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Surface reconstructions in molecular beam epitaxy of SrTiO₃

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We show that reflection high-energy electron diffraction (RHEED) can be used as a highly sensitive tool to track surface and resulting film stoichiometry in adsorption-limited molecular beam epitaxy of (001) SrTiO₃ thin films. Even under growth conditions that yield films with a lattice parameter that is identical to that of stoichiometric bulk crystals within the detection limit of high-resolution x-ray diffraction (XRD), changes in surface reconstruction occur from (1 × 1) to (2 × 1) to c(4 × 4) as the equivalent beam pressure of the Ti metalorganic source is increased. These surface reconstructions are correlated with a shift from mixed SrO/TiO₂ termination to pure TiO₂ termination. The crossover to TiO₂ surface termination is also apparent in a phase shift in RHEED oscillations observed at the beginning of growth. Comparison with prior results for carrier mobilities of doped films shows that the best films are grown under conditions of a TiO₂-saturated surface [c(4 × 4) reconstruction] within the XRD growth window. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4901726]
at TTIP/Sr = 60.0, which was determined to be Ti-rich, all films lie within the XRD growth window. The patterns taken along the (100) and (110) azimuths are four-fold symmetric in all cases. The RHEED image taken for a film grown with TTIP/Sr = 37.5 indicates a (1×1) unreconstructed surface. The emergence of a 1/2-order reflection only along the (100) azimuths in the film grown with TTIP/Sr = 39.5 is indicative of mixed (1×2) and (2×1) reconstructed lattice domains. At TTIP/Sr = 45.0, the 1/2-order reflections along the (100) azimuth are more pronounced, and 1/4-order reflections are apparent along the (110) azimuth, consistent with a c(4×4) reconstruction. The c(4×4) reconstruction persists up to a TTIP/Sr ratio of 60.0 (Ti-rich conditions, see Fig. 2), though clearly defined chevrons along the (110) azimuths and dim 1/4-order reflections along (100) azimuths are also observed at TTIP/Sr = 60.0. Both features are very similar to what is observed for mixed (1×4) and (4×1) anatase TiO2 (001) domains grown epitaxially on SrTiO3 (001).23

Figure 2 shows a map of the growth conditions that result in different reconstructed surfaces at growth temperatures of 810°C and 850°C, respectively, as well as the XRD生长窗口at each temperature as determined from measured film lattice parameters. Figure 3 shows RHEED intensity oscillations obtained at the beginning of growth for samples grown at 850°C were either non-existent or decayed after no more than 6 oscillation periods, due to the transition from layer-by-layer to step-flow growth as a result of the higher growth temperature.14,15

We first discuss the observed surface reconstructions seen in Figs. 1 and 2 in terms of their stoichiometry. In particular, these reconstructions indicate a systematic change in

FIG. 1. RHEED recorded along the [100] and [110] azimuths after the growth of SrTiO3 films grown at different values of TTIP/Sr with a substrate temperature of 810°C.

FIG. 2. Out-of-plane lattice parameters of SrTiO3 films grown at 810°C and 850°C as a function of the TTIP/Sr ratio and the corresponding observed reconstructions at each growth condition. The dashed lines correspond to the bulk lattice parameter of cubic SrTiO3. The field labeled (2×1) refers to a multi-domain (2×1)/(1×2) surface.

FIG. 3. RHEED intensity oscillations measured along the [100] azimuth at the beginning of growth for SrTiO3 films grown at various TTIP/Sr with a substrate temperature of 810°C. Black arrows mark the approximate onset of each phase shift. The beginning of each growth involved compensation of a Sr source flux transient to maintain constant TTIP/Sr in the early stages of growth.
TiO$_2$ coverage of the growing surface. Previous scanning tunnel microscopy studies of bulk (001) SrTiO$_3$ surfaces have shown that a (1 × 1) reconstruction, observed here at the Sr-rich side of the growth window, are comprised of approximately equal fraction of SrO- and TiO$_2$-terminated sites.\textsuperscript{19,24} The onset of a multi-domain (2 × 1) and (2 × 1) surfaces at higher TTIP/Sr values corresponds to expanding regions of coherent TiO$_2$ coverage, with uniformly distributed SrO-terminated sites.\textsuperscript{24} Higher-order reconstructions, such as the c(4 × 4) observed here, or c(2 × 4) and c(2 × 6) observed by others, have been associated with purely TiO$_2$-terminated (001) SrTiO$_3$ surfaces.\textsuperscript{19,20,24} Thus, an increasing TTIP/Sr flux ratio during growth is closely tracked by the surface composition as exhibited by the different reconstructions. Most importantly, the boundary between the multi-domain (2 × 1) and the c(4 × 4) growth regimes marks the relative TTIP flux at which the growing surface is saturated with TiO$_2$. The shift of this boundary to higher TTIP/Sr at 850 °C compared to 810 °C is consistent with a higher desorption rate for TTIP at higher growth temperatures.\textsuperscript{15,25}

For growth conditions far outside the XRD growth window, the observed surface reconstructions are similar to those reported in previous studies of (001)SrTiO$_3$ surfaces. In the instance of substantial TiO$_2$ excess, either a weak (2 × 1) reconstruction (Fig. 2) or (1 × 1) surface (not shown) is typically observed, consistent with previous reports from both solid-source MBE\textsuperscript{16,17} and hybrid MBE growth of SrTiO$_3$ (001),\textsuperscript{14} and the diffraction pattern becomes increasingly diffuse, most likely due to amorphous excess TiO$_2$.\textsuperscript{26} In the SrO-excess regime, a c(2 × 2) is often observed, consistent with reports on SrO-rich surfaces.\textsuperscript{16,17} These features are thus useful for determining the surface stoichiometry when growing outside the growth window, but such films are likely of limited practical use.

The changing character of the surface reconstruction with increasing TTIP flux suggest a substantial variation in the surface stoichiometry within the XRD growth window that likely reflects the growing film’s stoichiometry. From Fig. 2, one concludes that for growth conditions within the growth window, the number of defects from non-stoichiometry incorporated into the bulk of the film is low enough such that the film and substrate lattice parameters are equal, despite these variations in surface stoichiometry. This conclusion is, however, dependent on the sensitivity of the lattice parameter to small deviations from stoichiometry, which is further complicated by substantial XRD peak overlap in homoepitaxy (i.e., no clearly defined separate film peak). In the (1 × 1) growth regime, the comparable fractions of SrO and TiO$_2$ surface terminations may result in a sufficiently low incorporation of defects to maintain film/substrate XRD peak overlap and thus fall within the XRD growth window. However, as a substantial portion of the surface is SrO-terminated and SrO has a low vapor pressure at typical growth temperatures, some defects may still be incorporated from SrO accumulation over time. Saturating the surface with volatile TTIP, which results in TiO$_2$ terminated surface reconstructions, precludes accumulation of defects by bringing the growth into a truly adsorption-controlled regime. The TiO$_2$ terminated surface is exposed to nonvolatile SrO, while excess TTIP desorbs to prevent excess TiO$_2$ accumulation. The higher-index c(4 × 4) reconstruction is a clear signature of this TiO$_2$ saturation. Although it is still present in excess TiO$_2$ conditions, outside the XRD growth window, the appearance of 1/2-order reflections along (100), combined with the dimming of 1/4-order reflections and the appearance of chevrons along (110), for TTIP/Sr = 60.0 (Fig. 1) suggests faceted anatase-like TiO$_2$ domains\textsuperscript{23} coexisting with c(4 × 4) TiO$_2$-saturated domains. These features can be used as a signature of Ti-excess conditions. The growth conditions that give optimal stoichiometry can be identified by the overlap of the XRD growth window with the c(4 × 4) regime. La-doped SrTiO$_3$ films with the highest recorded electron mobilities for unstrained films, exceeding 50 000 cm$^2$V$^{-1}$s$^{-1}$ were grown in this regime.\textsuperscript{27}

The boundary between growth conditions yielding mixed termination and TiO$_2$ saturation is also apparent in the RHEED intensity oscillations at the beginning of growth, shown in Fig. 3. For TTIP/Sr ≤ 42.5, within the growth window, an abrupt phase shift in the intensity oscillations after ~5 monolayers from the specular 00 reflection puts the 00 reflected intensities almost π rad out-of-phase with the 10 reflected intensities. For TTIP/Sr > 42.5, the 00 reflected intensities remain 0 to π/2 rad out-of-phase with the 10 reflected intensities without any obvious, abrupt phase shift, even for TTIP/Sr values slightly outside the XRD window (e.g., TTIP/Sr = 55.4). The phase shift is only observed for the 00 reflected intensities, which do not require surface features to have lateral symmetry to produce diffraction features (e.g., defects, steps).\textsuperscript{28} Thus it is likely that this phase shift is associated with the growth dynamics involving the boundaries between SrO- and TiO$_2$-terminated regions during layer-by-layer growth below the TTIP/Sr ratio corresponding to full TiO$_2$ surface coverage. Determining the exact origin of this phase shift would require more detailed investigation of the dynamics of SrTiO$_3$ growth by hybrid MBE, but within the scope of this study, this empirical observation serves as another indicator of the onset of TiO$_2$ saturation.

In summary, we have shown that MBE in an adsorption-limited regime allows for detailed monitoring changes in surface reconstructions even within the XRD growth window, where film lattice parameters indicate stoichiometric films. Both surface reconstructions and RHEED intensity oscillations provide insight into the extent of TiO$_2$ coverage on the growing surface. This enables precise control of the surface and resulting film stoichiometry, with a greater sensitivity than XRD alone, and thus enables the growth of highly perfect, stoichiometric SrTiO$_3$.

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\textsuperscript{1} J. Appel, \textit{Phys. Rev.} \textbf{180}, 508 (1969).
\textsuperscript{2} X. Lin, Z. W. Zhu, B. Fauque, and K. Behnia, \textit{Phys. Rev. X} \textbf{3}, 021002 (2013).
\textsuperscript{3} J. A. Sulpizio, S. Ilani, P. Irvin, and J. Levy, \textit{Ann. Rev. Mater. Res.} \textbf{44}, 117 (2014).
\textsuperscript{4} S. Stemmer and S. J. Allen, \textit{Ann. Rev. Mater. Res.} \textbf{44}, 151 (2014).
5N. Nakagawa, H. Y. Hwang, and D. A. Muller, Nat. Mater. 5, 204 (2006).
6N. Erdman, K. R. Poeppelmeier, M. Asta, O. Warschkow, D. E. Ellis, and L. D. Marks, Nature 419, 55 (2002).
7G. Koster, G. Rijnders, D. H. A. Blank, and H. Rogalla, Phys. C 339, 215 (2000).
8J. H. Neave and B. A. Joyce, J. Cryst. Growth 44, 387 (1978).
9C. Deparis and J. Massies, J. Cryst. Growth 108, 157 (1991).
10F. Briones, D. Golmayo, L. Gonzalez, and J. L. Demiguel, Jpn. J. Appl. Phys., Part 2 24, L478 (1985).
11J. H. Haeni, C. D. Theis, and D. G. Schlom, J. Electroceram. 4, 385 (2000).
12C. M. Brooks, L. F. Kourkoutis, T. Heeg, J. Schubert, D. A. Muller, and D. G. Schlom, Appl. Phys. Lett. 94, 162905 (2009).
13T. Ohnishi, K. Shibuya, T. Yamamoto, and M. Lippmaa, J. Appl. Phys. 103, 103703 (2008).
14B. Jalan, R. Engel-Herbert, N. J. Wright, and S. Stemmer, J. Vac. Sci. Technol. A 27, 461 (2009).
15B. Jalan, P. Moetakef, and S. Stemmer, Appl. Phys. Lett. 95, 032906 (2009).
16P. Fisher, H. Du, M. Skowronski, P. A. Salvador, O. Maksimov, and X. Weng, J. Appl. Phys. 103, 013519 (2008).
17Z. Yu, Y. Liang, C. Overgaard, X. Hu, J. Curless, H. Li, Y. Wei, B. Craigo, D. Jordan, R. Droopad et al., Thin Solid Films 462, 51 (2004).
18J. A. Enterkin, A. K. Subramanian, B. C. Russell, M. R. Castell, K. R. Poeppelmeier, and L. D. Marks, Nat. Mater. 9, 245 (2010).
19M. R. Castell, Surf. Sci. 505, 1 (2002).
20N. Erdman, O. Warschkow, M. Asta, K. R. Poeppelmeier, D. E. Ellis, and L. D. Marks, J. Am. Chem. Soc. 125, 10050 (2003).
21S. Gerhold, Z. Wang, M. Schmid, and U. Diebold, Surf. Sci. 621, L1 (2014).
22R. Shimizu, K. Iwaya, T. Ohsawa, S. Shiraki, T. Hasegawa, T. Hashizume, and T. Hitosugi, ACS Nano 5, 7967 (2011).
23Y. Du, D. J. Kim, T. C. Kaspar, S. E. Chamberlin, I. Lyubinetsky, and S. A. Chambers, Surf. Sci. 606, 1443 (2012).
24Q. D. Jiang and J. Zegenhagen, Surf. Sci. 425, 343 (1999).
25C. J. Taylor, D. C. Gilmer, D. G. Colombo, G. D. Wilk, S. A. Campbell, J. Roberts, and W. L. Gladfelter, J. Am. Chem. Soc. 121, 5220 (1999).
26S. Stemmer, S. K. Streiffer, N. D. Browning, and A. I. Kingon, Appl. Phys. Lett. 74, 2432 (1999).
27T. A. Cain, A. P. Kajdos, and S. Stemmer, Appl. Phys. Lett. 102, 182101 (2013).
28W. Braun and K. Ploog, Appl. Phys. A 60, 441 (1995).