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Influence of the interfacing with an electrically inhomogeneous bottom electrode on the ferroelectric properties of epitaxial PbTiO$_3$

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The influence of an electrically inhomogeneous epitaxial bottom layer on the ferroelectric and electrical properties has been explored in epitaxial PbTiO$_3$ (PTO)/La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) submicron structures using atomic force microscopy. The submicron LSMO-dot structures underneath the ferroelectric PTO film allow exploring gradual changes in material properties. The LSMO interfacial layer influences significantly both electrical and ferroelectric properties of the upper PTO layer. The obtained results show that the as-grown polarization state of an epitaxial ferroelectric layer is strongly influenced by the properties of the layer on top of which it is deposited. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4828743]

Recently, considerable interest in functional oxide interfaces and sub-micron and nanostructures has been aroused, facilitated by the developments in fabrication and patterning techniques.$^1$ The epitaxial interfaces between various oxides show interesting physical phenomena, e.g., two dimensional electron gas in LaAlO$_3$/SrTiO$_3$, and magneto-electric coupling in BiFeO$_3$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO), etc.$^4$–$^6$ In particular, since the interfacial layer can also alter the ferroelectric properties via strain and/or electrical effects, there have been many reports on interfacing ferroelectric materials with dissimilar materials.$^7$–$^9$ Among them, ferroelectric/LSMO layered structures such as PbTiO$_3$ (PTO)/LSMO and Pb(Zr,Ti)O$_3$/LSMO have been concerned because these structures show a couple of different physical phenomena including magnetoelectric coupling and changes in electrical and ferroelectric properties.$^7$–$^9$ Moreover, as-grown epitaxial ferroelectric thin films with tetragonal structure that are c-axis grown have often a preferential orientation of the polarization. The phenomena determining the as-grown polarization state are not fully understood, but most likely the type of bottom electrode onto which the ferroelectric film is deposited plays a crucial role.$^8$–$^{11}$ That is, the bottom electrode can control functionality of the upper ferroelectric layer. However, exploring influence of interfacial layer can be somewhat difficult if there are very small changes in the material properties. If two different film structures can be prepared on the same substrates, even small influence of interfacial layers on the material properties can be easily addressed. Here, we explore the influence of the interfacing between an electrically inhomogeneous bottom electrode on the electrical and ferroelectric properties in epitaxial LSMO submicron dots embedded in epitaxial ferroelectric PTO film using atomic force microscopy (AFM). Ordered 180° domains of both upward and downward polarization formed in the ferroelectric film, allowing the study of both type of domains in one sample.

Epitaxial submicron dot structures were fabricated on semiconductive Nb-doped SrTiO$_3$ (STON) (100)-oriented substrates by pulsed-laser deposition. The 30 nm thick LSMO dots were grown through SiN stencil masks on the substrates. After removing the stencil mask, a 50 nm thick PTO film was deposited on the area. The detailed information can be found elsewhere.$^7$ AFM studies were performed with a commercial system (Asylum Research Cypher) additionally equipped with a Labview/MATLAB based band-excitation (BE) controller. BE-piezoresponse force microscopy (BE-PFM) and BE piezoresponsescopy (BEPS) were carried out with about 300 kHz of 0.4 V$_{pp}$ BE signal applied to a Pt/Cr-coated probe (Budget sensors Multi75E-G).$^{12}$–$^{14}$ Current AFM (CAFМ) was simultaneously performed with the BEPS measurements using a current amplifier (FEMTO DLPCA-200).

Figure 1(a) shows a topographic AFM image of uniformly distributed PTO/LSMO dot structures. As-grown domain structures depend on the existence of LSMO dots. The LSMO dotted regions show upward polarization, whereas the outside of the dots presents downward polarizations. As previously reported,$^7$ the different orientation of the polarization may originate from the different electrical properties and charge carrier densities of the LSMO. As shown in Figs. 1(b) and 1(c), the PTO film region shows clear switching event and hysteresis loop. In particular, we were able to see switching current at near −3 V, which occurs at the negative coercive voltage, even in the voltage-current loop. Since the as-grown domain structures of the region are downward, the switching current can be only observed during the negative bias sweep. Furthermore, the voltage-current loop shows higher leakage current only at the negative bias. The n-type PTO/n-type STON interface constitutes an Ohmic junction,
whereas Pt/n-type PTO interface shows a Schottky junction. Thus, this diode behavior is dominantly affected by the Schottky junction between the Pt/Cr coated tip and the PTO film.

We further explored local switching properties using BEPS measurements. The high resolution BE-PFM images of Fig. 2(a) revealed that the PTO film in the area between the LSMO dots partially shows also tiny regions with upward polarizations and the PTO film grown on center of the dot shows slightly higher response compared to the outside and the boundary of the dot. By comparing the BEPS spatial maps [Figs. 2(b)–2(d)] with the BE-PFM images, it was found that the switching properties of the PTO film strongly depend on the existence of the interfacial layer underneath. The PTO on top of the LSMO dot regions has higher positive coercive voltage, lower negative coercive voltage, and higher switchable polarization, respectively. We note that the other switching parameters, e.g., imprint and remnant polarization, are very similar to them (not shown here). However, even inside the LSMO dot regions, switching properties of PTO on the center of the dot are slightly different from those of the PTO on the boundary of the dot, i.e., electrically inhomogeneous switching properties. In particular, the change in the coercive voltage is more significant than the change in the remnant polarization. Since the boundary of the dot has thinner LSMO bottom layer, its different electrical properties can affect the switching properties of the PTO. Indeed, Jiang et al. reported that thinner LSMO layer
shows higher resistivity. Slight stoichiometry variations may also exist between the center of the LSMO dot and the edges due to the LSMO deposition being performed through a stencil mask. The electronic and magnetic properties of LSMO are known to be sensitive to the stoichiometry, in particular to the La/Sr ratio and oxygen content. Hence, it appears that the polarization switching properties are affected by the changes in the electric properties of the LSMO layer underneath the PTO layer. The area between LSMO dotted regions also shows very different switchable polarization as shown in Fig. 2(d). In this area, there may still be a very thin LSMO layer or particle-like LSMO layer formed by material that diffused sideways during the stencil-deposition of the LSMO dots. Thus, the PTO film partially is not in direct contact with the STON substrate but with this diffused LSMO layer. Consequently, the area shows two different polarization states which can be observed from the BE-PFM images of Fig. 2. Overall, the LSMO layer led the switching properties of the PTO films to positive shift for the coercive voltage as well as high switchable polarization. This indicates that the interfacial bottom layer underneath the ferroelectric layer can dictate the switching properties of the ferroelectric layer.

In order to explore in more detail the switching properties of the PTO film grown between LSMO dots, we have compared the switching properties at different close neighboring sites. As shown in Fig. 3(b), switching properties of the PTO film depend on the location and thus on the properties of the bottom submicron-structured LSMO layer, confirming the results of Fig. 2. It can be deduced that the outside of the LSMO dotted region has upward polarized pinning layer near the interfacial layer [see orange and blue regions in Fig. 3(a)]. Indeed, it was reported that PTO or PZT thin films/nanostructures grown on STON substrates are hardly switched due to the pinning layer near the interface. The PTO film on the LSMO dotted regions has hysteresis loops with larger remnant polarization and more symmetric shape. Notably, the hysteresis loop at the green region is obviously very symmetric for both coercive voltage and remnant polarization. It indicates that the thick LSMO dotted-layer beneath the PTO film influences the ferroelectric properties through the modification of the interfacial properties. In addition, we explored the local voltage-current properties as shown in Figs. 3(c) and 3(d). The voltage-current behavior is simultaneously monitored during the BEPS measurements. The negative leakage current strongly depends on the existence of the structured bottom layer, i.e., LSMO layer. As explained above, the electrical behavior of the orange and blue regions without the LSMO layer is dominantly affected by the Schottky junction between the Pt/Cr coated tip and the PTO film. As a result, high leakage current was observed under a negative bias for those regions. However, as clearly seen in Fig. 3(d), the green region with the LSMO layer shows very different electrical behavior. Even though the LSMO interfacial layer makes a bit increase for the positive current, both leakage current spectroscopy and map under a negative bias show that it makes the leakage current significantly decrease, i.e., influence electrical properties. In this case, the n-type PTO/p-type LSMO interface constitutes an Ohmic junction. Although the Pt/n-type PTO interface still shows a Schottky junction, the rough surface of those regions might affect the poor junction property. As a result, the opposite diode behavior of the green regions might be dominantly affected by the p-n junction between the PTO film and the LSMO layer.

In conclusion, we have explored the influence of electrical properties of the bottom layer on the ferroelectric and electrical properties in epitaxial PTO/LSMO submicron dot structures using BE-PFM and CAFM. Since two different interfacial structures can be fabricated on the ferroelectric layer through the submicron dot structures, we were able to explore small changes in material properties. It was found that the LSMO interfacial layer can influence significantly both electrical and ferroelectric properties through the modification of the pinning layer and junction property. The results indicate that the significant influence on material properties can be achieved through control of the interfacial layer and can provide an effective way for tuning material properties.

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![Image](image_url)

FIG. 3. Spatial maps of (a) positive remnant polarization and (c) log scale current map at $-5\,\text{V}$. (b) Averaged hysteresis and (d) voltage-current loops of each colored region in Fig. 3(a).

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