

## Coercive field of ultrathin $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ epitaxial films

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The polarization reversal in single-crystalline ferroelectric films has been investigated experimentally and theoretically. The hysteresis loops were measured for  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  films with thicknesses ranging from 8 to 250 nm. These films were grown epitaxially on  $\text{SrRuO}_3$  bottom electrodes deposited on  $\text{SrTiO}_3$  substrates. The measurements using Pt top electrodes showed that the coercive field  $E_c$  increases drastically as the film becomes thinner, reaching values as high as  $E_c \approx 1200$  kV/cm. To understand this observation, we calculated the thermodynamic coercive field  $E_{\text{th}}$  of a ferroelectric film as a function of the misfit strain  $S_m$  in an epitaxial system and showed that  $E_{\text{th}}$  strongly depends on  $S_m$ . However, the coercive field of ultrathin films, when measured at high frequencies, exceeds the calculated thermodynamic limit. Since this is impossible for an intrinsic coercive field  $E_c$ , we conclude that measurements give an apparent  $E_c$  rather than the intrinsic one. An enormous increase of apparent coercive field in ultrathin films may be explained by the presence of a conductive nonferroelectric interface layer. © 2003 American Institute of Physics.  
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The use of ferroelectric thin films in high-density non-volatile random access memories is based on the ability of ferroelectrics to switch between two opposite polarization states.<sup>1</sup> The coercive electric field  $E_c$ , which characterizes the polarization reversal in a ferroelectric film, usually increases significantly with decreasing film thickness.<sup>2–5</sup> Several different explanations have been proposed earlier for this size effect,<sup>6</sup> including the surface pinning of domain walls<sup>7</sup> and the influence of an internal electric field on the domain nucleation in depleted films.<sup>3</sup> At present, it is believed that the thickness dependence of the coercive field in  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  films with metallic electrodes is caused mainly by the presence of a nonferroelectric layer at the film/electrode interface.<sup>4,8</sup> Although an insulating dielectric layer was shown to have no significant influence on the coercive field,<sup>4,9</sup> the charge injection through a nonferroelectric layer gives a reasonable explanation of the discussed size effect at film thicknesses larger than  $t \approx 100$  nm.<sup>4,8</sup>

It is of great interest to study the thickness dependence of  $E_c$  for ultrathin films with  $t \sim 10$  nm. Up to now, detailed investigations in this nanoscale range have been performed only for Langmuir–Blodgett films of ferroelectric polymers.<sup>5</sup> In this letter, we present the polarization switching measurements carried out for  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  (PZT 52/48) films with thicknesses ranging from 250 nm down to 8 nm. The observed thickness dependence of the coercive field is analyzed theoretically in the light of two phenomena, which are expected to be important for ultrathin epitaxial perovskite films. First, in an ultrathin film grown epitaxially on a dissimilar “compressive” substrate, the crystal lattice may be highly strained, which stabilizes the out-of-plane polarization

state<sup>10</sup> and so may increase the coercive field considerably. Second, since perovskite ferroelectrics exhibit a finite conductivity, the leakage current through a capacitor must increase with decreasing film thickness which may influence an apparent coercive field in ultrathin films.

High-quality single-crystalline PZT 52/48 thin films have been grown epitaxially on (001)-oriented  $\text{SrTiO}_3$  substrates by high-pressure on-axis sputtering.<sup>11,12</sup> The substrate surface has been covered by a thin layer of  $\text{SrRuO}_3$ , a conducting oxide deposited by the same technique to serve as a bottom electrode. The ferroelectric capacitors were fabricated by evaporating Pt through a shadow mask to pattern the top electrode. The polarization–field ( $P$ – $E$ ) hysteresis loops were obtained using an aixACCT TF Analyzer 2000. Though a different patterning technique has been used here, the observed  $P$ – $E$  curves are very similar to the loops reported in our previous study for the ion-beam etched capacitors (see Fig. 3 in Ref. 13). The coercive field  $E_c$  has been extracted from the  $P$ – $E$  curves measured at 20 kHz in a manner described earlier.<sup>13</sup> The dependence of  $E_c$  on the film thickness is shown in Fig. 1. It can be seen that the coercive field increases drastically as the thickness of a PZT film is decreased.

Since the observed coercive field of the thinnest capacitors is extremely high, it is of interest to calculate the thermodynamic coercive field  $E_{\text{th}}$  of an epitaxial ferroelectric film. In contrast to the previous calculations of  $E_{\text{th}}$  performed for bulk crystals<sup>14</sup> and polymer films,<sup>5</sup> in our case it is necessary to take into account the influence of lattice strains induced in an epitaxial layer by a dissimilar thick substrate. The mechanical substrate effect on  $E_c$  is expected to be pronounced due to electrostrictive coupling between polarization  $\mathbf{P}$  and strain in ferroelectrics.

For the tetragonal  $c$  phase, which represents the energetically most favorable state in PZT films grown on compressive substrates,<sup>15</sup> the thermodynamic coercive field can

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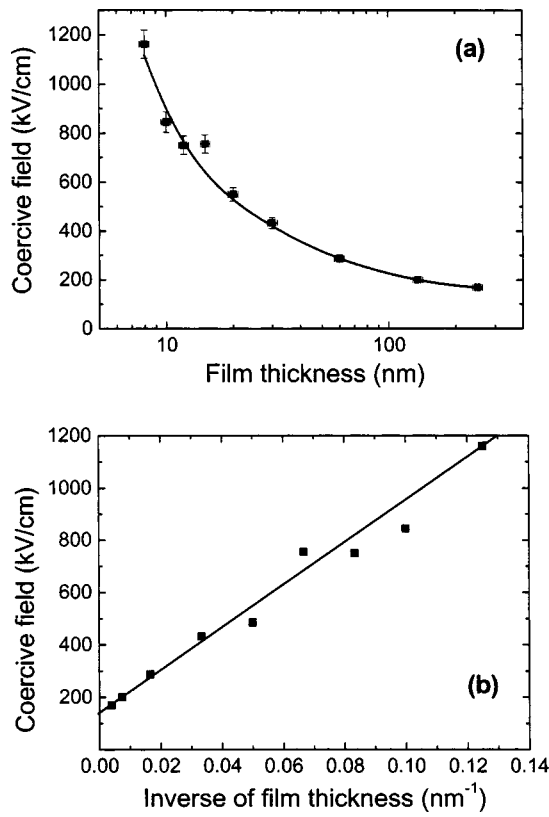


FIG. 1. Coercive field of PZT 52/48 epitaxial films measured at 20 kHz and plotted versus the film thickness  $t$  (a) and the inverse of film thickness  $1/t$  (b). The straight line in (b) shows a linear fit to the experimental data, whereas the curve in (a) is a guide to the eyes.

be calculated analytically. According to the nonlinear thermodynamic theory,<sup>15</sup> the energy density of this out-of-plane polarization state ( $P_1 = P_2 = 0$ ,  $P_3 \neq 0$ ) is given by  $\tilde{G} = S_m^2/(s_{11} + s_{12}) + a_{33}^* P_3^2 + a_{33}^* P_3^4 + a_{111} P_3^6 - P_3 E_3$ , where  $a_3^* = a_1 - S_m 2Q_{12}/(s_{11} + s_{12})$ ,  $a_{33}^* = a_{11} + Q_{12}^2/(s_{11} + s_{12})$ ,  $S_m$  is the misfit strain in the film/substrate system,  $\mathbf{E}$  is the applied electric field,  $a_1$ ,  $a_{11}$ , and  $a_{111}$  are the dielectric stiffness and higher-order stiffness coefficients at constant stress,  $s_{ln}$  are the elastic compliances at constant polarization, and  $Q_{ln}$  are the electrostrictive constants in polarization notation. The dependence of the polarization  $P_3$  on the electric field  $E_3$  can be calculated from the condition  $\partial \tilde{G} / \partial P_3 = 0$ , which gives  $E_3 = 2P_3(a_3^* + 2a_{33}^* P_3^2 + 3a_{111} P_3^4)$ . If the field is directed against the polarization ( $E_3 < 0$ ),  $P_3$  decreases with increasing field intensity. The stability condition  $\partial^2 \tilde{G} / \partial P_3^2 = \chi_{33} > 0$  of the ferroelectric phase makes it possible to calculate the minimum polarization, which can exist in an antiparallel electric field. From the equation  $\chi_{33} = 0$ , we obtain the critical polarization  $P_{cr}(E_3)$  as

$$P_{cr}^2 = -\frac{a_{33}^*}{5a_{111}} + \sqrt{\frac{a_{33}^{*2}}{25a_{111}^2} - \frac{a_3^*}{15a_{111}}}. \quad (1)$$

The critical field  $E_{th}$ , which makes the antiparallel orientation of polarization unstable, equals

$$\begin{aligned} E_{th} &= 2P_{cr}(a_3^* + 2a_{33}^* P_{cr}^2 + 3a_{111} P_{cr}^4) \\ &= -8P_{cr}^3(a_{33}^* + 3a_{111} P_{cr}^2). \end{aligned} \quad (2)$$

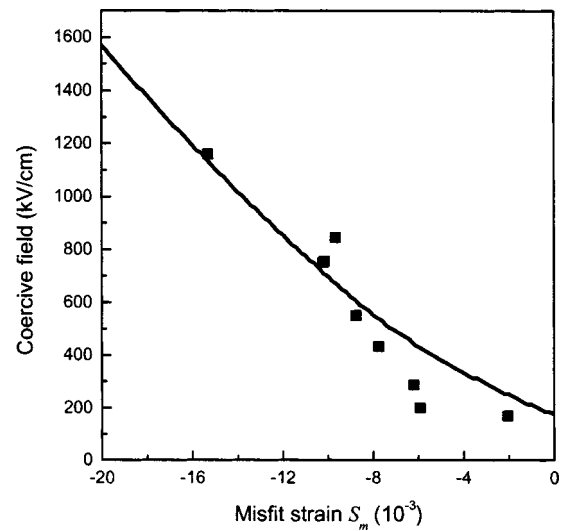


FIG. 2. Coercive field of single-crystalline PZT films as a function of misfit strain  $S_m$  in the epitaxial system. The solid line shows the thermodynamic coercive field  $E_{th}$  calculated for PZT 50/50 films. The experimental data points represent the coercive fields  $E_c$  of PZT 52/48 films of different thicknesses measured at 20 kHz.

The substitution of Eq. (1) into Eq. (2) makes it possible to calculate the thermodynamic coercive field  $E_{th}$  of the  $c$  phase as a function of the misfit strain  $S_m$ .

In the general case, when all of the polarization components  $P_1$ ,  $P_2$ , and  $P_3$  differ from zero, the coercive field  $E_{th}(S_m)$  can be computed numerically. We performed these calculations for single-domain PZT 50/50 films at room temperature using numerical values of the involved material parameters given in Refs. 16 and 15. In our calculations, it was taken into account that the ground state of a strained PZT 50/50 film changes at  $S_m = -2.82 \times 10^{-3}$  from the tetragonal  $c$  phase, which is stable at larger negative  $S_m$ , to the monoclinic  $r$  phase.<sup>15</sup> Figure 2 shows the dependence  $E_{th}(S_m)$  for the relevant strain range  $S_m < 0$ . It can be seen that the coercive field varies strongly with the misfit strain in an epitaxial system. Remarkably, the stability of out-of-plane polarization state enhances with the increase of compressive in-plane strains in the film. Since the magnitude of the out-of-plane spontaneous polarization  $P_r = P_3(E=0)$  grows with the lattice strains in a similar way,<sup>10</sup> the increase of  $E_{th}$  must be correlated with that of  $P_r$ . Indeed, the calculations demonstrate that  $E_{th}$  scales almost linearly with the cube of polarization:  $E_{th} \sim P_r^3$ . It should be emphasized that a similar strong dependence of the coercive field  $E_c$  on polarization  $P_r$  is expected for thermally activated switching processes governed by the nucleation of antiparallel  $180^\circ$  domains (owing to a rapid increase of the domain-wall energy with increasing polarization<sup>17,18</sup>). Therefore, the measured coercive field in epitaxial films may vary markedly with the misfit strain as well.

To compare the observed coercive field  $E_c$  with the calculated thermodynamic one, it is necessary to determine the misfit strain in our epitaxial system as a function of film thickness  $t$ .<sup>19</sup> To this end, we performed x-ray diffraction measurements of the lattice constants of our PZT films. The misfit strain  $S_m = (a - a_0)/a_0$  has been evaluated from the measured in-plane lattice parameter  $a(t)$ , taking the equivalent cubic cell constant  $a_0$  of a free-standing PZT 52/48 film

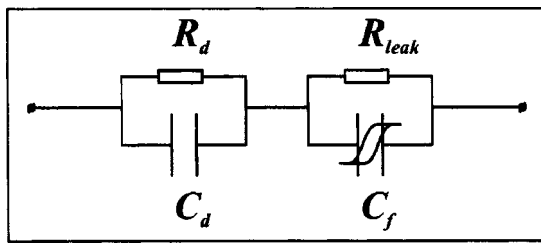


FIG. 3. Equivalent circuit modeling of a leaky ferroelectric capacitor with a conductive nonferroelectric layer at the film/electrode interface.

to be  $a_0=0.4065$  nm.<sup>20</sup> Using the determined thickness-dependent values of  $S_m(t)$  and the data given in Fig. 1, we obtained the set of experimental points shown in Fig. 2. It can be seen that the observed coercive field  $E_c$  exhibits misfit-strain dependence similar to that of the thermodynamic field  $E_{th}$ . Although at film thicknesses  $t \gg 10$  nm the  $E_c$  values measured at 20 kHz are well below the thermodynamic limit, in ultrathin films ( $t \sim 10$  nm) they become close to  $E_{th}$ . Moreover, the coercive fields displayed by our capacitors increase significantly at high frequencies, exceeding markedly the thermodynamic field in the case of ultrathin films (e.g., for  $t=12$  nm,  $E_c=1065$  kV/cm at 200 kHz, whereas  $E_{th}=700$  kV/cm).

This result indicates that the performed hysteresis measurements give an apparent coercive field rather than the intrinsic one. Indeed, the intrinsic coercive field  $E_{ci}$  could only tend to  $E_{th}$  at high frequencies and low temperatures, where the thermally activated switching processes may be largely suppressed, but cannot exceed this thermodynamic limit.

We believe that enormous increase of apparent coercive field in ultrathin films is partly caused by the presence of a *conductive nonferroelectric layer* at the interface between the film and Pt electrode. Our hypothesis is supported by the observed linear dependence of  $E_c$  on the inverse of film thickness [see Fig. 1(b)]. This dependence has the form  $E_c(t) = E_{ci}^{\infty} + \text{const}/t$ , which is similar to the one predicted in Refs. 4 and 8 for the size effect controlled by the charge injection through an interface layer. However, high leakage currents displayed by capacitors involving ultrathin films ( $t \sim 10$  nm) indicate that the interface layer does not behave as an insulator even at small electric fields, contrary to the supposition made in Refs. 4 and 8. Based on this observation, we propose another model (see Fig. 3) that could possibly explain a drastic increase of the coercive field in ultrathin PZT films. Here, finite conductivities of the ferroelectric film and the interface layer are modeled by resistors  $R_{leak}$  and  $R_d$  connected in parallel to the ferroelectric capacitor  $C_f$  and the dielectric-layer capacitor  $C_d$ , respectively. A voltage drop  $V_d = I_d R_d$  across a thin interfacial layer, which is created by a current  $I_d$  flowing through this layer, reduces the voltage applied to a ferroelectric film. Hence, the apparent coercive field  $E_c = E_{ci} + I_d R_d / t$  becomes larger than the intrinsic coercive field  $E_{ci}$ . The actual variation of  $E_c$  with the film thickness  $t$  depends on the resistivities of ferroelectric

and interface layers, thickness and capacitance  $C_d$  of the latter, and on the displacement current through the ferroelectric capacitor  $C_f$ .

In addition, the observed size effect (see Fig. 1) may be partly due to a strain-induced increase of the intrinsic coercive field  $E_{ci}$  in ultrathin films. Based on our measurements of the remanent polarization  $P_r$  in PZT films and the relation  $E_{ci} \sim P_r^n$  with  $n \approx 3$ , we estimate that  $E_{ci}$  may be about two times larger at  $t \sim 10$  nm than at  $t \sim 100$  nm. The extrapolation of the plot  $E_c(1/t)$  shown in Fig. 1(b) to  $1/t=0$  gives  $E_{ci}^{\infty} \approx 140$  kV/cm. This value represents the coercive field of a very thick strained film, where the interface effect becomes negligible, and the misfit strain relaxes to a thickness-independent value, which in our films equals  $S_m \approx -(2-4) \times 10^{-3}$ . All in all, the strain effect may increase the intrinsic coercive field to about 300 kV/cm at  $t \sim 10$  nm, which is much smaller than the thermodynamic limit  $E_{th} \approx 1200$  kV/cm.

Thus, the observed drastic increase of the coercive field in ultrathin PZT films may be caused by the effect of a conductive nonferroelectric interface layer combined with the in-plane compression of the crystal lattice. Additional influence of intrinsic size effects and structural factors, however, cannot be ruled out.

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- <sup>19</sup>The misfit strain depends on the film thickness due to the strain relaxation caused by generation of misfit dislocations at the film/substrate interface.
- <sup>20</sup>This value of  $a_0$  was chosen based on the measured lattice constants  $c_b$  and  $a_b$  of bulk PZT 50/50 ceramics and their electrostrictive constants  $Q_{1n}$  and polarization  $P_s=0.5$  C/m<sup>2</sup> given in Ref. 16, using the theoretical relations  $(c_b - a_0)/a_0 = Q_{11}P_s^2$  and  $(a_b - a_0)/a_0 = Q_{12}P_s^2$ .