

Molecular beam epitaxy of SrTiO₃ with a growth window

Bharat Jalan^{a)}, Pouya Moetakef and Susanne Stemmer^{b)}

Materials Department, University of California, Santa Barbara, CA 93106-5050, U.S.A.

Abstract

Many complex oxides with only nonvolatile constituents do not have a wide growth window in conventional molecular beam epitaxy (MBE) approaches, which makes it difficult to obtain stoichiometric films. Here it is shown that a growth window in which the stoichiometry is self-regulating can be achieved for SrTiO₃ films by using a hybrid MBE approach that uses a volatile metal-organic source for Ti, titanium tetra isopropoxide (TTIP). The growth window widens and shifts to higher TTIP/Sr flux ratios with increasing temperature, showing that it is related to the desorption of the volatile TTIP. We demonstrate stoichiometric, highly perfect, insulating SrTiO₃ films, which can easily be adapted for other complex oxides that previously were believed to have no wide MBE growth window.

a) Electronic address: bjalan@mrl.ucsb.edu

b) Electronic address: stemmer@mrl.ucsb.edu

The atomic level control of layer thicknesses, structural perfection, low defect densities and high purity afforded by molecular beam epitaxy (MBE) promises highly perfect oxide heterostructures. The structural quality of oxide films grown by MBE now matches that of epitaxial semiconductors [1]. Stoichiometry control, however, remains a major challenge [2]. A number of approaches have been developed to avoid oxygen deficiency, including, for example, the use of reactive oxidants such as ozone [3] or sources that supply transition metals already bonded to oxygen [4]. However, unlike III-V semiconductors, many important complex oxides do not have a volatile constituent, such as As, which results in the absence of a wide “MBE growth window” [5] that would allow for a range of fluxes in which only the stoichiometric phase grows. For example for growth of SrTiO₃, if only stoichiometric SrTiO₃ is to condense within a range of metal fluxes, growth conditions must allow for excess Sr or SrO to desorb; Ti has a sticking coefficient of nearly one if it is evaporated from conventional elemental metal sources [6], such as Knudsen cells, electron beam evaporators or sublimation sources. As can be seen from Fig. 1, only a relatively narrow growth window exists for stoichiometric SrTiO₃; in contrast, the growth window for GaAs spans many orders of magnitude of As gas pressure [6]. Even more importantly, the window exists only at very high growth temperatures and unpractical low SrO gas pressures. MBE growth experiments confirm this [2]; for example, it has been shown that SrO desorption is negligible at growth temperatures up to 750 °C [7]. Therefore, conventional MBE of SrTiO₃ and related materials, such as many high-temperature superconductors or ferroelectrics, requires precise flux control and stability to obtain a stoichiometric oxide. Flux control is possible on the order of 0.1 – 1% [8,9], which corresponds to defect concentrations of 10²⁰ cm⁻³ or higher. This sharply contrasts with high-quality

semiconductor films, where defect concentrations are in the ppm range or better (corresponding to concentrations of less than 10^{17} cm^{-3}).

An alternative to the conventional solid metal sources is the use of metal organic sources; in III-V MBE this technique has become known as chemical beam epitaxy. We have recently shown that by using a metal-organic source for Ti, insulating SrTiO_3 films can be grown by MBE with excellent structural quality [10]. The metal organic source, titanium tetra isopropoxide [$\text{Ti}(\text{OC}_3\text{H}_7)_4$ or TTIP], has several advantages over a solid Ti source. These include orders of magnitude of higher vapor pressure [11,12], allowing for high growth rates, ease of flux control and supplying additional oxygen that already comes bonded to Ti, thereby eliminating oxygen deficiency and allowing for insulating films at typical MBE growth pressures. For example, phase-pure TiO_2 films can be grown even in the absence of an oxygen source [4]. At high temperatures, growth from this source becomes desorption-limited [4,13,14]. In this Letter, we show that a major consequence of desorption is that it opens an MBE growth window within which stoichiometric SrTiO_3 films can be grown within a range of practical substrate temperatures and metal fluxes.

Epitaxial SrTiO_3 films were grown on (001) SrTiO_3 and $(\text{La}_{0.3}\text{Sr}_{0.7})(\text{Al}_{0.65}\text{Ta}_{0.35})\text{O}_3$ (LSAT) single crystals, respectively, using an oxide MBE system (GEN 930, Veeco Instruments) with a base pressure of 10^{-10} torr. The substrates were ultrasonically cleaned in acetone, isopropanol and de-ionized water before and after deposition of a Ta backing layer, which served to improve the heat transfer between heater and the substrate. Each substrate was baked at 200°C in the entry/exit chamber for 1.5 hrs and cleaned in the growth chamber at the growth temperature for 20 min using an oxygen rf plasma source operated at 250 W. Films were grown with two different oxygen beam equivalent pressures (BEPs) of 5.0×10^{-6} and 8.0×10^{-6} torr,

respectively. Titanium tetra isopropoxide (99.999%, Sigma-Aldrich, USA) was supplied by thermal evaporation from a “bubbler” that was connected through a gas inlet system to the growth chamber. No carrier gas was used. Strontium was supplied from a low temperature effusion cell. The Sr flux showed an initial transient (2 - 3 minutes) after opening the shutter, because of cell cooling [15]. This transient was compensated by controlling the linear leak valve that supplied the TTIP to keep the TTIP/Sr flux ratio at the desired value. A series of samples was grown at different TTIP/Sr BEP ratios by varying the TTIP BEP between 2.49×10^{-6} torr and 2.70×10^{-6} torr and the Sr BEP between 4.54×10^{-8} torr and 7.24×10^{-8} torr. The substrate temperature was kept at 700 °C, 725 °C or 800 °C, respectively (measured using an Ircon Modline 3 pyrometer). The oxygen plasma was left on during cooling until the sample reached a temperature of 260 °C.

Reflection high-energy electron diffraction (RHEED) was used to monitor the growth mode and surface morphology in-situ. All films grew initially in a layer-by-layer growth mode that transitioned to step-flow mode [10,16]. RHEED intensity oscillations were also used to estimate the film thickness, which were also calibrated using x-ray reflectivity measurements of SrTiO₃ on LSAT. Films were characterized ex-situ using on-axis high-resolution x-ray diffraction (XRD) 2θ - ω and ω -scans with a Philips X'PERT Panalytical MRD Pro Thin-Film diffractometer equipped with a duMond-Hart-Partels Ge(440) incident beam monochromator. All films were epitaxial with a cube-on-cube orientation relationship with the substrates and showed extremely narrow on-axis rocking curve widths (i.e. 34 arcsec on LSAT [16]) that were limited by those of the substrates. Secondary ion mass spectroscopy (SIMS) profiling using 6 kV Cs⁺ primary ions was used to measure carbon concentrations. For films grown at 800 °C, the carbon content was at or below the level in the substrate [16]. Atomic force microscopy (AFM)

showed near ideal surfaces with unit cell step heights [10,16]. All the films were insulating consistent with the absence of oxygen vacancies, which would cause n-type conductivity [17].

The lattice parameter of homoepitaxial SrTiO₃ films is a sensitive measure of cation stoichiometry. In particular, the lattice parameter of nonstoichiometric SrTiO₃ is larger than that of stoichiometric SrTiO₃ ($a = 3.905 \text{ \AA}$) independent of whether films are Sr or Ti-rich [10,18,19]. Thus lattice parameter measurements as a function of MBE growth parameters can be used to investigate if a growth window exists. For the stoichiometric films, x-ray diffraction showed perfect overlap between film and substrate reflections (see Fig. 2). Figure 3 shows the out-of-plane lattice parameter of the SrTiO₃ films as a function of cation flux ratio. For all three substrate temperatures a growth window is obtained for which stoichiometric SrTiO₃ grows, i.e. with a lattice parameter that is equivalent to that of the SrTiO₃ substrate, independent of the TTIP/Sr BEP ratio (see grey-shaded areas in Fig. 3). With increasing substrate temperature the growth window expanded and shifted towards higher TTIP/Sr BEP ratios. This shift demonstrates that the volatile Ti metal-organic source is the primary cause for the existence of the growth window and its expansion at higher temperatures: TTIP desorption increases with temperature [13,14], so higher TTIP/Sr flux ratios are required for a stoichiometric film. At the same time, easier desorption at higher temperature widens the window of flux ratios for which stoichiometric films are obtained.

To further investigate the range of growth parameters for which an MBE growth window exists, Fig. 4 shows the range of TTIP/Sr ratios for stoichiometric films as a function of substrate temperature for two different oxygen BEPs (5×10^{-6} and 8×10^{-6} torr). With decreasing oxygen BEP the growth window expands into what was the Ti-rich regime at higher oxygen BEP; furthermore the widening is more pronounced at higher temperatures. Within the growth

window, the growth rates were not strongly affected by the oxygen BEP, indicating that the films grew in a metal-limited regime, consistent with their insulating properties. Prior studies of TiO_2 growth using the same source have shown that the growth mode is influenced by the oxygen BEP [4,14]. Higher oxygen BEPs may assist in the break-down of the TTIP molecule, which would be consistent with a lowering of the desorption, or an increase in the sticking coefficient, and thus a narrowing of the growth window. Again, these results confirm that desorption of the metal-organic Ti source is the primary reason for existence of a growth window in hybrid MBE. Future studies should address if at higher temperatures SrO also begins to desorb, as predicted in Fig. 1.

In summary, we have demonstrated that a hybrid MBE approach, which uses a volatile metal-organic source to supply Ti, allows for SrTiO_3 MBE with self-regulating stoichiometry for practical growth parameters, not possible in conventional MBE from solid sources. The approach can easily be implemented for other perovskite titanates, such as ferroelectric BaTiO_3 , the rare-earth Mott titanates, or indeed any other complex oxide for which a volatile transition metal precursors exists. The combination of structural perfection, high purity and precise control of oxygen and cation stoichiometry afforded by the hybrid MBE approach sets the stage for revealing the intrinsic physics of this exciting class of materials and their heterostructures.

The authors thank Mr. Nick Wright for some of the AFM studies and Dr. Tom Mates for the SIMS analysis. This research was supported by the National Science Foundation through the UCSB MRL (Award No. DMR 05-20415) and by DOE (DE-FG02-06ER45994). Acquisition of the oxide MBE system was made possible through a NSF MRI grant (NSF DMR-0619698).

References

- [1] M. D. Biegalski, D. D. Fong, J. A. Eastman, P. H. Fuoss, S. K. Streiffer, T. Heeg, J. Schubert, W. Tian, C. T. Nelson, X. Q. Pan, M. E. Hawley, M. Bernhagen, P. Reiche, R. Uecker, S. Trolier-McKinstry, and D. G. Schlom, *J. Appl. Phys.* **104**, 114109 (2008).
- [2] D. G. Schlom, J. H. Haeni, J. Lettieri, C. D. Theis, W. Tian, J. C. Jiang, and X. Q. Pan, *Mater. Sci. Eng. B* **87**, 282 (2001).
- [3] D. D. Berkley, B. R. Johnson, N. Anand, K. M. Beauchamp, L. E. Conroy, A. M. Goldman, J. Maps, K. Mauersberger, M. L. Mecartney, J. Morton, M. Tuominen, and Y. J. Zhang, *Appl. Phys. Lett.* **53**, 1973 (1988).
- [4] B. Jalan, R. Engel-Herbert, J. Cagnon, and S. Stemmer, *J. Vac. Sci. Technol. A* **27**, 230 (2009).
- [5] J. Y. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic Press, Boston, 1993).
- [6] C. D. Theis, J. Yeh, D. G. Schlom, M. E. Hawley, and G. W. Brown, *Thin Solid Films* **325**, 107 (1998).
- [7] S. Migita, Y. Kasai, and S. Sakai, *J. Low Temp. Phys.* **105**, 1337 (1996).
- [8] M. E. Klausmeier-Brown, J. N. Eckstein, I. Bozovic, and G. F. Virshup, *Appl. Phys. Lett.* **60**, 657 (1992).
- [9] J. H. Haeni, C. D. Theis, and D. G. Schlom, *J. Electroceram.* **4**, 385 (2000).
- [10] B. Jalan, R. Engel-Herbert, N. J. Wright, and S. Stemmer, *J. Vac. Sci. Technol. A* **27**, 461 (2009).
- [11] K. L. Siefering and G. L. Griffin, *J. Electrochem. Soc.* **137**, 1206 (1990).
- [12] P. D. Desai, *Int. J. Thermophys.* **8**, 781 (1987).

- [13] C. J. Taylor, D. C. Gilmer, D. G. Colombo, G. D. Wilk, S. A. Campbell, J. Roberts, and W. L. Gladfelter, *J. Amer. Chem. Soc.* **121**, 5220 (1999).
- [14] K.-H. Ahn, Y.-B. Park, and D.-W. Park, *Surface and Coatings Technology* **171**, 198 (2002).
- [15] F. G. Celii, Y. C. Kao, E. A. Beam, W. M. Duncan, and T. S. Moise, *J. Vac. Sci. Technol. B* **11**, 1018 (1993).
- [16] See EPAPS supplementary material at [URL will be inserted by AIP] for further information about the structural quality of the films, growth modes and carbon impurity concentration.
- [17] J. F. Schooley, W. R. Hosler, and M. L. Cohen, *Phys. Rev. Lett.* **12**, 474 (1964).
- [18] T. Ohnishi, K. Shibuya, T. Yamamoto, and M. Lippmaa, *J. Appl. Phys.* **103**, 103703 (2008).
- [19] C. M. Brooks, L. F. Kourkoutis, T. Heeg, J. Schubert, D. A. Muller, and D. G. Schlom, *Appl. Phys. Lett.* **94**, 162905 (2009).
- [20] R. H. Lamoreaux, D. L. Hildenbrand, and L. Brewer, *J. Phys. Chem. Ref. Data* **16**, 419 (1987).
- [21] I. Barin, *Thermochemical Data of Pure Substances*, Vol. I and II, 3rd ed. (VCH, Weinheim, 1995).

Figure Captions

Figure 1 (color online):

Estimated MBE growth window for SrTiO₃ in conventional MBE using solid metal sources. The diagram was calculated using thermodynamic data from refs. [20] and [21], following the same approach as in ref. [6]. A sticking coefficient of one is assumed for Ti, consistent with experimental data in the literature [6]. At the oxygen pressures used in MBE, Sr is assumed to oxidize immediately to SrO, consistent with experiments [7] and thermodynamic data [16]. Shown are the equilibrium lines for two reactions SrO_(s) ↔ SrO_(g) (red dashed lines) and SrO_(g) + TiO_{2(s)} ↔ SrTiO₃ (blue solid lines). The two lines for each reaction indicate the uncertainty in the thermodynamic data used for the estimates. Above the lower solid line, SrO_(g) condenses to react with TiO_{2(s)} to SrTiO₃ and below the dashed line any excess SrO_(s) will evaporate. Thus phase-pure stoichiometric SrTiO₃ films grow in the window (hatched area) between the lines.

Figure 2 (color online):

High-resolution 2θ-ω x-ray diffraction scans around the 002 reflections of homoepitaxial SrTiO₃ films and substrates. The arrows indicate the film peak. All films were grown at a substrate temperature of 800 °C with an oxygen BEP of 8×10⁻⁶ torr and at TTIP/Sr ratios of (a) 55.4 (b) 53.3 (c) 42.13 (d) 41 and (e) 39.5, respectively. The film thicknesses were between 120 and 170 nm. The scans are displayed in order of increasing nonstoichiometry away from the middle scan for the stoichiometric film shown in (c).

Figure 3 (color online):

Out-of-plane lattice parameter as a function of TTIP/Sr BEP ratio for epitaxial SrTiO₃ films grown on (001)SrTiO₃ at (a) 800 °C, (b) 725 °C and (c) 700 °C. All films were grown using an oxygen BEP of 8×10^{-6} torr. The darker grey-shaded region shows the growth window for stoichiometric films with a lattice parameter that is equivalent to that of the substrate at each temperature.

Figure 4 (color online):

Growth window for stoichiometric SrTiO₃ films for two different oxygen BEPs of 5×10^{-6} (black circles) and 8×10^{-6} torr (green triangles). Shown is the range of TTIP/Sr ratios that results in stoichiometric films as a function of temperature and oxygen BEP. The lines are shown a guide to the eye.







