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Citation: *Appl. Phys. Lett.* **98**, 142902 (2011); doi: 10.1063/1.3569137

View online: <http://dx.doi.org/10.1063/1.3569137>

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Strong strain dependence of ferroelectric coercivity in a BiFeO₃ film

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(Received 16 July 2010; accepted 2 March 2011; published online 5 April 2011)

The ferroelectric polarization loop of an epitaxial BiFeO₃ film on a piezoelectric substrate has been investigated as a function of continuously and reversibly varied biaxial strain of $\varepsilon = 0.36\% - 0.51\%$. Over this range, the ferroelectric coercive field (E_C) at 80 K increases reversibly by 36% with the increasing tensile strain. In contrast, phase-field simulations predict the opposite trend of $dE_C/d\varepsilon < 0$. Therefore, we attribute the observed $E_C(\varepsilon)$ dependence to the strain dependence of domain dynamics, which are not included in thermodynamic models. The strain dependence of the remanent polarization agrees with previous results. © 2011 American Institute of Physics. [doi:10.1063/1.3569137]

Ferroelectric switching is of practical and fundamental interest. Advances in epitaxial growth techniques have led to well-defined strain states of ferroelectric oxide films,¹ providing the grounds for the recent discoveries of strong strain effects.¹⁻⁴ *Ab initio* theories are increasingly effective in predicting the strain dependence of ferroelectric polarization^{2,3,5} and strain-induced ferroelectric phases.^{1,6,7} This includes several magnetic oxides which, hence, may display strain-induced multiferroicity.^{6,7} Ferroelectric domain configurations have been controlled by epitaxial strain⁸ and modeled, e.g., by phase-field simulations,⁹ providing a foundation for the analysis of domain processes during ferroelectric switching. On the other hand, switching dynamics have been studied by time-resolved switching current measurements¹⁰ and by imaging domain growth using piezoresponse force microscopy.¹⁰⁻¹² The ferroelectric coercivity (E_C) depends on both the energetically favorable domain configuration predicted by thermodynamic relations and the kinetic pathways that are necessary to reach the energetically most favorable state.

The measurement of strain-dependent coercivity has been notoriously difficult since the common approach of utilizing the thickness-dependent strain relaxation in epitaxial films leads to a strong direct thickness dependence of E_C (Refs. 2 and 13-16) which is hard to separate from the strain dependence. In the present study, a piezoelectric monocrystalline substrate of $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - x\text{PbTiO}_3(001)$ with $x=0.28$ (PMN-PT) is employed to reversibly strain an epitaxial BiFeO₃ film¹⁷ and, thereby, to directly record the strain dependence of ferroelectric polarization loops. Such loops are measured on a BiFeO₃ film at 80 K as a function of biaxial tensile in-plane strain. Strikingly, E_C shows a strong increase with tensile strain, whereas the phase-field simulation conducted for strained BiFeO₃ predicts a *decrease*. We suggest that at the measuring conditions ferroelectric switching is governed by the dynamics of domain nucleation and

wall propagation with the consequence that the dynamics show strong strain dependence. The strain response of the remanent polarization agrees with previous experimental and theoretical results.

To perform the measurements leading to these observations, a 200 nm thick film of BiFeO₃ was grown by pulsed laser ablation from a 10% Bi-rich target in 100 mTorr O₂ at 650 °C onto a polished PMN-PT(001) substrate covered with a 4 nm thick La_{0.7}Sr_{0.3}MnO₃ (LSMO) electrode layer. Voltages up to 450 V were applied between the LSMO layer and a gold electrode on the back of the substrate, resulting in a maximum reversible biaxial in-plane strain of 0.15%.¹⁷ The lattice parameters of the film in various strain states were determined by four-circle x-ray diffraction.¹⁷ Polarization measurements were performed in a parallel plate geometry with 50 μm diameter Cr/Au top electrodes using an Aixact TF 2000 analyzer at a frequency of 1 kHz. Since the leakage through the BiFeO₃ layer increases strongly with temperature, measurements were taken at 80 K in a cryogenic probe station. This leakage may be related to an excess of semiconducting bismuth oxide and is a well-known problem for BiFeO₃ films. However, the temperature dependence of the ferroelectric polarization of BiFeO₃ is weak between 80 and 300 K,¹⁸ and our values of remanent polarization (P_r) agree with previously published room-temperature data.

The BiFeO₃ film shows a pseudocubic cube-on-cube epitaxy on LSMO/PMN-PT, a monoclinic lattice structure without signs of a structural transition in the range of applied strain. The three dimensional strain of the film was measured at room temperature as described previously in Ref. 17. The sample was then cooled in cryogenic stage and the out-of-plane lattice constant was measured to determine the strain due to cooling from room temperature to 80 K. The relative change in the in-plane lattice constant was calculated using the out-of-plane strain due to cooling to 80K and the Poisson ratio for this film from Ref. 17. The BiFeO₃ film was found to have an as-grown strain of $\varepsilon=0.51\%$ at 80 K with respect to the bulk lattice constant of ferroelectric BiFeO₃.^{13,17} This

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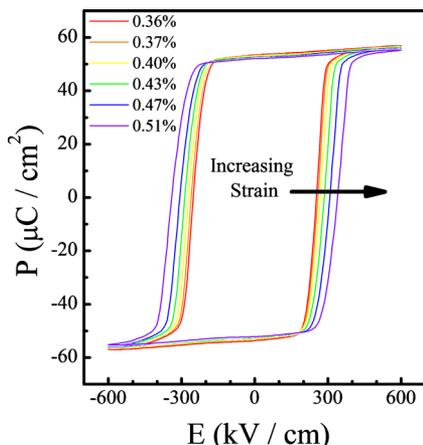


FIG. 1. (Color online) Ferroelectric polarization vs electric field of a BiFeO₃ film measured in the denoted biaxial tensile strain states at 80 K and 1 kHz.

tensile strain results from the lower thermal expansion of the substrate compared to that of the film, coupled with cooling from growth temperature to 80 K. A square polarization loop is observed (Fig. 1) which allows an accurate determination of P_r and E_C , in agreement with our earlier report.¹³ The frequency (f) dependence of $P(E)$ is weak, similar to the films in Ref. 13 which were grown under the same conditions. Application of a bias field to the substrate does not shift the hysteresis loops, indicating that the grounded LSMO bottom electrode shields the film from the ferroelectric polarization and the electric field applied to the substrate. The major effects of the reversible substrate compression, which reduces the tensile strain of the film, are a reversible reduction in E_C and a small enhancement of P_r . Figure 2 shows an increase in E_C by 36% when the tensile strain is decreased by 0.15%. Before discussing the strain effect on E_C , the strain dependence of P_r [Fig. 2] is compared to previous room-temperature data. Jang *et al.*³ have reported polarization loops for BiFeO₃ films grown on SrTiO₃ and Si substrates as well as for a membrane released from the substrate. These experimental data and their model of a polarization rotation mechanism³ are compared with our result in Fig. 3. The good agreement between the slopes of the data sets provides strong cross-validation for both results, with the slope of the linear fit ($dP_r/d\varepsilon$) of $13.5 \pm 0.3 \mu\text{C}/\text{cm}^2\%$ for our data at 80 K, and $13.8 \pm 0.7 \mu\text{C}/\text{cm}^2\%$ for the experimental room-temperature data from Ref. 3.

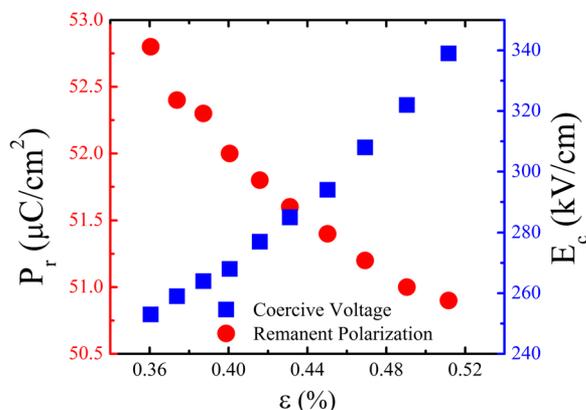


FIG. 2. (Color online) Coercive field and remanent polarization vs biaxial in-plane strain as derived from the data in Fig. 1.

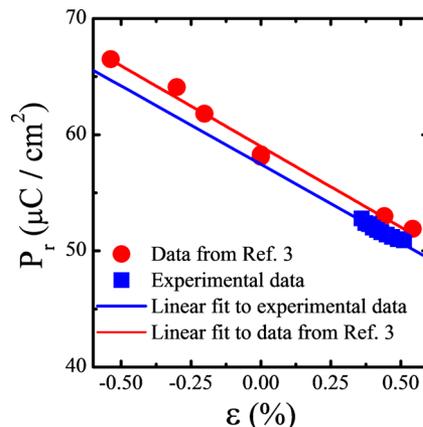


FIG. 3. (Color online) Comparison of the measured strain dependence of the remanent polarization at 80 K with room-temperature data from Ref. 3.

We now discuss the large strain dependence of E_C . In a simple model considering thermodynamic aspects alone¹⁶ one would expect E_C and the projection of P_r onto the direction of the electric field to have a similar dependence on strain since switching involves the nucleation of domains, and domain-wall energies increase with polarization. To gain a description of the strain dependence of E_C and P_r resulting from such thermodynamic considerations, we perform phase-field calculations^{9,19} on a (001)-oriented epitaxial BiFeO₃ thin film under in-plane biaxial tensile strain (0% to 0.6%) and at a temperature of $T=77$ K. As is seen in the results shown in Fig. 4, both the coercive voltage and P_r decrease with an increase in biaxial strain, i.e., we find that $dE_C/d\varepsilon < 0$ and $dP_r/d\varepsilon < 0$. While we note that similar trends ($dE_C/d\varepsilon < 0$ and $dP_r/d\varepsilon < 0$) were observed in BaTiO₃ thin films in the tensile strain regime,⁹ these results are clearly in contradiction with our experimental finding of $dE_C/d\varepsilon > 0$. Note, however, that for the polarization a negative slope $dP_r/d\varepsilon < 0$ is obtained in both experiment and calculations confirming the model.

To understand the intriguing difference between $dE_C/d\varepsilon$ predictions from our phase-field simulations and the experimental results at 80 K, we recall that simulations of $E_C(\varepsilon)$ for other perovskite oxide ferroelectrics^{9,20–22} all find $dE_C/d\varepsilon < 0$. The present simulations for BiFeO₃ thus yield similar results to those found for other materials. On the other hand, our experimental data, showing the opposite trend of $dE_C/d\varepsilon > 0$, is in agreement with the experimental BiFeO₃ data from Ref. 3. The difference between simulations

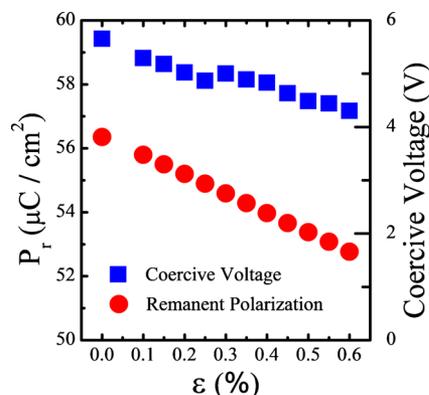


FIG. 4. (Color online) Phase field modeling of the strain dependence of remanent polarization and coercive voltages at 77 K.

and experiment must be attributed to a different dominant mechanism in the two cases. The E_C derived in the phase field simulations, denoted as E_C^S hereafter, corresponds to the field above which there is a thermodynamic driving force for the switching. In contrast, the experimentally determined E_C corresponds to the field where this driving force exists *and* switching occurs on a time scale faster than the experimental measurements, i.e., thermodynamic *and* kinetic conditions (related to domain wall velocities v and domain nucleation rates n) must be satisfied. Recalling that we observe only a very weak frequency dependence (much weaker than the changes with strain), we conclude that above E_C both domain nucleation and domain wall motion must be fast processes compared to the measurement frequency. However, both v and n are known to be strongly and nonlinearly dependent on the electric field, nearly vanishing below a threshold value.¹⁰ In the case of v , this threshold value corresponds to a depinning field and can depend on strain.²³ Then, at higher fields corresponding to the depinning and flow regimes, a weak frequency dependence is recovered.¹⁰ Both experimental measurements and first principle modeling of strain effects on n and v are difficult due to the role of defects in the process and the previous lack of reliable experimental data on strain dependencies. Based on the fact that the measured $E_C(\epsilon)$ is different in sign from E_C^S , our combined experimental and numerical investigation strongly suggests that the switching and its strain dependence in BiFeO₃ at the experimental conditions are governed by domain dynamics.

Finally we note that we have carefully eliminated potential sources of error for E_C^S : first, the reversible tensile strain leads to a thickness reduction by 0.15%¹⁷ which is too small to account for the large enhancement of E_C .^{2,14} Second, an unknown structural change might occur but structural data for the investigated film and strain range indicate an unchanged monoclinic symmetry.¹⁷ Third, the multiferroic nature and magnetoelectric coupling in BiFeO₃ have not been included in the simulations.²⁰ However, a strong strain-dependent magnetoelectric influence on E_C is not likely since the magnetic moment is weak.

In summary, applying reversible strain from a piezoelectric substrate onto an epitaxial BiFeO₃ film allows us to directly probe the strain dependence of the ferroelectric polarization and the coercive field. The strain dependence of the polarization agrees with data from films grown on various substrates and with the polarization rotation model. A large reversible enhancement of the coercive field with tensile strain is observed, in contrast to the result of our phase-field simulations that predict a decreasing E_C in the tensile regime. We suggest that the polarization reversal in the BiFeO₃ film is governed by domain *dynamics* and propose a dynamic origin for the observed strain-enhanced coercivity. The application of reversible strain may ultimately allow experiments that directly study the strain dependences of domain nucleation and wall velocity. Since fast switching and a low

switching voltage are essential for applications, these strain effects may become an important factor for the choice of materials. This work will motivate the development of models for strain-dependent domain nucleation and wall motion, and inspire local investigations of switching under reversibly controlled strain. Together with the presented results, this will yield a better understanding of ferroelectric switching and new designs of functional heterostructures that utilize this strain dependence.

The research at the CNMS was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. DOE. K.D. acknowledges funding by the Deutsche Forschungsgemeinschaft, FOR520. The work at Pennsylvania State University was supported by DOE under grant DE-FG02-07ER46417.

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