Time-resolved Surface X-ray Diffraction Study of $SrTiO_3$ Homoepitaxy during Pulsed-laser Deposition

G. Eres,[1] J. Z. Tischler,[1] M. Yoon,[2] B. C. Larson,[1] C. M. Rouleau,[1] D. H. Lowndes,[1] P. Zschack[3]
[1]Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A.
[2]University of Rhode Island, Kingston, RI, U.S.A.
[3]University of Illinois at Chicago, Chicago, IL, U.S.A.

Introduction

Pulsed-laser deposition (PLD) is employed widely to grow complex oxide films and multilayered structures as well as to rapidly and efficiently search for novel oxide materials [1]. Although a great deal is known about the ablation plume's dynamics in the gas phase, the subsequent processes that occur on the growing surface and affect nucleation and epitaxial growth of films are less well understood. PLD, simply by its pulsed nature, has a singular advantage for fundamental growth studies in that it naturally separates film growth into a deposition step followed by a phase of surface rearrangement. In this work, a study of homoepitaxial oxide thin film growth kinetics was carried out by employing time-resolved surface x-ray diffraction (SXRD) during strontium titanate (STO) PLD.

Methods and Materials

Pulsed-KrF laser deposition (PLD) was performed in a film growth chamber specially designed for SXRD and based on the so-called 2+2 diffraction geometry. The direction of the ablation laser beam was synchronized with the chamber rotation to maintain a fixed PLD configuration as the sample orientation was changed for x-ray diffraction measurements. The vacuum in the chamber was maintained by a turbomolecular pump (base pressure of 6×10^{-8} Torr). Sample heating was accomplished by radiative heating from a pyrolytic boron-nitride-encapsulated graphite-filament planar heating element. The STO sample temperature was derived from measurements of the (002) Bragg angle by using a Ge analyzer and the thermal expansion data. The background oxygen pressure during STO PLD ranged from 10^{-5} to 15 mTorr.

The samples were 001-oriented TiO_2-terminated STO purchased from Escete and AFM imaging *ex vacuo* prior to film growth and showed a clean and well-developed step and terrace structure with step heights of 3.9Å, a height corresponding to one STO unit cell. The samples were attached without additional cleaning to a Mo sample platen by using Ag paste. PLD was performed by ablating a single-crystal STO target through O_2 at an energy density of 3 J/cm^2 with a typical repetition rate of 0.03 to 1 Hz. The substrate was placed 7 cm from the target and heated to a growth temperature that ranged from 310 to 780ºC.

The experiments were performed on the University-National Laboratory-Industry Collaborative Access Team (UNI-CAT) undulator beamline by using a monochromatic 10-keV x-ray beam. Measurements of the diffracted intensity were performed simultaneously at the (00½) and (01½) surface truncation rod positions by using scintillation detectors. Before deposition, the substrates were characterized at room temperature by measuring these reflections, and count rates on the order of 10^5 and 10^4 counts per second were achieved, respectively. Because of the well-known tendency of STO to undergo continuous structural and compositional changes during vacuum annealing [2, 3], the samples were heated in oxygen at a pressure of 5×10^{-5} Torr; the rod intensities remained stable under these conditions.

Results

The periodic intensity oscillations observed at the (00½) specular rod in Fig. 1 are representative of the long-time behavior of STO PLD, while the inset shows the evolution of the rod intensity over one growth cycle. The initial damping of growth oscillations with increasing film thickness (<25 monolayers) is attributed to a gradual buildup of surface roughness due to incomplete interlayer

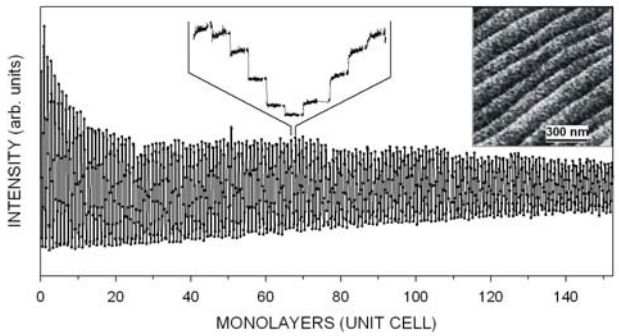

FIG. 1. Illustration of typical growth intensity oscillations at both the (00½) and the (01½) surface truncation rods by SXRD of STO homoepitaxy during PLD. The inset shows an antiferromagnetic (AFM) image of a PLD STO film that is 150 unit cells thick.

mass transport, while the loss in oscillation contrast after this stage (>25 monolayers) is attributed to small variations in film thickness over the projected length of the x-ray beam on the sample. In terms of one growth cycle, we note that the rod intensity dropped abruptly after each laser pulse and reached a minimum when the surface was half covered, a condition corresponding to nearly complete destructive interference between those x-rays reflected from newly deposited islands and those reflected from the smooth underlying terrace. In addition to prompt (<100 msec) intensity changes resulting from coverage increments, rather sluggish intensity transients with timescales on the order of seconds were observed.

Figure 2 shows specular (00½) and off-specular (01½) surface truncation rod transients measured during PLD of STO at temperatures ranging from 310 to 780ºC. It was observed that at temperatures below 600ºC, the specular and off-specular rod intensities were remarkably similar, indicating that surface-normal and in-plane atomic registry are essentially concurrent for the timescale of the measurement (~100 msec).

Discussion

We have used a simple rate equation described by Cohen et al. [4] to initiate quantitative analysis of SXRD measurements in terms of crystallization, island nucleation, and interlayer transfer. After modifying the model to include multiple levels of film growth and coverage-dependent interlayer mass transport, comparisons of model simulations with our data reveal STO PLD behaves like a nearly perfect two-level system. For instance, Fig. 3(a) shows a model calculation for 40 growth oscillations, illustrating that the general features of STO PLD in Fig. 1 can be simulated by a model in which the growing layer is about 75% complete before

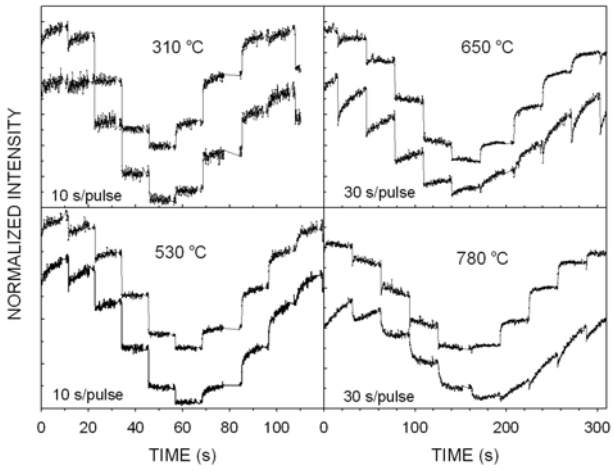

FIG. 2. High-resolution-time resolved SXRD at both the (00½) surface truncation rod (top) and (01½) surface truncation rod (bottom) at four temperatures.

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 coverage increases roughly 1% with each additional 10 layers. Such behavior is characteristic of systems with weak interlayer diffusion barriers.

Figure 3(b) shows that the simulated response of the model for individual deposition pulses is in qualitative agreement with the *specular* rod intensity transients measured in Figs. 1 and 2 — especially when the interlayer transport rate is scaled by 10. When coupled with the lack of a temperature dependence in the specular rod intensity transients, this observation suggests essentially unimpeded interlayer diffusion in the present temperature regime.

The relative sensitivity of the *off-specular* rod intensity transients to changes in substrate temperature, however,

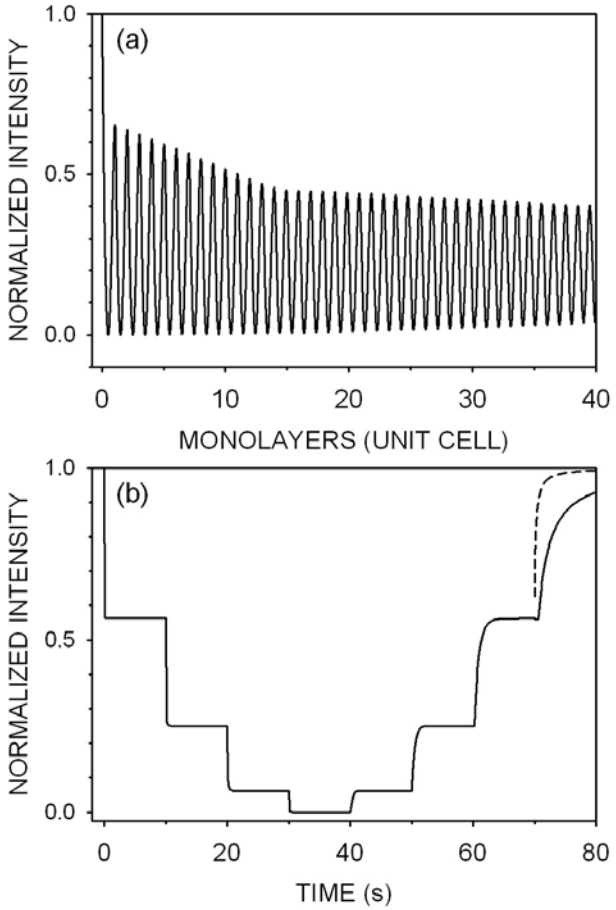

FIG. 3. (a) Illustration of growth intensity oscillations from using the rate equation in Reference 5. (b) Time-dependent specular reflectivity following laser shots according to the two-level model [4]. The dashed line illustrates the effect of increasing the interlayer transport rate by 10 times.

indicates the presence of structural displacements limiting in-plane registry within the growing layer. The onset of the temperature dependence coincides roughly with the temperature (~500ºC) above which substantial oxygen loss has been measured during STO surface annealing [2]. STO surfaces are known to accommodate the loss of oxygen by formation of oxygen-vacancy-induced superstructures, and the resulting surface reconstructions typically show reduced long-range order and are quite unstable. They can be quenched easily by oxygen adsorption, leading to random structure formation and surface roughening. Since the growing surface during PLD consists of incomplete layers, it is likely susceptible to oxygen loss at elevated temperatures, leading to transient surface rearrangements, as observed here.

This work demonstrates the capabilities and advantages of time-resolved SXRD to study interlayer transfer in real time. The use of time-resolved SXRD ensures that simple kinematic single-scattering analysis can be used to provide direct physical insights that go well beyond those afforded by reflection high-energy electron diffraction studies, for example. Interlayer mass transfer is a key process that affects interfacial broadening and surface roughness, characteristics that are of crucial importance in the technological application of oxide thin films.

Acknowledgments

This research was sponsored by Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC05-00OR22725. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-13-109-ENG-38. The UNI-CAT facility at the APS is operated by the University of Illinois, ORNL, the National Institute of Standards and Technology, and UOP Research, Inc.

References

[1] D. H. Lowndes, D. B. Geohegan, A. A. Puretzky, D. P. Norton, and C. M. Rouleau, Science **273**, 898 (1996).

[2] T. Nishihara, O. Ishiyama, S. Hayashi, M. Shinohara, M. Yashimoto, T. Ohnishi, and H. Koinuma, Mat. Res. Soc. Symp. Proc. **474**, 389 (1997).

[3] T. Nishimura, A. Ikeda, H. Namba, T. Mroshita, and Y. Kido, Surf. Sci. **421**, 273 (1999).

[4] P. I. Cohen, G. S. Petrich, P. R. Pukite, G. J. Whaley, and A. S. Arrott, Surf. Sci. **216**, 222 (1089).

[5] H. A. van der Vegt et al., Phys Rev. Lett. **68**, 3335 (1992).