

## Domain ordering of strained 5 ML SrTiO<sub>3</sub> films on Si(001)

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(Received 16 February 2007; accepted 7 May 2007; published online 30 May 2007)

High resolution x-ray diffraction data indicate ordered square shaped coherent domains,  $\sim 1200$  Å in length, coexisting with longer,  $\sim 9500$  Å correlated regions in highly strained 5 ML SrTiO<sub>3</sub> films grown on Si(001). These long range film structures are due to the Si substrate terraces defined by the surface step morphology. The silicon surface “step pattern” is comprised of an “intrinsic” terrace length from strain relaxation and a longer “extrinsic” interstep distance due to the surface miscut.  
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The commensurate growth of high dielectric constant crystalline oxide films on semiconductor substrates may change the scaling limits for very large scale integration transistor architecture due to reduced “leakage” currents through the insulator region.<sup>1</sup> The prototypical system continues to be SrTiO<sub>3</sub> on Si(001). The ordered growth of this structure was reported by Mckee *et al.* in 1998.<sup>2</sup> Suppression of interfacial amorphous SiO<sub>x</sub> during the film growth is tantamount to creating an ordered interface. The SrTiO<sub>3</sub> (STO)–Si(001) samples studied were grown using kinetically controlled sequential deposition, whereby the film growth is achieved with the suppression of amorphous interfacial SiO<sub>x</sub> by controlling the substrate temperature and oxygen partial pressure as each layer of SrO and TiO is separately deposited.<sup>3</sup> These films having a high degree of commensuration with the Si substrate are under significant compressive strain.<sup>4</sup> How the nature of the film order is maintained over relatively long length scales will have an impact on the electrical characteristics of any subsequent device.

The experiment was performed at the 6-ID-B, Midwestern Universities Collaborative Access Team, medium energy beamline at the Advanced Photon Source (APS). Incident energy photons of 9.8 KeV were used to perform grazing incident diffraction and specular reflectivity using a six-circle diffractometer. A  $200 \times 200 \mu\text{m}^2$  beam spot size was used along with matching detector slit settings for reflectivity measurements. For high resolution sample rocking curves, a postsample Si(111) analyzer crystal was employed with open detector slits. The experiment was performed *ex situ* at room temperature. The 5 ML samples are highly strained ( $-1.66\%$ ) with a high degree of lattice matching between the STO films and the Si(001) substrate.<sup>4</sup> Full details of the growth process are presented elsewhere.<sup>3</sup> The films are rotated  $45^\circ$  with respect to the Si(001) substrate,  $[001]_{\text{Si}} \parallel [001]_{\text{STO}} : [100]_{\text{Si}} \parallel [110]_{\text{STO}}$ . Photoelectron spectroscopy

copy indicated no evidence of amorphous SiO<sub>x</sub> at the Si 5 ML STO interface but does show both interfacial metal-silicon (Sr–Si) and O–Si bonding indicating the initial SrO layer.

Figure 1 illustrates low  $Q$  reflectivity measurements for both the strained 5 ML film and a semirelaxed 8 ML film fit using the Parratt method with surface and interface distributions (Sigma, rms roughness).<sup>5</sup> The STO film roughness is twice that for the highly strained 5 ML film than for the semirelaxed 8 ML film, measuring 8 and 4 Å, respectively (with a  $\sim 4$  Å STO unit cell). Scanning tunneling microscopy studies of an earlier 5 ML STO film showed both single and double unit cells with 4 and 8 Å steps, along the  $[110]_{\text{Si}}$  direction.<sup>3</sup> Compressive strain in this system promotes three-dimensional film growth. With strain relief, the film growth is smoother.

Strong in-plane satellite features are identified in rocking curves of the STO(002) Bragg reflections, shown in Fig. 2. With every  $45^\circ$  in-plane azimuthal rotation, the position of the satellite peaks oscillates in and out from the STO(002) reflection by a factor of  $\sqrt{2}$ . The fourfold symmetry with wings elongated along the  $H_{\text{Si}}$  and  $K_{\text{Si}}$  directions reflects the presence of coherent square domains in real space with the domain edges following the  $[100]_{\text{STO}}$  and  $[010]_{\text{STO}}$  directions. These coherent regions may be treated similarly to islands. The interregion “real space” distance is equivalent to  $2\pi/\Delta Q$ , with  $\Delta Q$ , in reciprocal units, measured between the satellite feature and center of the reflection. Along  $[100]_{\text{STO}}$ , the correlated distances measure  $\sim 1200$  and  $\sim 1700$  Å along the diagonal  $[110]_{\text{STO}}$ . Rocking curves of the STO(002) reflection from both films are also presented in Fig. 2. The satellite features of the 8 ML system measure a coherency length around  $\sim 1460$  Å, equivalent to the average of the square edge length of the 5 ML film domains (1200 Å) and the corresponding diagonal (1700 Å). The satellites pattern a uniform ring in the  $HK$  plane around the 8 ML STO(002) reflection. Thus, the aligned square domain order-

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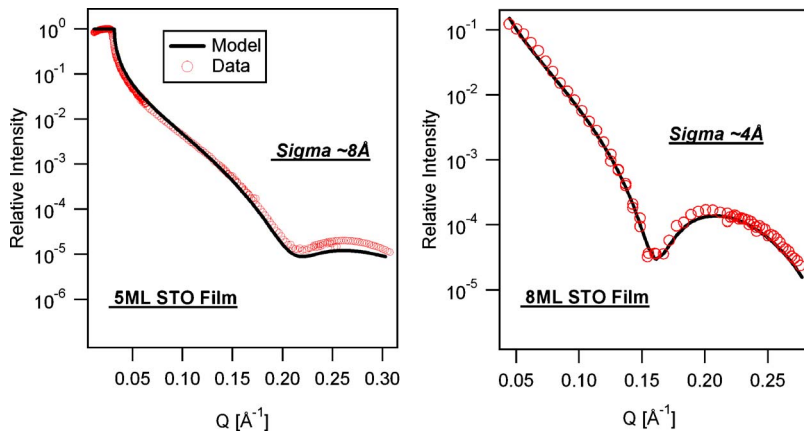


FIG. 1. (Color online) Low  $Q$  reflectivity scans compared with modeled fits for both the 5 and 8 ML STO films.

ing for the 5 ML film is not evident in the semirelaxed 8 ML film.

It is believed that the domain boundaries are initiated by Si surface steps. Hu *et al.*<sup>6</sup> presented transition electron microscopic images showing such a step and subsequent in-plane lattice discontinuity running vertically through the STO film. The same effect occurs in the highly strained 5 ML film. The 8 ML STO film has partially relaxed as compressive strain from the substrate subsides and the effect of the surface step morphology no longer retains the directional order of the steps through the film. As a result, the STO domains lose directional order.

Figure 3 presents a rocking curve through the bulk forbidden Si(110) reflection, overlapping the STO(100) reflection in grazing geometry. The broad satellite features are a result of the STO coherent regions discussed above. The strong sharp doublet at the center results from crossing the tails of the tilted crystal truncation rods from both the Si(111) and Si(11-1) substrate reflections, indicating the existence of an ordered series of step edges induced by a surface miscut. The net miscut runs close to the  $[100]_{\text{Si}}$  direction and is comprised of regular steps running along the orthogonal but equivalent  $[110]_{\text{Si}}$  and  $[-110]_{\text{Si}}$  directions. Peak separations indicate the extent of the macroscopic miscut induced tilt angle in the particular azimuthal direction. Assuming single Si step heights, one may estimate an average separation length between steps. The surface slope in the measured direction may be estimated by the following:  $\Delta Q = ml2\pi/d$ , where  $\Delta Q$  is the reciprocal measure from the center to either peak position,  $d$  is the Si cubic lattice parameter,  $l$  is the out-of-plane distance of the Bragg reflection position in re-

ciprocal lattice units, and  $m$  is the miscut (slope) in the measured direction.<sup>7</sup> Terrace lengths of  $\sim 6200$  and  $\sim 8000$  Å are measured for the  $[1-10]_{\text{Si}}$  and  $[110]_{\text{Si}}$  directions, respectively. As such, these lengths are far larger than the coherent domain size of the STO film, 1200 Å.

In order to explain the domains of 1200 Å in size and square in shape, we refer to previously performed energy calculations of the Si(100) surface, considering the effect of step related strain relaxation.<sup>8</sup> Calculations revealed an interstep distance of 1500 Å for single layer step heights for infinitely flat surfaces at 0 K. The step directions are calculated for both  $[110]_{\text{Si}}$  orthogonal directions. This interstep calculation is in reasonable agreement with the measured STO film domain size. Thus, the resulting Si surface contains both an “extrinsic” regular array of step edges, due to the surface miscut with a large correlated distance, and smaller “intrinsic” interstep distances with no net surface tilt.

The inset of Fig. 3 compares rocking curves across the Si(110) reflection for both the 5 and 8 ML films. The 8 ML film shows a single peak indicating a miscut in the  $[1-10]_{\text{Si}}$  orthogonal direction. The weak satellite intensities of the 5 ML film were first postulated to be second order substrate truncation rod effects. However, similar signatures evident in the 8 ML film with a single central peak suggest these to be related to long range order. This coexisting coherence length for the 5 ML film measures  $\sim 9500$  Å. The 8 ML film satellites identify a distribution of correlation lengths around 1.2  $\mu\text{m}$ , associated with the miscut interstep distances, even though the miscut is in the orthogonal direction. This longer range order exists simultaneously with the  $\sim 1460$  Å domain

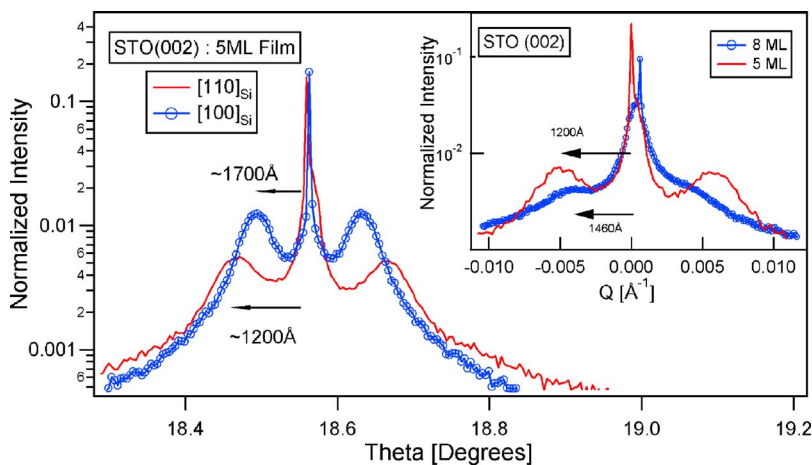


FIG. 2. (Color online) Rocking curves across the 5 ML STO(002) Bragg reflection, along the  $[100]_{\text{Si}}$  and  $[110]_{\text{Si}}$  directions. The inset compares the satellite features around the STO(002) reflection in the same reciprocal direction for both the 5 and 8 ML films.

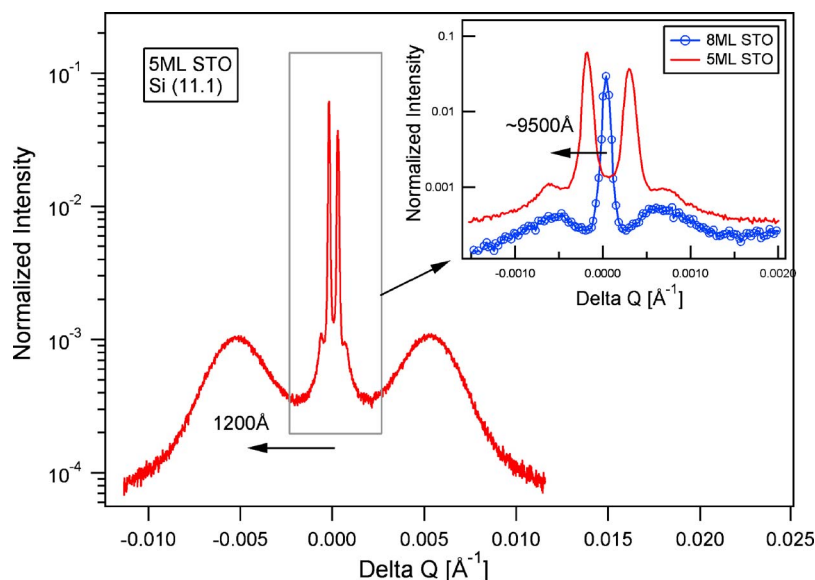


FIG. 3. (Color online) Rocking curve taken in grazing geometry of the bulk forbidden Si(110) reflection, overlapping the STO(010) reflection taken of the 5 ML film. The inset compares a narrow range of the same scan with that for the 8 ML film.

length and is not confined to the miscut direction. With reduced strain, there is no in-plane directional order of the domain boundaries through the film.

In conclusion, the domain structure of both fully and partially strained SrTiO<sub>3</sub> films grown on Si(001) was investigated. Low  $Q$  reflectivity data indicate reduced film roughness with strain relief. The strained 5 ML film measured a surface roughness of 8 Å and the semirelaxed 8 ML film a roughness of 4 Å. These measurements correspond to double and single STO unit cell step heights, suggesting that strain promotes three-dimensional growth. Square coherent domains are evident in the 5 ML film with a side length of 1200 Å. The regions align along the [110]<sub>Si</sub> Si step directions, while similar sized domains in the semirelaxed 8 ML film lose their directional alignment. The domain boundaries are essentially in-plane lattice discontinuities through the STO film caused by Si surface steps. The calculated intrinsic step separation of 1500 Å, resulting from strain relaxation, is postulated to explain the smaller STO domain size. The extrinsic miscut related step separations of ~9500 Å account for the larger correlated regions.

The MUCAT sector at the APS is supported by the U.S. DOE Office of Basic Energy Sciences, Office of Science

through Ames Laboratory under Contract No. W-7405-Eng-82. The use of the advanced photon source is supported by the U.S. DOE, Basic Energy Sciences, Office of Science under Contract No. DE-AC02-06CH11357. One of the authors (P.R.) would like to thank Paul Micelli, Edward Conrad, and Douglas Robinson for their important contributions to this work.

<sup>1</sup>C. J. Först, C. R. Ashman, K. Schwarz, and P. E. Blochl, *Nature (London)* **427** (2004).

<sup>2</sup>R. A. McKee, F. J. Walker, and M. F. Chrisholm, *Phys. Rev. Lett.* **81**, 3014 (1998).

<sup>3</sup>H. Li, X. Hu, Y. Wei, Z. Yu, X. Zhang, R. Droopad, A. A. Demkov, J. Edwards, Jr., K. Moore, W. Ooms, J. Kulik, and P. Fejes, *J. Appl. Phys.* **93**, 4521 (2003).

<sup>4</sup>J. C. Woicik, H. Li, P. Zschack, E. Karapetrova, P. Ryan, C. R. Ashman, and C. S. Hellberg, *Phys. Rev. B* **73**, 024112 (2006).

<sup>5</sup>L. G. Parratt, *Phys. Rev.* **95**, 359 (1954).

<sup>6</sup>X. Hu, H. Li, Y. Liang, Y. Wei, Z. Yu, D. Marshall, J. Edwards, Jr., R. Droopad, X. Zhang, A. A. Demkov, and K. Moore, *Appl. Phys. Lett.* **82**, 203 (2003).

<sup>7</sup>G. Renaud, P. H. Fuoss, J. Bevk, and B. S. Freer, *Phys. Rev. B* **45**, 9192 (1992).

<sup>8</sup>O. L. Alerhand, A. Nihat Berker, J. D. Joannopoulos, and David Vanderbilt, *Phys. Rev. Lett.* **64**, 2406 (1990).