Time-resolved study of $SrTiO_3$ homoepitaxial pulsed-laser deposition using surface x-ray diffraction

G. Eres,[a] J. Z. Tischler, M. Yoon,[b] B. C. Larson, C. M. Rouleau, and D. H. Lowndes
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

P. Zschack
Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 13 December 2001; accepted for publication 8 March 2002)

Homoepitaxy of $SrTiO_3$ by pulsed-laser deposition has been studied using *in situ* time-resolved surface x-ray diffraction in the temperature range of 310 °C to 780 °C. Using a two-detector configuration, surface x-ray diffraction intensities were monitored simultaneously at the $(0\ 0\ \frac{1}{2})$ specular and the $(0\ 1\ \frac{1}{2})$ off-specular truncation rod positions. Abrupt intensity changes in both the specular and off-specular rods after laser pulses indicated prompt crystallization into $SrTiO_3$ layers followed by slower intra- and interlayer surface rearrangements on time scales of seconds. Specular rod intensity oscillations indicated layer-by-layer growth, while off-specular rod intensity measurements suggested the presence of transient in-plane lattice distortions for depositions above 600 °C. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1477279]

Pulsed-laser deposition (PLD) is a method used widely for thin-film deposition of complex and nonequilibrium materials.[1] In PLD, an intense laser pulse is used to vaporize a solid target and create a plume of dense plasma. The plume has a sharp spatial profile, exists for a few microseconds, and consists of rapidly expanding ionic and neutral species. The fact that film deposition occurs from a brief, high intensity pulse of vaporized solid differentiates PLD from thermal equilibrium growth techniques such as molecular-beam epitaxy and chemical vapor deposition.

Although a great deal is known about the time structure of ablation plumes used in PLD film growth,[1] the details of the aggregation, crystallization, and surface kinetics involved in the epitaxial growth process are less well understood. Reflection high-energy electron diffraction (RHEED) has been used for time-resolved monitoring PLD of complex oxides[2,3] and interval deposition techniques have been investigated to control the growth mode.[4] So far, quantitative analysis of RHEED-oscillation transients have been made under the simplifying assumption of a single-exponential process.[3,4]

In this letter, we describe the use of surface x-ray diffraction (SXRD) for real-time monitoring of oxide thin-film growth and testing of two time-scale growth models. The use of SXRD ensures that simple kinematic single-scattering analysis can be used[5,6] to provide direct physical insight beyond that afforded by RHEED measurements.

PLD was performed in a film growth chamber specially designed for SXRD and based on the so-called $2+2$ diffraction geometry.[7] Details of the capabilities and operation of this apparatus have been provided elsewhere,[8] and only the salient features of the experimental setup are discussed here. The direction of the ablation laser beam was synchronized with the chamber rotation to maintain a fixed PLD configuration as the sample orientation is changed for x-ray diffraction. The vacuum in the chamber was maintained by a turbomolecular pump at a typical background pressure of 6×10^{-8} Torr. Sample heating was accomplished by a pyrolytic boron nitride encapsulated graphite filament heater. The sample temperature was derived from a measurement of the (0 0 2) Bragg angle using a Ge analyzer and the thermal expansion data for $SrTiO_3$. The background oxygen pressure during PLD ranged from 1×10^{-5} Torr to 15 mTorr.

The samples were (001) $SrTiO_3$ ($10\times10\ mm^2$, 0.5 mm thick, and typical miscut below 0.2°), TiO_2 terminated epiready wafers purchased from Escete. Atomic force microscopy (AFM) imaging prior to film growth showed a clean and well developed step and terrace structure with step heights of 3.9 Å which correspond to the height of one unit cell (bilayer) of $SrTiO_3$. The samples were attached without additional cleaning to a molybdenum sample platen using silver paint. PLD was performed in a substrate temperature range from 310 °C to 780 °C, using a KrF (248 nm) pulsed excimer laser (Compex 301, Lambda Physik), and a single-crystal $SrTiO_3$ target. An energy density of 3 J/cm^2 and typical repetition rates ranging from 0.03 to 1 Hz were used.

The experiments were performed on the UNICAT undulator beamline at the Advanced Photon Source using a monochromatic 10 keV x-ray beam. Continuous measurements of the diffracted intensity were performed simultaneously at the $(0\ 0\ \frac{1}{2})$ and $(0\ 1\ \frac{1}{2})$ anti-Bragg reflections using scintillation detectors. Before deposition the substrates were characterized at room temperature by measuring both the $(0\ 0\ \frac{1}{2})$ and the $(0\ 1\ \frac{1}{2})$ rod intensities. Typical count rates for surfaces with well developed initial terrace structure as determined by AFM imaging were on the order of 10^5 cps (specular) and 2×10^4 cps (off specular). Because of the well known tendency of the $SrTiO_3$ surface to undergo continuous structural and compositional changes during vacuum annealing, the samples were heated in oxygen at a pressure of 5×10^{-5} Torr.[9,10] Under these conditions, the rod intensities remained stable at elevated temperature.

[a]Electronic mail: eresg@ornl.gov
[b]Present address: Department of Physics, University of Rhode Island, Kingston, RI 02881.

 © 2002 American Institute of Physics
Downloaded 06 Sep 2009 to 160.91.157.167. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

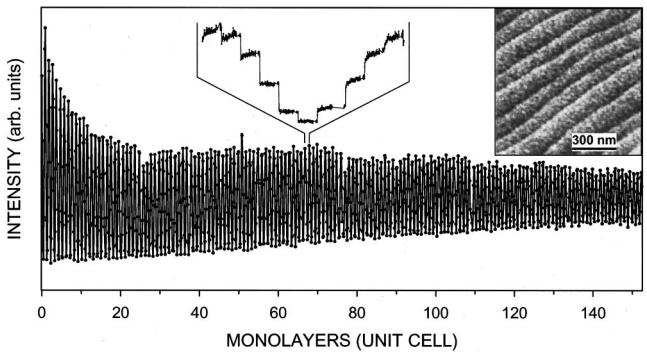

FIG. 1. Illustration of typical growth intensity oscillations at both, the (0 0 $\frac{1}{2}$) and (0 1 $\frac{1}{2}$) rods in SXRD of $SrTiO_3$ homoepitaxy by PLD. These oscillations were obtained at 650 °C using a laser power density of 3 J/cm^2 at 1 Hz repetition rate and oxygen pressure of 12.4 mTorr. The growth oscillation period corresponds to unit cells of 3.9 Å. Each dot represents deposition from one laser shot. The line is only a guide for the eye. The high-resolution scan illustrates the fine structure associated with one growth cycle and consists of single-laser pulses. The inset shows an AFM image of a $SrTiO_3$ PLD film that is 150 unit cells thick. The terrace structure is intact, but the appearance of 10–20 nm single-unit cell high islands on the terraces is clearly visible.

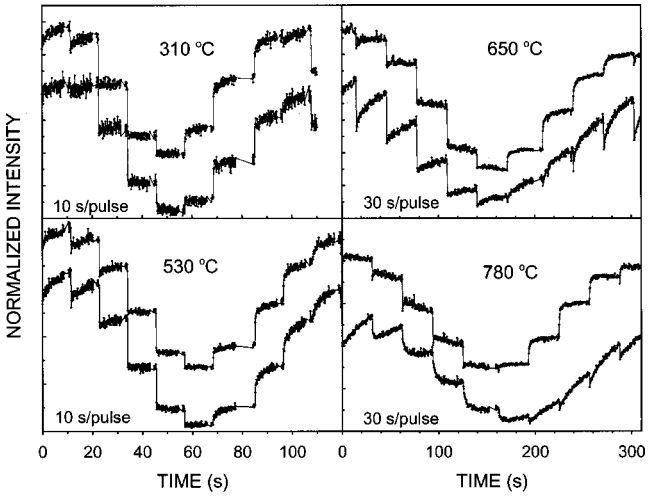

FIG. 2. High-resolution time resolved x-ray reflectivity for a single-oscillation period at the specular (top trace) and off-specular (bottom trace) rods at four different substrate temperatures. The evolution of the deposited layer was monitored for 10 s at low—and 30 s at high—temperatures. The lines represent guides for the eye.

The periodic intensity oscillations observed at the (0 0 $\frac{1}{2}$) specular rod in Fig. 1 are representative of the long time behavior of $SrTiO_3$ PLD. Since these RHEED-like oscillations result from the destructive interference between x rays reflected from newly deposited islands and the smooth terrace, the intensity would recover to its initial value if the growing layer were filled completely before island nucleation began. The damping of growth oscillations with increasing film thickness in the initial 20–25 oscillations in Fig. 1 is attributed to a gradual buildup of surface roughness due to incomplete interlayer mass transport. The loss of contrast in the oscillations that occurs without appreciable damping between 50 and 150 oscillations is attributed to small variations in deposition uniformity over the several millimeter projection of the x-ray beam on the sample, which causes oscillations to get out of phase.

An expanded view of intensity oscillations is shown in the inset of Fig. 1 where the data points correspond to 100 ms time slices. We note that the rod intensity drops abruptly after each laser pulse and reaches a minimum when the surface is half covered, corresponding to nearly complete destructive interference. As the deposition continues (after the minimum), the intensity rises abruptly after each laser pulse as island coverage increases. In addition to the prompt ($<$100 ms) intensity changes resulting from the coverage increments, rather sluggish intensity transients with time scales of seconds are observed. As will be discussed next in connection with a multiple layer deposition/evolution model, these longer time-scale transients are the signature of interlayer transfer.

Figure 2 shows specular (0 0 $\frac{1}{2}$) and off-specular (0 1 $\frac{1}{2}$) truncation rod transients measured during PLD of $SrTiO_3$ at temperatures ranging from 310 °C to 780 °C. For temperatures below 600 °C, the specular and off-specular intensities are observed to be remarkably similar (apart from differences in absolute magnitude). This indicates that in-plane and surface-normal atomic registration are essentially concurrent on the 100 ms time scale of the measurements. The measurements made at 650 °C and 780 °C (with 30 s dwell time) show specular rod intensity transients similar to those at the lower temperatures. However, the off-specular intensity transients depart noticeably from the specular rod transients at 650 °C and they depart markedly at 780 °C. The response of the off-specular intensities at elevated temperatures suggests the presence of in-plane lattice distortions or defect structures that anneal on time scales of $\sim$10 s.

We have used a simple rate equation model described by Cohen *et al.*[11] to initiate quantitative analysis of SXRD measurements. The rate equation model describes film growth in terms of layer coverages. Therefore, it is only applicable for modeling the specular rod intensities. Application of a modified version of Cohen's model described by van der Vegt[12] reveals that $SrTiO_3$ PLD behaves like a nearly perfect two-level system. The modified model includes multiple levels of film growth and coverage dependent interlayer mass transport characterized by the parameters α and β.[12] For instance, Fig. 3(a) shows a model calculation for 40 growth oscillations, and illustrates that the general features of $SrTiO_3$ PLD in Fig. 1 can be simulated by a model in which the growing layer is about 75% complete before significant nucleation occurs on top of the growing layer. This level of nucleation results in 10% island coverage on the growing layer at the time of its completion and increases roughly 1% with each additional ten layers. Such behavior is characteristic of systems with a weak interlayer diffusion barrier.

Figure 3(b) shows that the simulated response of the unmodified Cohen model for individual deposition pulses is in qualitative agreement with the specular rod intensity transients measured in Figs. 1 and 2. The curvature of the simulated pulses is inversely related to the rate of interlayer mass transport. Interlayer mass transport slows down past half coverage because there are fewer holes available in the growing layer. This effect is best seen near full coverage. For example, see the sixth through the eighth pulse in Fig. 3(b). The lack of a temperature dependence in the specular rod intensity transients is remarkable considering the large temperature range, suggesting essentially unimpeded interlayer diffusion.

Downloaded 06 Sep 2009 to 160.91.157.167. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

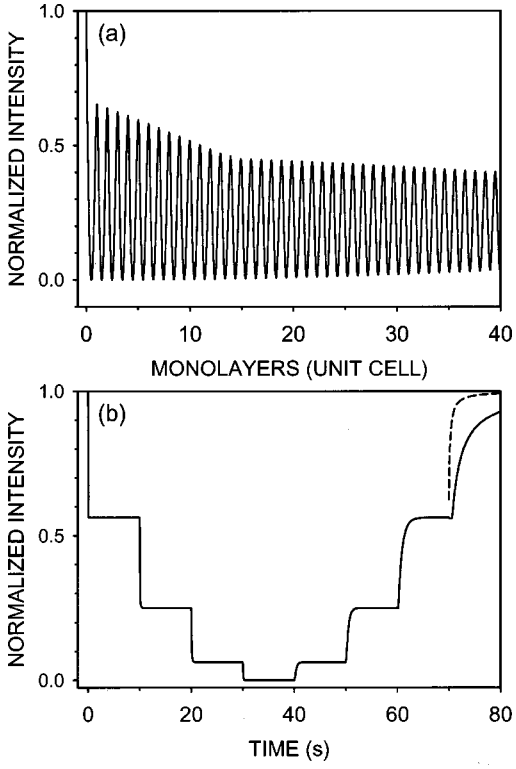

FIG. 3. (a) Illustration of growth intensity oscillations using the rate equation model (described in Ref. 12), with $\alpha=3.8$ and $\beta=0.97$ for oscillations 0–15, $\alpha=2.5$ and $\beta=0.999$ for oscillations >15 and a 0.5% variation in the deposition rate. (b) Time-dependent specular reflectivity following laser shots according to a two-level model described by Cohen *et al.* (see Ref. 11). There are eight laser shots per a $SrTiO_3$ monolayer. At $t=0$ (after the laser pulse), the plume from each pulse is distributed in proportion to the fractional coverage of the two layers. The dashed line illustrates the effect of increasing the interlayer transport rate by $10\times$.

Information about the incorporation of atoms with in-plane registry with the crystalline lattice and subsequent evolution of structural features of the growing surface is obtained from measurements of the off-specular rod intensity at $(0\ 1\ \frac{1}{2})$, which has an in-plane momentum transfer component.[5,6] Therefore, the changes in the off-specular rod intensity transients with the substrate temperature suggest the presence of structural displacements limiting in-plane registry within the growing layer at elevated substrate temperatures. The onset of the temperature dependence coincides roughly with the temperature (500 °C) above which substantial oxygen loss has been measured by medium-energy ion scattering during $SrTiO_3$ surface annealing in an ultrahigh vaccum.[9] $SrTiO_3$ surfaces are known to accommodate the loss of oxygen by formation of oxygen-vacancy induced superstructures[10,13] and the resulting surface reconstructions typically show reduced long-range order and are quite unstable.[13] They can be easily quenched by oxygen adsorption, leading to random structure formation and roughening of the surface.[13] Since the growing surface during PLD consists of incomplete layers, it is likely to be susceptible to oxygen loss at elevated substrate temperatures, leading to transient surface rearrangements. We anticipate that these surface rearrangements would be temporarily quenched by reactive oxygen species during succeeding deposition pulses.

In summary, we have described SXRD real-time monitoring of homoepitaxial PLD growth of $SrTiO_3$. Time-slice measurements with 100 ms resolution suggest $SrTiO_3$ unit cell formation concurrent with the arrival of the ablation plume, followed by interlayer transfer with a time scale of seconds and (at temperatures above 600 °C) in-plane structural rearrangements that occur on time scales of tens of seconds. The observation of persistent growth oscillations for PLD between 550 °C–650 °C is consistent with essentially unimpeded interlayer mass transport during film growth, a characteristic behavior necessary to sustain a two level system. We have further shown that SXRD can be used in combination with simple kinematic modeling for direct testing of film growth models and obtaining new physical information on nonequilibrium growth processes.

This research was sponsored by the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under Ccontract No. DE-AC05-00OR22725. The Advanced Photon Source is supported by the DOE (BES W-31-109-ENG-38). The UNI-CAT facility at the APS is operated by the University of Illinois, ORNL, NIST, and UOP Research, Inc.

[1] D. H. Lowndes, D. B. Geohegan, A. A. Puretzky, D. P. Norton, and C. M. Rouleau, Science **273**, 898 (1996).
[2] D. H. A. Blank, G. J. H. M. Rijnders, G. Koster, and H. Rogala, Appl. Surf. Sci. **138**, 17 (1999).
[3] M. Lippmaa, N. Nakagawa, M. Kawasaki, S. Ohashi, and H. Koinuma, Appl. Phys. Lett. **76**, 2439 (2000).
[4] D. H. A. Blank, G. Koster, G. A. J. H. M. Rijnders, E. van Setten, P. Slycke, and H. Rogalla, J. Cryst. Growth **211**, 98 (2000).
[5] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).
[6] I. K. Robinson and D. J. Tweet, Rep. Prog. Phys. **55**, 599 (1992).
[7] K. W. Evans-Lutterodt and M. T. Tang, J. Appl. Crystallogr. **28**, 318 (1995).
[8] J. Z. Tischler, G. Eres, D. H. Lowndes, B. C. Larson, M. Yoon, T.-C. Cheng, and P. Zschack, in *Proceedings of the 11th U.S. National Synchrotron Radiation Instrumentation Conference (SRI'99)*, edited by P. Pienetta, J. Arthur, and S. Brennan (AIP, New York, 2000), p. 151.
[9] T. Nishihara, O. Ishiyama, S. Hayashi, M. Shinohara, M. Yoshimoto, T. Ohnishi, and H. Koinuma, Mater. Res. Soc. Symp. Proc. **474**, 389 (1997).
[10] T. Nishimura, A. Ikeda, H. Namba, T. Morishita, and Y. Kido, Surf. Sci. **421**, 273 (1999).
[11] P. I. Cohen, G. S. Petrich, P. R. Pukite, G. J. Whaley, and A. S. Arrott, Surf. Sci. **216**, 222 (1989).
[12] H. A. van der Vegt, H. M. van Pinxteren, M. Lohmeier, E. Vlieg, and J. M. C. Thornton, Phys. Rev. Lett. **68**, 3335 (1992).
[13] J. Zegenhagen, T. Haage, and Q. D. Jiang, Appl. Phys. A: Mater. Sci. Process. **67**, 711 (1998).

Downloaded 06 Sep 2009 to 160.91.157.167. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp