

Piezoelectric response hysteresis in the presence of ferroelastic 90° domain walls

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Piezoelectric response hysteresis curves of $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ -based capacitors have been measured by piezoresponse force microscopy. The piezoelectric coefficient d_{33} was found to vary considerably depending on the position of the probing tip on the top electrode for films possessing a $c/a/c$ domain structure. d_{33} values up to 125 pm/V, which is twice the theoretical value for a clamped film, have been measured. The spatial variations of the piezoelectric response amplitude is explained by a local movement of ferroelastic 90° a domains. This work experimentally proves the local enhancement of the polarization near the 90° wall boundaries, as predicted by Ishibashi *et al.* [Jpn. J. Appl. Phys. **44**, 7512 (2005)]. © 2007 American Institute of Physics. [DOI: 10.1063/1.2430681]

The movement of ferroelastic twin walls plays an important role in determining the physical properties of many materials of interest.^{1–3} In the case of ferroelectric materials, the 90° domain switching results in an enhancement of the piezoelectric and dielectric coefficients, as well as the polarization.⁴ However, controversial reports about 90° ferroelastic domain wall motion in ferroelectric thin films exist, most probably due to results obtained on samples of different quality. In particular, the analyzed samples may have different concentrations of both extended structural defects and point defects (vacancies). These defects are known to pin the domain walls and thus to reduce their mobility.^{5–9} This is one of the main reasons, which together with the clamping effect of the substrate,^{10,11} is used to explain the often reported immobility or low mobility of twins in ferroelectric films.¹²

Recently, we reported unambiguous data showing the relatively high mobility of ferroelastic domain walls in epitaxial $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (PZT) thin films.¹³ In the past few years, several publications were dedicated to theoretical and experimental investigations of atomistic structure^{14–16} and polarization reversal processes^{17,18} of 90° domain walls. It has been shown, for instance, that the trapping of point defects is responsible for the broadening of the twin walls, and thus results in different twin mobility.¹⁶ In addition, the barrier height for the 90° domain wall motion calculated by Meyer *et al.*¹⁵ was found to be extremely small. The authors concluded that the twin walls may fluctuate rather freely in the absence of pinning centers. Using the Ginzburg-Landau theory, Ishibashi *et al.*¹⁷ demonstrated in a simplified model that there are various modes of polarization reversal in the presence of 90° domain walls, depending on the degree of anisotropy of the local free energy. In agreement with the analysis of Ishibashi, Franck *et al.*¹⁸ found that the polarization width of a 90° domain wall is much thicker (about 7.5 times) than the physical width, which was estimated to be 10 nm. In this letter, we report experimental work based on piezoelectric response hysteresis measurements showing enhancement of polarization in the vicinity of twin walls, and supporting the theoretical studies briefly described above.

The system of choice on which the experimental work has been carried out is high quality single crystal epitaxial PZT films. Epitaxial $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ thin films (20–250 nm thick) were grown in layer-by-layer mode on $\text{SrRuO}_3/\text{SrTiO}_3(001)$ using pulsed-laser deposition (PLD). The deposition procedure, described in detail elsewhere,¹⁹ has enabled the fabrication of low defect density epitaxial films. Circular SrRuO_3 (SRO) top electrodes ($\sim 50 \mu\text{m}$ diameter and $\sim 50 \text{ nm}$ thick) were deposited by PLD at room temperature through a shadow mask. In order to ease the contacting of the capacitor pads, platinum was sputtered on top of the SRO electrodes. Domain switching and piezoelectric behavior were investigated using a scanning probe microscope (ThermoMicroscopes) equipped with PtIr coated tips (Nanosensors, ATEC-EFM) with an elastic constant of about 2.5 N m^{-1} . Local piezoelectric hysteresis loops were measured by positioning the probing tip at various sites on the top electrode and recording the piezoresponse signal as a function of an applied dc voltage superimposed on the probing ac voltage. In this configuration, the measurements are performed under homogeneous electric field.^{13,20}

Figure 1 shows piezoresponse hysteresis loops obtained through the top electrode for two different $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ films, with and without 90° domains, respectively. The pi-

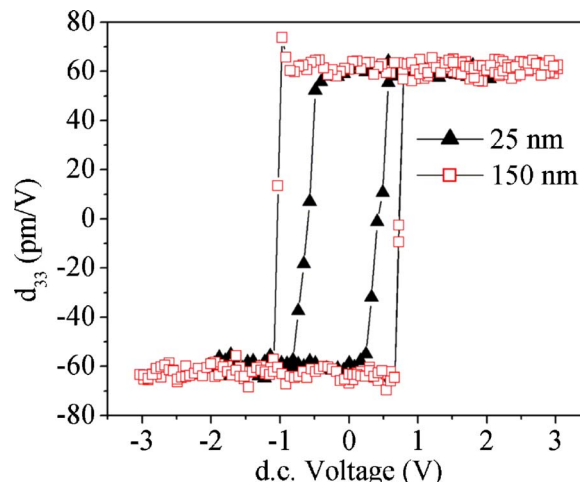


FIG. 1. (Color online) Piezoelectric coefficient as a function of dc bias voltage for 25 and 150 nm thick PZT films.

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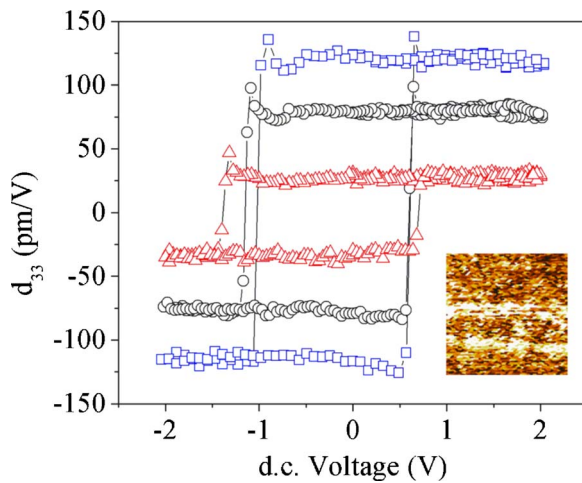


FIG. 2. (Color online) Piezoelectric hysteresis loops, which show the spatial variation of the d_{33} coefficient on the same capacitor. The inset is a piezoresponse image ($400 \times 400 \text{ nm}^2$) showing the local enhancement of d_{33} along twins ($d_{33} \sim 125 \text{ pm/V}$, bright contrast). Note that the dark contrast corresponds *here* to a d_{33} value of $\sim 60 \text{ pm/V}$ (c domain).

ezoelectric coefficient, d_{33} , of both films is about 60 pm/V , which is similar to the theoretical value of a continuous clamped film calculated by Ouyang *et al.*²¹ We note that the d_{33} coefficients obtained when measuring through a top electrode are slightly higher than those measured on a free surface (~ 60 – $\sim 45 \text{ pm/V}$, respectively).^{13,19} This confirms that a more accurate quantitative measurement is obtained by probing through a top electrode, which improves the electrical contact between the tip and the surface, as previously pointed out by Zavala *et al.*²² However, while the d_{33} amplitude value is constant for the 25 nm thick film wherever we positioned the tip on the electrode, extremely large variations of the piezoelectric constant have been obtained in the case of thick films ($>100 \text{ nm}$) by probing at different sites on the same electrode. This is illustrated in Fig. 2 for a 215 nm thick film. Piezoelectric hysteresis loops with d_{33} coefficient values between 20 and 125 pm/V have been systematically measured on the same electrode. It is worth noting that for PZT films with a thickness above 100 nm , a $c/a/c$ domain structure²³ was observed by piezoresponse force microscopy (PFM), as well as by transmission electron microscopy (TEM) on cross-sectional and plan-view samples.^{9,13,19} On the other hand, films thinner than 100 nm were fully c -axis oriented.¹⁹ We believe that the spatial variation of the d_{33} coefficient is related to the domain structure of the films. Imaging of the domain structure through a top electrode is rather difficult as noted by Gruvermann *et al.*²⁴ The electric field applied through the top electrode is uniform within the film so that the PFM tip probes the whole thickness of the film. The lateral resolution remains as usual for PFM, which is about 10 – 30 nm . As a result, the amplitude of the piezoelectric vibration is either a contribution of c domain or an averaged contribution of the a and c domains within the probing volume underneath the tip. For tetragonal c -oriented PZT films the piezoelectric coefficient d_{33} can be expressed as a function of the spontaneous polarization P_s through the following relation:³

$$d_{33} = 2Q\epsilon_{33}P_s,$$

where Q is the electrostriction coefficient and ϵ_{33} the dielectric constant of the ferroelectric material along the c axis.

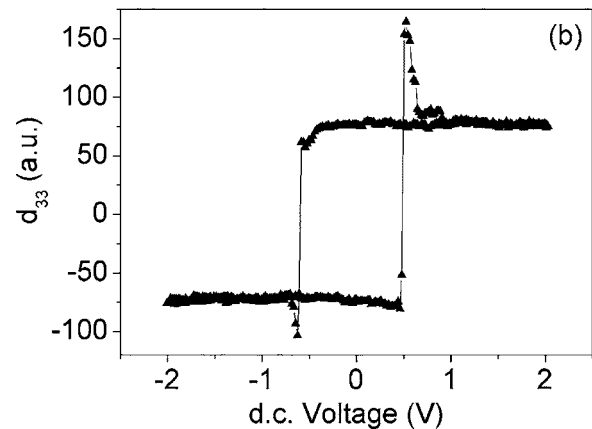
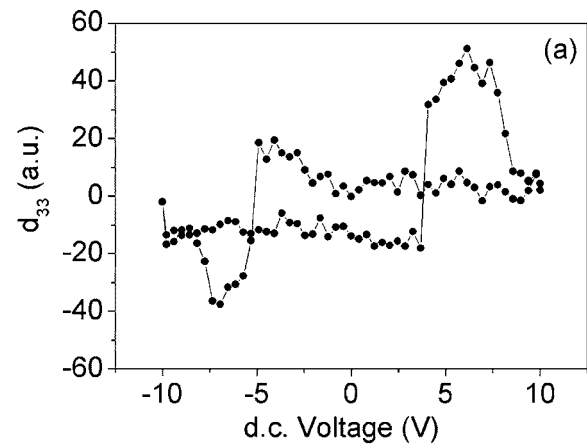


FIG. 3. Piezoelectric loops measured in the vicinity of $90^\circ a$ domain (a) on the bare film surface and (b) on a top electrode showing extrinsic effects due to ferroelastic domain switching.

Therefore, the piezoresponse signal probed by PFM is proportional to the normal component of the local polarization. When the probing volume is a mixture of a and c domains, the resulting d_{33} coefficient is reduced compared with the probing of a single c domain, since the polarization vector in the $90^\circ a$ domain is parallel to the film surface. This explains the smaller d_{33} for the piezoelectric loop presented in Fig. 2, if we consider immobile twins. On the other hand, the larger d_{33} values ($>60 \text{ pm/V}$) measured can result from the effect of extrinsic contribution that causes additional displacement in the film under the applied electric field. The extrinsic contribution is mainly due to the ferroelastic-ferroelectric domain wall motion. Moreover, it is known that, even under weak field conditions, the external applied electric field can cause vibrations or small displacements of the domain walls.²⁵ Therefore, it is reasonable to attribute the enhancement of the piezoelectric coefficient shown through the largest d_{33} - V curve in Fig. 2 to the local 90° domain wall oscillations, under the applied ac voltage ($\sim 30 \text{ kV/cm}$). The inset in Fig. 2 is a piezoresponse image showing the local enhancement of d_{33} along two movable twins (bright contrast). The enhanced value is about 125 pm/V , which is twice the value measured on a bare c domain (dark region on the image). We emphasize that the piezoelectric coefficients measured locally (PFM tip in a fixed position) were well correlated with the different contrasts obtained in the piezoresponse images.

Figure 3(a) shows a piezoelectric loop measured after positioning the PFM tip in the vicinity of a $90^\circ a$ domain on the bare film surface. Figure 3(b) shows a piezoelectric loop measured on a top electrode showing extrinsic effects due to ferroelastic domain switching.

the free surface of the 215 nm thick PZT film (without top electrode). A strong increase of the d_{33} is observed near the coercive voltage, i.e., after the switching of the 180° c domain. This was also observed by measuring through the top electrode, as it is exemplified in Fig. 3(b). The peaks near the coercive voltages in both loops result most probably from the ferroelastic 90° a -domain switching. Indeed, if a 90° a domain switches to a c domain, the polarization, and thus the piezoelectric coefficient, will be significantly enhanced, as it is theoretically analyzed by Ishibashi *et al.*¹⁷ As a consequence, our experimental data are a direct proof of the theoretical prediction of the aforementioned authors. In addition, it is interesting to note that the extrinsic contribution to the piezoelectric coefficient d_{33} is comparable to the intrinsic piezoelectric response (~ 60 pm/V) in a clamped film (see Fig. 1). This was predicted by Pertsev *et al.*²⁶ in a calculation for a lead titanate film with a c/a domain structure. However, the extrinsic contribution to d_{33} from the 90° domain wall motion might be more or less pronounced depending on the strength and homogeneity of the applied voltage,¹⁷ but also on the variation of the structure of a single twin wall.^{16,18,27}

In summary, a spatial variation of the d_{33} piezoelectric coefficient measured on ferroelectric capacitors was observed for PZT films possessing a $c/a/c$ domain structure. The high values of the piezoelectric constant are attributed to ferroelastic 90° a -domain motion. Two cases were encountered: (1) the 90° domain wall oscillates under a weak ac field, thus contributing permanently to the d_{33} value; (2) the 90° domain switches together with 180° domain reversal, resulting in a transient increase of the d_{33} coefficient. In addition, since the d_{33} value obtained by PFM is the result of a *local* measurement, even when probing through a flattop electrode, the determination of a unique value of the piezoelectric coefficient for a capacitor is difficult as it could vary considerably depending on the structure of the film. Therefore, due care should be taken when reporting quantitative values for the piezoelectric coefficient, if the structure of the film is not uniform, i.e., not single domain. In that respect, the use of switching spectroscopy PFM might be an interesting and useful tool to image the spatial variation of the piezoelectric properties of the ferroelectric capacitors.²⁸

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