanocapacitors, two neighboring nanocapacitors were polarized by applying +5 V and −5 V through an AFM tip, respectively. Figures 9(c) and (d) illustrate the phase images of PZT nanocapacitors before and after switching by external electric field, which show that the orientation of nanodomain

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**Figure 8.** Band excitation (BE) PFM mapping for the self-assembled PZT film and nanoislands structures: amplitude (a) and phase (b), resonance frequency (c), and quality factor (d) mappings.
can be written by the applied electric field. It is also found that the switching process does not affect the neighboring domains, which implies no apparent crosstalk between the switched and neighboring domains. The stability of polarization in the PZT nanocapacitors was also confirmed by a retention test for various durations after the electrical writing, as shown in figures 9(d), (e) and (f). It was found that written domains inside the PZT nanocapacitors can be well preserved for a long period of 12 h. This good retention without obvious deterioration of properties for a long time is a critical criterion for applications in microelectronic devices. From the above observations, the self-assembled nanocapacitors exhibit unique anti-domain structures and enhanced piezoelectric properties, which may find opportunities for application in high-density recording devices. Besides that, the nanocapacitors also exhibit excellent retention behavior, which is promising for high-density non-volatile memories.

4. Conclusion

In summary, self-assembled epitaxial BFO and PZT nanocapacitor cell structures with 10–150 nm lateral size were fabricated by a single-step PLD process. Each capacitor consists of a nanoisland of conductive bismuth or lead oxide as the top electrodes, a ferroelectric functional layer and a conducting substrate layer as the bottom electrode. It is revealed that the nanocapacitor structures not only prefer to accommodate ferroelectric anti-domains in contrast to the opposite orientated uniform polarization state for the naked film, but also apparently lower the switching fields and lead to enhanced piezoelectricity. Besides that, the nanocapacitors also exhibit excellent retention behavior, which is promising for high-density non-volatile memories.

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