

Photochemical switching of ultrathin PbTiO₃ films

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The ferroelectric domain ground state of PbTiO₃ thin films on Nb:SrTiO₃ substrates has been studied as a function of film thickness. High resolution linear Q_x x-ray diffraction profiles were recorded in order to probe the presence of stripe domains, which were invariably observed for as-grown samples. After photochemical treatment, films thinner than 50 unit cells were switched to a monodomain state that could be reversed upon subsequent annealing. The stripe-domain state is linked to a Q_x modulation of the Q_z parameter in the reciprocal space, which disappears upon switching. © 2008 American Institute of Physics. [DOI: 10.1063/1.2890485]

Ferroelectric materials are interesting for electromechanical and optoelectronic applications.¹⁻⁵ The presence of ferroelectric domains will effectively alter the response of a sample, as compared to the monodomain state, reducing the piezoelectric and pyroelectric response. Recently, there has been a strong focus on the ferroelectric stripe-domain ground state.⁴⁻⁶ In order to optimize the functional performance of thin films, a key point is to develop techniques to impose a monodomain state. For example, it has been shown that the electrostatic environment can affect the domain state of ferroelectric films, producing monodomain samples if appropriate electrodes are used.⁷ One challenge with ultrathin films is to switch between the different polarization states, preferably controlling the entire film area. For example, *ab initio* calculations have shown that ionic adsorbates can help stabilize a monodomain state in ultrathin PbTiO₃ film samples.⁸

In this letter, we show how photochemistry can be used to switch thin films from a ferroelectric stripe-domain state into a monodomain state. We also demonstrate how this switching is linked to a change in the crystalline symmetry, and that the transition can be reversed upon annealing.

PbTiO₃ samples were grown by off-axis magnetron sputtering⁹ on annealed, conductive 0.5 wt % Nb-doped (001) oriented SrTiO₃. The film thicknesses investigated ranged between 8 and 227 unit cells, as determined from the thickness fringes observed in $\theta-2\theta$ x-ray diffraction (XRD) around the (001) reflection and low-angle reflectometry measurements. Rocking curve measurements of the (001) reflection typically displayed a full width at half maximum of less than 0.03°. The (001) lattice parameter varied as a function of film thickness, from 4.16 Å for thick samples to 4.05 Å for the thinnest samples, in accordance with previously reported values.^{9,10} Atomic force microscopy showed flat surfaces with a step-and-terrace structure of one unit cell height. In order to probe the intrinsic domain structure, linear Q_x profiles were recorded around the (001) reflection, revealing a ferroelectric stripe-domain ground state for all films in this

study, as proven by the presence of diffuse satellite peaks coexistent with the specular reflection.⁴⁻⁶ The photochemical experiments were performed by dipping the samples in a 0.01M AgNO₃ solution under UV irradiation from a high pressure Hg lamp at 500 W.¹¹⁻¹⁶ All samples were immersed for 30 min.

Figure 1(a) displays linear Q_x scans of a 39 unit cell thick sample before and after the photochemical processing. Prior to immersion, a satellite peak appears on each side of the specular (001) reflection due to a stripe-domain ground state. XRD analyses carried out after the photochemical treatment reveal that the satellite peaks are missing, suggesting an effective switching from a stripe-domain to a monodomain state. This demonstrates that surface chemistry can be adopted to suppress the stripe-domain ground state typically found in PbTiO₃ grown on Nb:SrTiO₃.⁸

In order to probe if this transition is reversible, we annealed a sample at 510 °C in an oxygen/argon (4:10) ambient, mimicking the growth atmosphere. This treatment effectively brought back the satellite peaks in the linear Q_x scans, albeit at a larger separation from the specular peak, see the inset in Fig. 1(a). This proves that the domain ground state can be reversibly switched back and forth. We note that even though the total film thickness is unaffected by the photochemical treatment, as determined by low-angle reflectometry, the thickness fringes on the PbTiO₃ Bragg peak, cf. Fig. 1(b), invariably suggest that the films have become three unit cells thinner. We tentatively attribute this inconsistency to formation of a surface reaction layer, brought about by the photochemical processing.¹⁷ Reciprocal space mapping of the (103) PbTiO₃ and SrTiO₃ reflections before and after the photochemical treatment reveal that the in-plane lattice constant is unchanged and equal to the substrate value, 3.905 Å.

In Fig. 1(b), the $\theta-2\theta$ diffractogram of the (001) reflection, before and after the photochemical treatment, shows that the (001) lattice parameter of the thin film increases in the monodomain state. The same procedure was carried out for a series of samples with different thickness. Figure 2 reports the thickness dependence of the (001) lattice parameter before and after photochemical processing. For films thinner than approximately 50 unit cells, we observe an effective increase in the (001) lattice constant. Samples thicker than 50 unit cells displayed both satellite peaks in the Q_x profiles and an unchanged (001) lattice parameter after the

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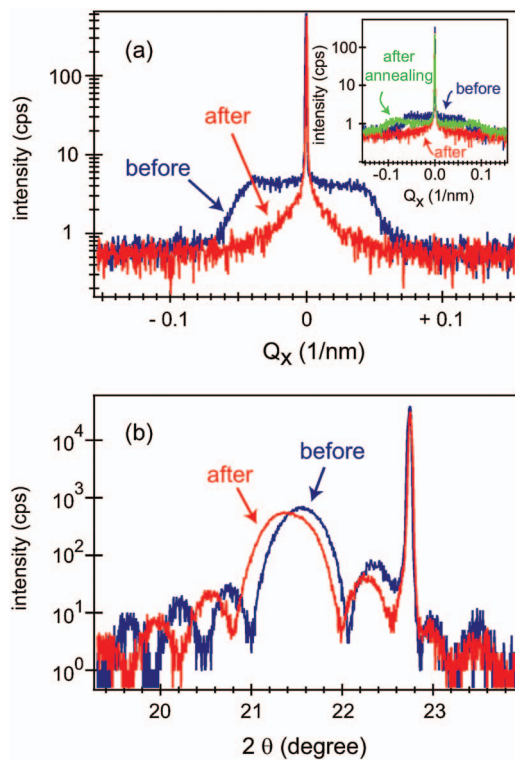


FIG. 1. (Color) (a) and (b) show high resolution linear Q_x and $\theta-2\theta$ scans before and after photochemical treatment, respectively. After treatment, the satellites are missing in the Q_x profiles, suggesting an effective switching from a stripe-domain to a monodomain state. The inset in (a) shows that annealing reintroduces the stripe-domain state in a thin film.

photochemical treatment. However, the XRD analyses reveal that the satellites move closer to the specular reflection after processing. As discussed elsewhere,¹⁸ the intensity of the diffuse reflections scales with the film thickness squared. The inset in Fig. 2 shows linear Q_x scans of the 8 and 14 unit cell thick samples, before (blue) and after (red) photochemical

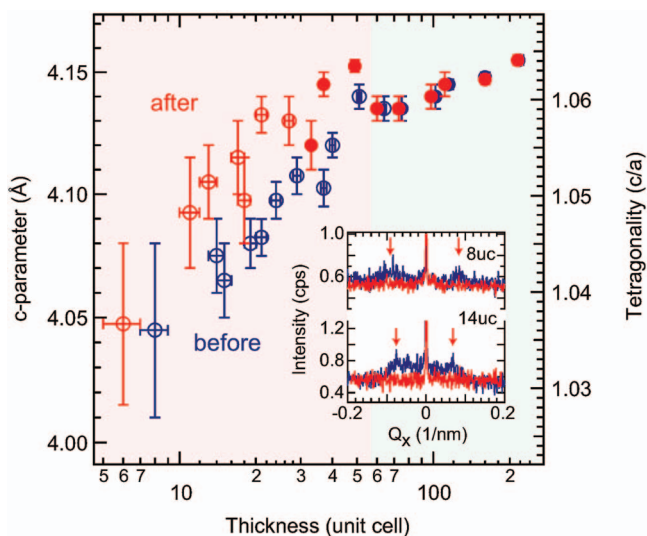


FIG. 2. (Color) Thickness dependence of the c -axis lattice constant and tetragonality of $\text{PbTiO}_3/\text{Nb}:\text{SrTiO}_3$ films before and after photochemical treatment. The photochemical treatment effectively increases the (001) lattice constant and hence the tetragonality, since the in-plane lattice constant is unchanged by this treatment. Open and solid circles refer to the tilted and non-tilted reciprocal lattice, respectively. The inset shows the linear Q_x profiles of 8 and 14 unit cell thick $\text{PbTiO}_3/\text{Nb}:\text{SrTiO}_3$ films, before (blue) and after (red) photochemical treatment.

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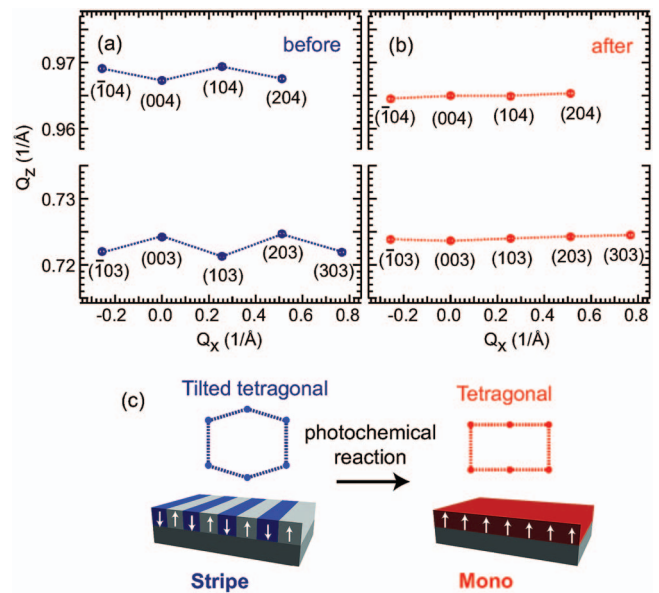


FIG. 3. (Color) (a) and (b) show the reciprocal space map of a 29 unit cell thick PbTiO_3 films before and after photochemical treatment, respectively. For the as-grown sample the Q_z value is modulated periodically with even and odd values of the Miller index h . This corresponds to a Q_x -modulated reciprocal space lattice. The (103) tilt angle is determined at 0.65° . (c) Schematic illustration of the photochemical switching linked with the change in crystalline symmetry.

treatment. We note that the satellite peaks are clearly missing after treatment for both samples.

When immersed in the AgNO_3 electrolyte, a galvanic potential is established across the thin ferroelectric layer. Relying on the theory developed by Scaife,¹⁹ the effective galvanic potential for $\text{Nb}:\text{SrTiO}_3$ in the AgNO_3 solution is estimated at approximately -1.3 V. If fully developed over the thin film, this potential corresponds to an effective field of 143 kV/cm and 4.1 MV/cm for the 227 and 8 unit cell thick samples, respectively. The local coercive field of a 100 nm sample was measured at 120 – 250 kV/cm. Hence, comparing the effective field induced by the photochemical treatment with the thickness dependent coercive field, as obtained

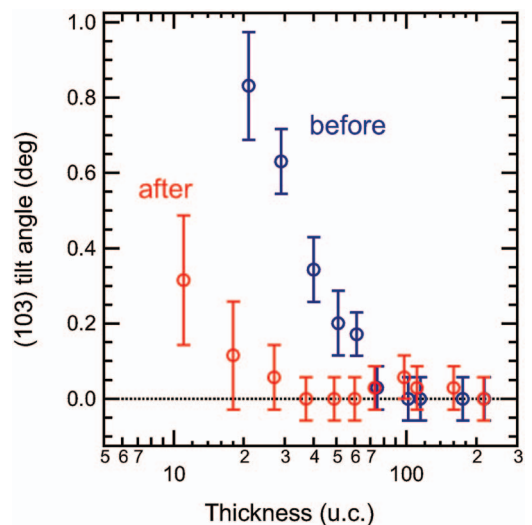


FIG. 4. (Color) Thickness dependence of the tilt angle between the (103) and (003) reflections, before and after photochemical treatment. After the photochemical treatment, the tilt angle is suppressed, although a small tilt distortion is still observed for the thinnest samples.

from Kay–Dunn scaling,²⁰ we find that for PbTiO₃ films thinner than 28–350 unit cells the chemically imposed field exceeds the coercive field. This is in good agreement with the measured data, where films thinner than 50 unit cells are effectively switched from a stripe-domain state to a monodomain state. We note that switching only takes place if samples are immersed in the AgNO₃ solution and illuminated, resulting in the photodeposition of Ag-rich species. Fong *et al.*⁸ demonstrated that ionic adsorbents may help stabilize a polar monodomain ground state in ultrathin films. Accordingly, we attribute the formation of a monodomain state to screening of the depolarization field by possible ionic adsorbents and the photo deposited particles. Additional screening from photogenerated carriers diffusing to the film surface and the PbTiO₃/Nb:SrTiO₃ interface under influence of the internal electric field in the ferroelectric cannot be ruled out.

Pyroelectric measurements¹⁸ (not shown) also support effective switching, as the pyroelectric response increases for the monodomain state relative to that of the stripe domains. The pyroelectric data reveal that the monodomain state corresponds to a negatively polarized thin film with respect to the top surface, in accordance with the sign of the estimated galvanic potential.

For samples of PbTiO₃ grown on insulating SrTiO₃ substrates, no galvanic potential developed over the thin film, when immersed in the electrolyte. Two PbTiO₃/SrTiO₃ samples, 19 and 35 unit cells thick, displaying diffuse peaks in the Q_x XRD scans, were treated by the photochemical treatment described above. After treatment, no change in domain structure was found, consistent with no galvanic potential across the thin film.

Crystalline structure is important to the application of thin ferroelectric materials. The crystal symmetry can affect piezoelectric and other functional properties of the ferroelectric. High resolution Q_z profiles of the (−103), (003), (103), (203), (303), (−104), (004), (104), and (204) reflections reveal that the normalized Q_z values for as-grown films vary. As shown in Fig. 3(a) for a 29 unit cell thick sample, the Q_z 's exhibit a periodic modulation with even and odd values of the Miller index h , i.e., a Q_x -modulated reciprocal lattice. The (103) tilt angle is determined at 0.65°. A corresponding (Q_x - Q_y) modulation in Q_z was observed for the (113), (223), and (114) reflections. In Fig. 3(b), Q_z is plotted as a function of Q_x after switching to a monodomain state by photochemical processing. It appears that switching from a stripe-domain state to a monodomain state is associated with a crystalline transition to the uniform tetragonal structure normally observed for bulk PbTiO₃, as illustrated in Fig. 3(c).

Figure 4 shows the thickness dependence of the (103) tilt angle. After photochemical treatment, the tilt angle is reduced, and samples between 30 and 60 unit cells thick become tetragonal, whereas the thinnest samples still display a small tilt distortion. Comparing this data with film thickness and tetragonality dependences of the characteristic stripe width,¹⁸ it is found that the tilt angle increases with decreasing stripe width. This tilt-modulated stripe state is only observed in thin samples where the tetragonality is less than that of bulk PbTiO₃.

It has been previously reported that the tetragonality is a good experimental measure of the polarization in ferroelectric thin films, with $P \propto (c/a - 1)^{1/2}$,¹⁰ suggesting that the tilt-modulated stripe state implies a weaker ferroelectric ground

state compared with the purely tetragonal monodomain state. Although the effective film thickness, as determined from finite size effects, decreases upon photochemical treatment, we obtain a larger c -axis lattice constant in the tetragonal phase, even in the regime where the tetragonality depends strongly on film thickness.^{9,10} The (001) lattice parameter decreases upon annealing, and the tilt-modulated tetragonal structure reappears. Prior to photochemical treatment, the slope in the thickness dependence of the (001) lattice constant is $-0.002 \text{ \AA}/\text{unit cell}$, increasing to $-0.004 \text{ \AA}/\text{unit cell}$ after such treatment, assuming linear fits to the data. Although the ferroelectricity is enhanced upon this photochemical treatment and the thickness defining the onset of an abrupt decrease in tetragonality is reduced compared to the stripe state, the (001) lattice parameter decreases rapidly with the film thickness once the reduction in polarization commences. This could be due to the larger depolarization field in the monodomain state.

In conclusion, it is possible to switch from a ferroelectric stripe-domain ground state to a monodomain state by photochemical treatment. This switching is limited to a transition in local crystal symmetry. The observation of a change in tetragonality between the monodomain state and the stripe-domain state provides evidence that ultrathin films in the stripe-domain state display a weakened ferroelectricity compared to that of monodomain films.

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¹C. H. Ahn, K. M. Rabe, and J.-M. Triscone, *Science* **23**, 488 (2004).

²R. Waser, U. Böttger, and S. Tiedke, *Polar Oxides: Properties, Characterization, and Imaging* (WILEY-VCH, Weinheim, 2005).

³N. Setter, D. Damjanovic, L. Eng, G. Fox, S. Gevorgian, S. Hong, A. Kingon, H. Kohlstedt, N. Y. Park, G. B. Stephenson, I. Stolitchnov, A. K. TagansteV, D. V. Taylor, T. Yamada, and S. Streiffer, *J. Appl. Phys.* **100**, 051606 (2006).

⁴S. K. Streiffer, J. A. Eastman, D. D. Fong, C. Thompson, A. Munkholm, M. V. R. Murty, O. Auciello, G. R. Bai, and G. B. Stephenson, *Phys. Rev. Lett.* **89**, 067601 (2002).

⁵D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, *Science* **304**, 1650 (2004).

⁶G. Catalan, A. Janssens, G. Rispens, S. Csiszar, O. Seeck, G. Rijinders, D. H. A. Blank and B. Noheda, *Phys. Rev. Lett.* **96**, 127602 (2006).

⁷C. Lichtensteiger, M. Dawber, N. Stucki, J.-M. Triscone, J. Hoffman, J.-B. Yau, C. H. Ahn, L. Despont, and P. Aebi, *Appl. Phys. Lett.* **90**, 052907 (2007).

⁸D. D. Fong, A. M. Kolpak, J. A. Eastman, S. K. Streiffer, P. H. Fuoss, G. B. Stephenson, C. Thompson, D. M. Kim, K. J. Choi, C. B. Eom, I. Grinberg, and A. M. Rappe, *Phys. Rev. Lett.* **96**, 127601 (2006).

⁹Ø. Dahl, J. K. Grepstad, and T. Tybell (unpublished).

¹⁰C. Lichtensteiger, J.-M. Triscone, J. Junquera, and P. Ghosez, *Phys. Rev. Lett.* **94**, 047603 (2005).

¹¹A. Sawada and R. Abe, *Jpn. J. Appl. Phys.* **5**, 401 (1966).

¹²J. L. Giocondi and G. S. Rohrer, *Chem. Mater.* **13**, 241 (2001).

¹³S. V. Kalinin, D. A. Bonnell, T. Alvarez, X. Lei, Z. Hu, J. H. Ferris, Q. Zhang, and S. Dunn, *Nano Lett.* **2**, 589 (2002).

¹⁴T. Abe, T. Ohsawa, M. Katayama, H. Koinuma, and Y. Matsumoto, *Appl. Phys. Lett.* **91**, 061928 (2007).

¹⁵K. Ohara, T. Ohsawa, H. Koinuma, and Y. Matsumoto, *Jpn. J. Appl. Phys., Part 2* **45**, L339 (2006).

¹⁶P. M. Jones and S. Dunn, *Nanotechnology* **18**, 185702 (2007).

¹⁷By changing the duration of the photochemical treatment the thickness of the surface reaction layer is altered, increasing with the treatment time.

¹⁸R. Takahashi, Ø. Dahl, E. Eberg, J. K. Grepstad, and T. Tybell (unpublished).

¹⁹D. E. Scaife, *Sol. Energy* **25**, 41 (1980).

²⁰H. F. Kay and J. W. Dunn, *Philos. Mag.* **7**, 2027 (1962).