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Effect of 90° domain movement on the piezoelectric response of patterned $PbZr_{0.2}Ti_{0.8}O_3/SrTiO_3/Si$ heterostructures

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The converse longitudinal piezoelectric responses of $PbZr_{0.2}Ti_{0.8}O_3/SrTiO_3/Si$ heterostructures have been studied for continuous films and for islands patterned by focused ion beam milling (typical dimension is $1\times1\times1$ μm). The intrinsic piezoelectric response of the island with an immobile polydomain structure is modeled using finite element analysis. The difference between the results of experimental measurement and modeling is explained by an extrinsic contribution to the piezoresponse from 90° domain movement. The contribution of 90° domain movement to the total piezoresponse is shown to be greatly enhanced in the patterned islands, and leads to an effective piezoelectric coefficient (~400 pm/V) which is five times larger than the theoretical bulk single domain value. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2012527]

Ferroelectric thin films such as lead zirconate titanate ($Pb(Zr,Ti)O_3$) are attractive for many applications requiring high piezoelectric coefficients, such as sensors and actuators in microelectrical-mechanical systems (MEMS).[1,2] The extrinsic contribution of 90° domain movement to the total piezoresponse has been extensively studied since the 1950's.[3–5] In bulk materials, this extrinsic contribution is equal to or greater than the intrinsic contribution from the lattice deformation of a single crystal.[6,7] Measurement of the dielectric and piezoelectric properties for thin polycrystalline films with thickness less than 1 μm showed negligible effect of 90° domain movement due to substrate clamping.[8] However, synchrotron x-ray analysis[9] has demonstrated that the 90° domains can move under applied electrical field in the continuous film.

Recently, 90° domain movement in $1\times1\times1$ μm islands microfabricated from $PbZr_{0.2}Ti_{0.8}O_3$ (PZT 20/80) film grown on (001) $SrTiO_3$ (STO) substrate has been observed.[10] Partially released clamping gives rise to a substantial increase in the effective piezoelectric coefficient up to three times larger than its theoretical bulk value. Since modern electronic industry including much MEMS has relied on the development of materials and processes compatible with silicon-based integrated circuits, in this letter we present the study of effect of 90° domain movement on piezoresponse of islands microfabricated from PZT 20/80 films grown on Si substrates. Comparing the results of finite element modeling of piezoresponse of an island with an immobile domain structure with the results of experiment allows us to estimate the contribution of 90° domain movement to the piezoresponse of islands.

Due to the difficulty of growing an epitaxial $Pb(Zr,Ti)O_3$ film directly on a Si substrate, a perovskite structured $SrTiO_3$ template layer is employed.[11] PZT 20/80 film of 1 μm thickness is grown by pulsed laser deposition (PLD) on the (001) Si substrate with a 200 Å predeposited $SrTiO_3$ (001) template layer. The films are deposited at 650 °C and then are slowly cooled down to room temperature to avoid cracking. Conductive $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) bottom and Pt top electrodes about 50nm thick each are also deposited by PLD to form capacitors for piezoelectric and polarization measurement. The detailed growth conditions have been described elsewhere.[12] X-ray diffraction analysis shows that PZT 20/80 film has epitaxial quality [Fig. 1(a)]. The film consists of *c*-axis-oriented domains (*c*-domains) and *a*-axis-oriented domains (*a* domains); no pyrochlore phase is observed. The volume fraction of *a* domains, about 60%, is determined by both ω-rocking curves [Fig. 1(b)] and transmission electron microscopy. The domain structure image obtained by piezoelectric force microscopy (PFM) in a multimode scanning force microscope (Digital Instruments, Nano IIIA) is presented in Fig. 2(a). It clearly shows a cellular domain structure consisting of $c/a_1/a_2$ polydomains in accordance with the theoretical prediction[13] and experimen-

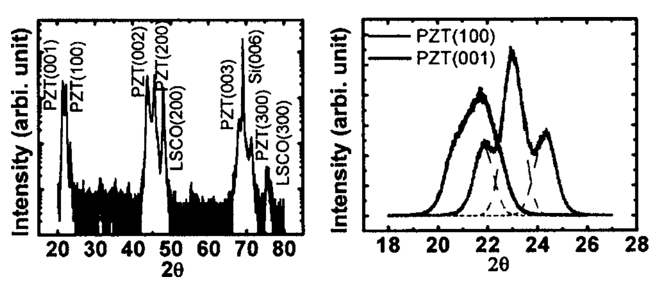

FIG. 1. X-ray diffraction analysis of the 1 μm thick $PbZr_{0.2}Ti_{0.8}O_3$ film on LSCO/STO/Si substrate : Left: θ–2θ scan; right: ω-rocking curve.

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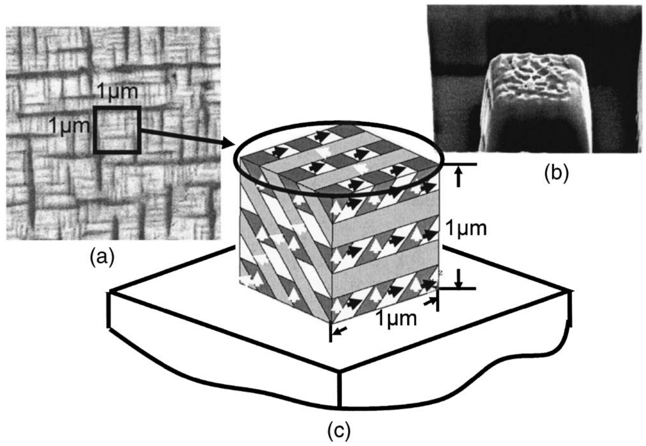

FIG. 2. (a) PFM image (5×5 μm) of 1 μm thick $PbZr_{0.2}Ti_{0.8}O_3$ film on LSCO/STO/Si; (b) a schematic model of a $1\times1\times1$ μm cubic island with three domain variants configuration on a rigid substrate (60% *a*-domain fraction); (c) scanning electron microscopy picture of a $1\times1\times1$ μm cubic island with Pt contact on top.

tal observation of PZT 20/80 films with thickness larger than 300 nm.[14] The *a*-domain fraction estimated from the PFM images is consistent with the results of x-ray diffraction. The films are then patterned to $1\times1\times1$ μm cubic islands by using a focused ion beam method with a Ga+ ion source (FEI DualBeam 610, 30 kV) in order to decrease substrate clamping effect [Fig. 2(b)].[15] The domain structure of the islands is found to be similar to that of the continuous film.[16] The fraction of *a* domains in islands estimated from PFM images is consistent with x-ray diffraction results for continuous films. The converse piezoelectric coefficients of the islands and the continuous films are measured by using a voltage modulated PFM method.[17] Polarization is measured using the same microscope setup with a TFA2000 system, by which the parasitic capacitance can be measured and subtracted from the total measured charge signal of the island.[18] For each measurement, a fresh virgin capacitor is used to exclude the influence of electric-field history.

Figure 3 shows the plot of the polarization and d_{33} versus electric field for the island and the continuous film. As shown in Fig. 3(a), d_{33} of the island has a peak value close to 400 pm/V at 12 MV/m. This value is nearly five times larger than the theoretical value of a bulk single crystal (87 pm/V), and eight times larger than d_{33} measured for the continuous film [$\sim$50 pm/V, Fig. 3(a)]. Decreased substrate clamping and constraint by surrounding material cannot explain why the d_{33} of islands dramatically increases, unless an extrinsic contribution of 90° domain movement is taken into account. Based on the PFM observations, we propose that the fraction of *a* domains start to decrease at about 10 MV/m, and most of *a* domains transform to *c* domains at about 12 MV/m. This hypothesis is verified by the polarization measurement. As shown in Fig. 3(b), the polarization of the island increases to that of the single domain ($\sim$80 μC cm^{-2}) at about the same field (12 MV/m), indicating that almost all *a* domains change to *c* domains via 90° domain-wall movement. On the contrary, there is no obvious change of polarization in the continuous film. The movement of *a* domain is observed to be partially reversible in islands: When the electric field is decreased from 40 MV/m, there is no jump of the d_{33}, but the d_{33} value is close to that of the continuous film, indicating that there should be some new

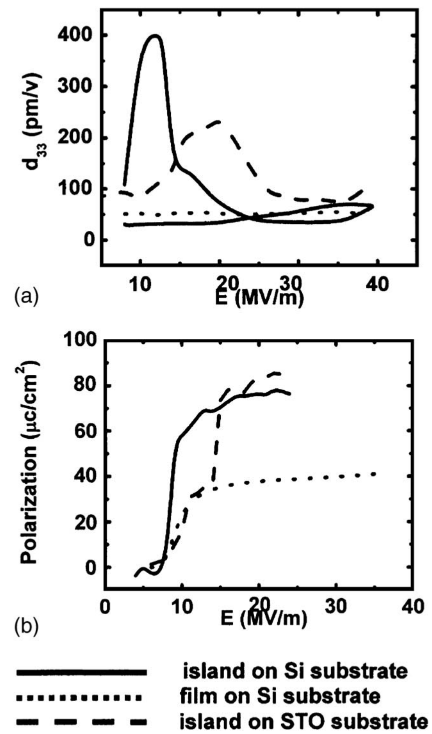

FIG. 3. (a) Change of d_{33} under electric field of the island and a continuous film on Si substrate measured by PFM, d_{33} of the same size island on STO substrate is shown for comparison; (b) change of polarization under electric field of the island and a continuous film on Si substrate, polarization curve of the same size island on an STO substrate is also shown for comparison.

90° domains formed when the applied field decreases.

For better interpretation of the experiment results, finite element modeling using a commercial software ANSYS was used to calculate the converse longitudinal piezoresponse of an island. A model of polydomain islands including all three-domain variants: *c*-domain [(001) oriented polarization], a_1- and a_2-domain [(100) and (010) oriented polarization] has been considered (Fig 2(c)). Domain thickness (50nm), period (137.5nm) and *a*-domain fraction (60%) in agreement with TEM and X-ray diffraction observation are used in this modeling. For simplicity, the polydomain ferroelectric is considered as isotropic elastic media with Young's modulus $Y = 148$ GPa, Poisson's ratio $\nu=0.3$.[19] Piezoelectric coefficients $d_{33}=87$ pm/V, $d_{31}=-26$ pm/V (Ref. 20) of PZT 20/80 bulk materials are employed for the calculation. The intrinsic piezoresponse is simulated for islands with fixed 90° domain boundaries. The substrate is assumed to be rigid to obtain the maximum possible intrinsic piezoresponse.[19] The normal surface strain of the island is calculated and compared with experimentally measured values (Fig. 4). For instance, the calculated strain of the island is 0.0336% at 12 MV/m, while the measured value is 0.1455% (obtained by integration of d_{33} data). So the contribution of 90° domain movement to the effective piezoelectric coefficient of the island is estimated to be $\sim$370 pm/V.

The extrinsic contribution to piezoresponse from 90° domain movement demonstrated in this work is similar to the results observed for PZT 20/80 film grown on a STO substrate,[10] but the peak value of d_{33} is higher. It shows that 90° domain movement is easier for the film grown on a Si substrate than on a STO substrate. The measured result of the polarization change under the electric field supports this argument. There are two steps on the polarization curve for

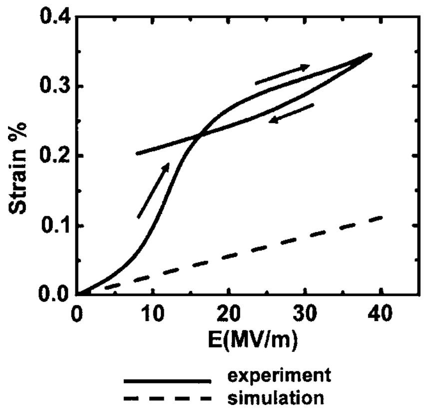

FIG. 4. Strain of the island of $PbZr_{0.2}Ti_{0.8}O_3$/LSCO film of STO/Si substrate under electric field and its simulation by finite element modeling. The solid line shows the strain of a cube island containing 60% volume fraction a-domain obtained by integration of experimental d_{33}, the dotted line shows the strain of surface of a cube island containing 60% a domain (finite element modeling).

islands grown on the STO substrate. The first jump of polarization near 10 MV/m is due to the saturation of c-domain polarizations, while the second jump of polarization around 15 MV/m shows that a domains have transformed into c domains. For the polarization evolution of the islands on Si substrates, only one step is shown around 10 MV/m. This means that the 90° domains on Si substrates can move at a lower voltage, which is close to the coercive voltage of the film.

In summary, the converse longitudinal piezoresponse of the $PbZr_{0.2}Ti_{0.8}O_3$ continuous films grown on Si substrates and island microfabricated from these films are measured by PFM. The piezoresponse has been calculated for an island with immobile domain boundaries by using finite element modeling. Comparison of the results of experiment and modeling points to a large extrinsic contribution from 90° domain movement to the piezoresponse of the island. Due to decreased substrate clamping the movement of 90° domain walls in $PbZr_{0.2}Ti_{0.8}O_3$ islands on Si substrate increases the effective d_{33} up to 400 pm/V, which is five times larger than the theoretical d_{33} value of a bulk single crystal.

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[1] J. F. Scott and C. A. Paz de Araujo, Science **246**, 1400 (1989).
[2] P. Muralt, J. Micromech. Microeng. **10**, 136 (2000).
[3] E. Little, Phys. Rev. **98**, 978 (1955).
[4] F. Jona and G. Shirane, *Ferroelectric Crystals* (Macmillan, New York, 1962).
[5] W. J. Merz, *Proceedings of the 1972 European Solid State Devices Research Conference* (1973), p. 3.
[6] Q. M. Zhang, W. Y. Pan, S. J. Jang, and L. E. Cross, J. Appl. Phys. **64**, 6445 (1988).
[7] R. Herbeit, U. Robels, H. Dederichs, and G. Arlt, Ferroelectrics **98**, 107 (1989).
[8] F. Xu, F. Chu, and S. Trolier-McKinstry, J. Appl. Phys. **86**, 588 (1999).
[9] K. S. Lee, Y. K. Kim, J. Kim, I. S. Jung, and S. Baik, Appl. Phys. Lett. **79**, 2444 (2001).
[10] V. Nagarajan, A. Roytburd, A. Stanishevsky, S. Prasertchoung, T. Zhao, L. Chen, J. Melngailis, O. Auciello, and R. Ramesh, Nat. Mater. **2**, 43 (2003).
[11] Y. Wang, C. Ganpule, B. T. Liu, H. Li, K. Mori, B. Hill, M. Wuttig, R. Ramesh, J. Finder, Z. Yu, R. Droopad, and K. Eisenbeiser, Appl. Phys. Lett. **80**, 97 (2002).
[12] V. Nagarajan, I. G. Jenkins, S. P. Alpay, H. Li, S. Aggarwal, L. Salamanca-Riba, A. L. Roytburd, and R. Ramesh, J. Appl. Phys. **86**, 595 (1999).
[13] A. L. Roytburd, Phys. Status Solidi A **37**, 329 (1976).
[14] C. S. Ganpule, V. Nagarajan, B. K. Hill, A. L. Roytburd, E. D. Williams, R. Ramesh, S. P. Alpay, A. Roelofs, R. Waser, and L. M. Eng, J. Appl. Phys. **91**, 1477 (2002).
[15] C. S. Ganpule, A. Stanishevsky, S. Aggarwal, and J. Melngailis, Appl. Phys. Lett. **75**, 3874 (1999).
[16] Observation on PZT islands ~1 μm grown by hydrothermal synthesis shows similar cellular domain structure as that of the continuous film. J. You, W. W. Jung, S. K. Choi, and Y. Cho, Appl. Phys. Lett. **84**, 3346 (2004).
[17] A. Gruverman, O. Auciello, and H. Tokumoto, Integr. Ferroelectr. **19**, 49 (1998).
[18] S. Tiedke, T. Schmitz, K. Prume, A. Roelofs, T. Schneller, U. Kall, R. Waser, C. S. Ganpule, V. Nagarajan, A. Stanishevsky, and R. Ramesh, Appl. Phys. Lett. **79**, 3678 (2001).
[19] J.-H. Li, L. Chen, V. Nagarajan, R. Ramesh, and A. Roytburd, Appl. Phys. Lett. **84**, 2626 (2004).
[20] M. J. Haun, E. Furman, S. J. Jang, and L. E. Cross, Ferroelectrics **99**, 63 (1989).