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Effect of residual stress on energy storage property in $PbZrO_3$ antiferroelectric thin films with different orientations

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The effect of residual stress on energy storage property was investigated for a series of $PbZrO_3$ thin films on $SrTiO_3$ and Si substrates. Compressive or tensile residual stress influences the critical electric field E_A for the ferroelectric-to-antiferroelectric phase transition, thus for films with (110)/(101) orientation, energy density W of films on $SrTiO_3$ is 38% larger than films on Si; in contrast, (001)-oriented $PbZrO_3$ films on $SrTiO_3$ show slightly smaller W compared to films on Si. We conclude that the different responses of W to stress are related to the different constrain states in films with different orientations. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4825336]

Dielectric materials that provide the capability of high-performance energy storage are of great importance for the power electronics in a wide range of technological applications. Among various dielectric materials, antiferroelectrics (AFEs) are promising candidates for dielectrics in high energy density electrical capacitors due to the field-induced phase transition into the ferroelectric state accompanied by large charge storage. In general, the recoverable energy density (W) can be calculated by the integral $W = \int EdD$, where E is the electric field and D is the electric displacement or charge density. Therefore, antiferroelectric thin films can develop greatly enhanced energy density compared with their bulk counterparts because they typically have higher dielectric strength and the electric displacement tends to saturate at higher electric field.[1,2] To further enhance the energy storage property of AFE film, much effort has been made including modification of film composition,[3–8] PbO content excess,[9,10] and using oxide top electrodes.[11] It was reported that a very high energy density of 37 and 56 J/cm^3 can be obtained in $Pb_{0.92}La_{0.08}(Zr_{0.95}Ti_{0.05})O_3$ and $Pb_{0.97}La_{0.02}(Zr_{0.55}Sn_{0.40}Ti_{0.05})O_3$ AFE films, respectively.[4,8]

Very recently, it has been shown experimentally that E_F for the antiferroelectric-to-ferroelectric phase transition and E_A for the reverse transition have been shifted to higher levels by compressive stresses in the Nb-doped lead zirconate titanate stannate (PNZST) bulk ceramic,[12,13] thus lead to an increase in the energy density of antiferroelectric capacitor. As a result, one may wonder if the stress, which is generally existed in films and can be controlled by a lot of parameters such as the choice of substrate, bottom electrode, annealing temperature, texture orientation, and so on can also influence the energy storage property of AFE films. However, reports on the effect of stress on polarization switching and energy storage properties in AFE films are rather limited so far. Xu *et al.* studied the field-induced phase switching of (111)-oriented lead zirconate titanate stannate (PZST) thick films on Si substrate and concluded that the tensile stress due to the thermal mismatch between film and substrate would make the films prone to the FE phase.[14,15] However, it appears that no report on strain dependency of AFE films on different substrates has been published. Hence, in this study, $PbZrO_3$ thin films, which are the prototype of AFE films, were deposited on $LaNiO_3$ (LNO) buffered $SrTiO_3$ and SiO_2/Si substrates and their strain-induced structure property and energy storage property as a function of temperature have been investigated.

The PZ/LNO heterostructures were grown on (001) $SrTiO_3$ and SiO_2/Si substrates by off-axis rf magnetron sputtering. The LNO electrodes were deposited at different oxygen partial pressure ($O_2/Ar + O_2 = 0\%$ and 20%, respectively) so that for the same LNO different orientations and lattice constants can be achieved.[16] 340-nm-thick PZ films were then deposited on LNO buffered SiO_2/Si and $SrTiO_3$ substrates using a 3-in.-diamater $PbZrO_3$ target made by uniaxial pressed mixed PbO and ZrO_2 powders in stoichiometric composition. The films were deposited on unheated substrate holder under the total pressure of 1×10^{-2} mbar (~1 Pa) (100% argon), with RF-power of 1.32 W/cm^2, and the target-substrate distance is 60 mm. These growth conditions yielded a deposition rate of about 570 Å/h for the PZ layer. The as-deposited films were amorphous and a post annealing treatment under air atmosphere at 625 °C was performed to crystallize the films into the perovskite phase.

The structure and phase purity of the films were checked using Rigaku SmartLab high resolution X-ray diffractometer (HRXRD). LNO top electrode (diameter of ~140 μm) was deposited by rf magnetron sputtering at RT through a photolithography process. The thickness of LNO top electrode is about 100 nm. The hysteresis loops were performed by aixACCT TF2000FE equipment.

Figure 1 shows X-ray diffraction (XRD, CuK_α radiation) patterns of PZ films deposited on LNO-buffered (001) $SrTiO_3$ and SiO_2/Si substrates. It should be noted that PZ possesses an orthorhombic structure below curie temperature (~230 °C) in which the orthorhombic cell is a multiple unit cell and contains eight primitive cells, which have a tetragonal structure ($a_0 = \sim 4.15$ Å, $b_0 = \sim 4.15$ Å, and $c_0 = \sim 4.10$ Å). Hence, for

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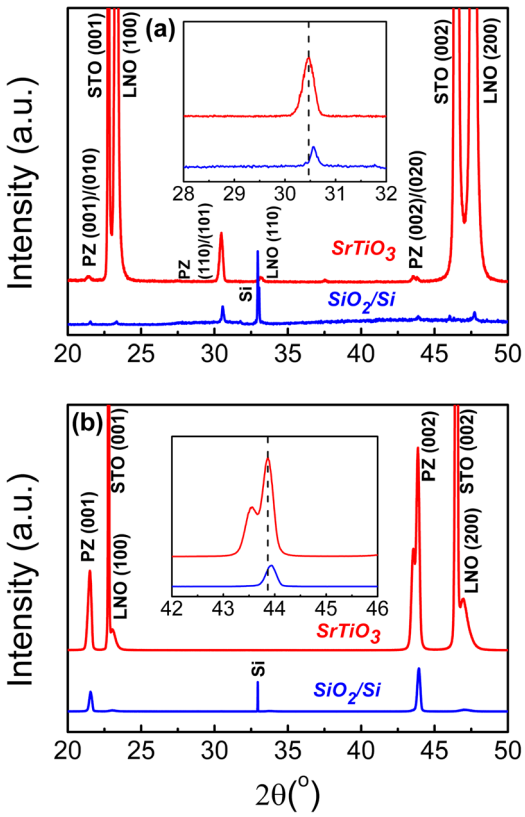

FIG. 1. Room temperature XRD θ-2θ of PZ films grown on (a) LNO (0% oxygen partial pressure) buffered (001) $SrTiO_3$ and SiO_2/Si, (b) LNO (20% oxygen partial pressure) buffered (001) $SrTiO_3$ and SiO_2/Si.

convenience all the peaks of PZ films are indexed based on the tetragonal structure. In Fig. 1(a), it is shown that LNO deposited on $SrTiO_3$ at 0% oxygen partial pressure is highly (100)-oriented, while on SiO_2/Si shows a (110)-preferred orientation. However, PZ films on both substrates have (110)/(101) preferred orientation and the reflections from the LNO electrodes indicate an out-of-plane lattice constant of 3.81 Å. The fact that PZ does not follow the (100) orientation of LNO on $SrTiO_3$ is maybe due to the large lattice misfit between LNO (3.81 Å) and PZ (~4.14 Å as a pseudo-cubic), which makes it difficult to facilitate grain-on-grain growth. In contrast, Fig. 1(b) shows LNO films deposited at 20% oxygen partial pressure are all highly (100)-oriented and yield a lattice constant of 3.87 Å, which indicates smaller lattice misfit with the overlaying PZ film. Consequently, PZ films follow the (100) orientation of LNO and show highly (001)-oriented fiber texture on both substrates. The out-of-plane c parameter of films with (001) orientation is 4.107 Å on SiO_2/Si substrates (calculated from the (002) peak from XRD patterns) and as on $SrTiO_3$ substrates, the (002) peak is more split, with a lattice parameter about 4.113 Å from the dominant peak, indicating the c_0 axis of the PZ unit cell lies perpendicular to the film plane and the a_0 and b_0 axes lie in plane. In addition, the rocking curve and Φ-scan confirm that PZ with LNO electrode deposited at 20% O_2 partial pressure on $SrTiO_3$ are epitaxially grown and the other PZ films are uniaxially textured.[16] Moreover, as we can see from the insets of Fig. 1, the peaks corresponding to PZ shift towards lower 2θ angle as the substrates change from Si to $SrTiO_3$, indicating an increase in the out-of-plane lattice parameter, which means films on $SrTiO_3$ receive a higher compressive stress compared to films on Si substrate.

In general, stress in a thin film can come from various sources including (1) intrinsic stress induced from a particular growth process, (2) transformation stress due to structural phase transition, (3) lattice mismatch stress due to epitaxial growth, and (4) thermal stress due to thermal expansion mismatch. Because all PZ films are deposited using the same parameters and the phase structures are essentially similar, the intrinsic and transformation stress can be treated as the same for all samples. Considering the thermal stress, the thermal expansion coefficients (TECs) of $SrTiO_3$ and SiO_2/Si substrates are 11.0[17] and 2.6[14] ppm/K, respectively, and assuming PZ films have a same value of TEC as PZ bulk ceramic (8.0[18] ppm/K), thus films on $SrTiO_3$ and SiO_2/Si are under compressive and tensile stress, respectively. As for lattice misfit stress, in view of only PZ films on LNO (20% of oxygen partial pressure) buffered $SrTiO_3$ were epitaxially grown and lattice parameter of LNO (3.87 Å) is smaller than that of PZ, it seems that the film will receive additional epitaxial compressive stress. However, there are also some reports argue that in epitaxial $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) films much thicker than the critical thickness (>80 nm), the lattice strain is completely relaxed.[17,19]

Polarization versus electric field hysteresis loops were measured on all four samples at a series of temperatures. Figures 2(a) and 2(b) show the loops of PZ films at 30 and 110 °C with a peak field of 700 kV/cm. It can be seen that with the temperature increasing, both critical electric fields E_F and E_A shift to lower value leading to a decrease in W, which is similar to our previous report on

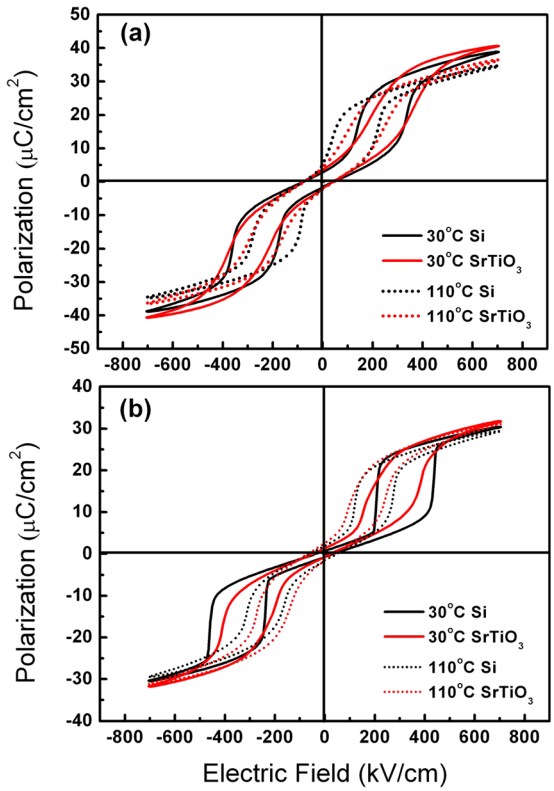

FIG. 2. Polarization versus electric field hysteresis loops of (a) (110)/(101)-oriented PZ films and (b) (001)-oriented PZ films on SiO_2/Si and $SrTiO_3$ at 30 and 110 °C (measured at 100 Hz).

$Pb_{0.97}La_{0.02}(Zr_{0.95}Ti_{0.05})O_3$ AFE films.[11] The effect of residual stress can be verified by the comparison of hysteresis loops of films on different substrates at the same temperature. It can be concluded that with the same orientation, films on $SrTiO_3$ appear to have slightly higher maximum polarization compared to films on SiO_2/Si. This is believed to result from the polarization rotating towards the film plane with tensile stress.[17] However, the relationships of E_F and E_A with thermal stress vary substantially as the orientations of films change. For PZ samples with (110)/(101) preferred orientation, the E_F and E_A of the sample on $SrTiO_3$ are slightly higher than that of the sample on SiO_2/Si. Considering the films on $SrTiO_3$ receive higher compressive stress, it is consistent with the report we mentioned before on PNZST AFE bulk ceramic[13] under compressive stresses. In contrast, when the orientation of PZ films changes to (001), our observation shows an opposite trend that the films on $SrTiO_3$ display lower E_F and E_A compared to films on SiO_2/Si. Furthermore, the phase transitions (both forward and reverse ones) appear to be more abrupt in sample on SiO_2/Si substrate.

From the hysteresis loops data at different electric fields and temperatures, energy storage density can be further extracted (Fig. 3). For samples with (110)/(101) orientation, films on $SrTiO_3$ substrate exhibit higher energy density in whole temperature range compared to films on SiO_2/Si, which means the compressive stresses enhance energy density of PZ films. For example, at 30 °C, W at 700 kV/cm is ~9.0 J/cm^3 in films on $SrTiO_3$ and ~6.5 J/cm^3 in films on SiO_2/Si, corresponding to a 38% increase. In contrast, for samples with (001) orientation, slightly higher energy density is achieved in films on SiO_2/Si compared to films on $SrTiO_3$ at room temperature, especially at relatively low electric field. For instance at 30 °C, W is ~6 J/cm^3 in films on $SrTiO_3$ and ~6.5 J/cm^3 in films on SiO_2/Si at 530 kV/cm. However, as the temperature increases, the energy density of films on SiO_2/Si decreases a little more rapidly and hence becomes smaller than that of films on $SrTiO_3$ at temperatures above 110 °C.

The fact that the PZ films with (110)/(101) orientation give larger energy density on $SrTiO_3$, while films with (001) orientation obtain better energy storage property on SiO_2/Si, can be explained by a consideration of the different constrain states in films with different orientations. Based on the model of Xu *et al.*,[14] we draw the schematic diagram of the primitive cells in AFE and FE phases with different orientations (Figure 4). The polar direction of the antiparallel dipoles is along the [110] direction of the tetragonal primitive cell. When changed to the FE phase, the tetragonal primitive cell becomes rhombohedral with the polar directions along the [111] direction. The lattice angle of the unit cell of the FE rhombohedral phase α_{Rh} is very close to 90° (89.8° or 89.95°). The lattice parameter a_{Rh} of FE rhombohedral phase is a little smaller than a_{tet} of the AFE tetragonal primitive cell, but obviously larger than c_{tet}. Fig. 4(a) shows the

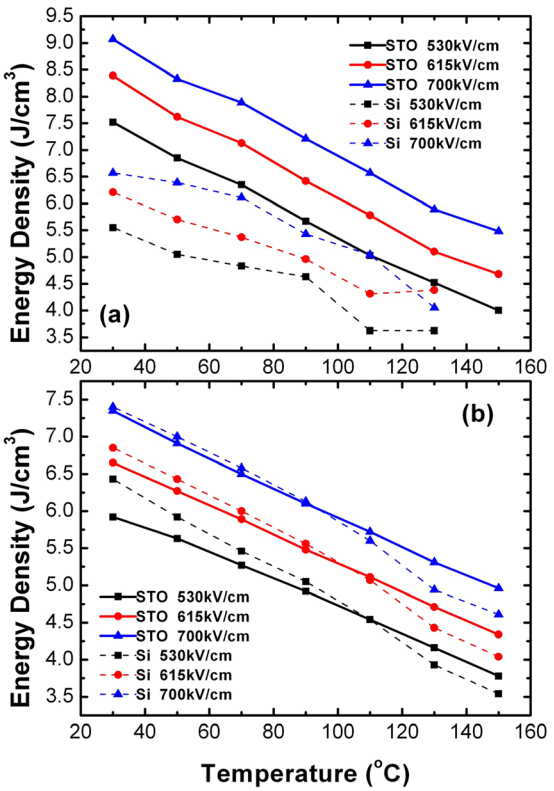

FIG. 3. The temperature dependence of W for (a) (110)/(101)-oriented PZ films and (b) (001)-oriented PZ films on SiO_2/Si and $SrTiO_3$ measured at 530, 615, and 700 kV/cm, respectively.

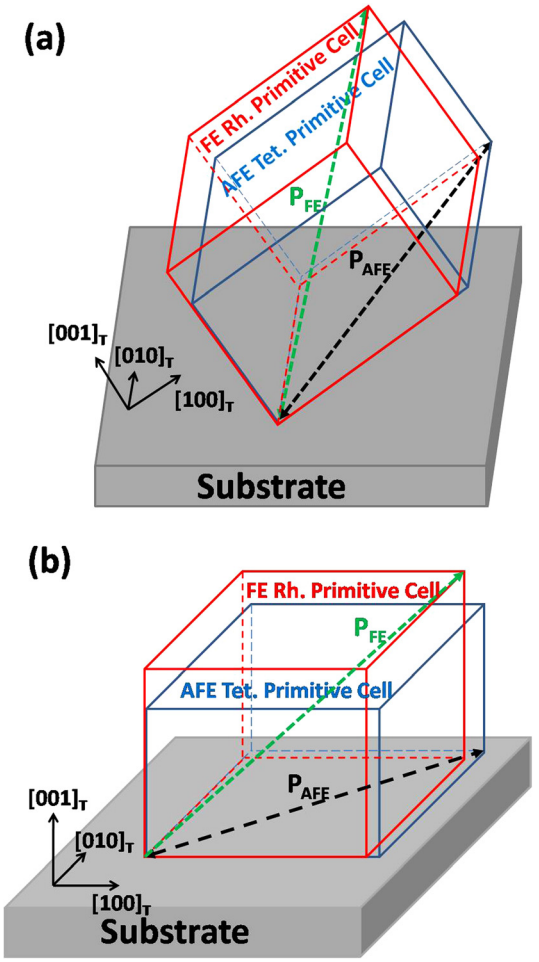

FIG. 4. Schematic diagram of the primitive cells with (a) (101) orientation and (b) (001) orientation in AFE and FE phases. The primitive cell is tetragonal (Tet.) structure in AFE phase and rhombohedral (Rh.) structure in FE phase.

primitive cells with (101) orientation in AFE and FE phases. The situation of primitive cells with (110) orientation would be similar. It can be seen that the films will expand in the plane parallel to the film surface after being switched to the FE phase. Hence, the residual compressive stress will make the films prone to the AFE phase, thus shifts the E_F and E_A to higher value. In contrast, if the films are (001)-oriented, as shown in Fig. 4(b), because a_{Rh} is a little smaller than a_{tet}, the films will contract along the in-plane direction and hence it is not compressive stress but tensile stress that will stabilize the AFE phase, leading to an increase in E_F and E_A of samples on SiO_2/Si in comparison to samples on $SrTiO_3$.

In summary, we have grown (110)/(101)- and (001)-oriented PZ films on both LNO buffered $SrTiO_3$ and SiO_2/Si substrates. It is observed that the critical electric fields E_F and E_A of films with (110)/(101) orientation increase as the substrate changes from SiO_2/Si to $SrTiO_3$ substrates, which lead to a higher energy density in films on $SrTiO_3$ substrate. However, for films with (001) orientation, the E_F and E_A decrease in films on $SrTiO_3$ substrate, which results in a higher energy density in films on SiO_2/Si substrate. These results demonstrate that the orientation of PZ films may heavily influence the relation between the energy density property and the stress field within the PZ films. We conclude that it is closely related to the different constrain states in films with different orientations.

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