Time-Resolved X-ray Scattering Study of Homoepitaxial Oxide Growth Using Pulsed-Laser Deposition

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Introduction

Epitaxial growth of a crystalline surface following atomic deposition is a complex, multistep process that includes atomic diffusion on the surface, crystallization into chemical units, and rearrangement of crystalline units. A complete experimental examination of these processes has been difficult to achieve because of their vastly different time scales and the fact that they occur concurrently in continuous deposition techniques such as molecular beam epitaxy and chemical vapor deposition. As a result, our present understanding of epitaxial surface growth remains rather approximate and phenomenological. Using the discontinuous nature of pulsed-laser deposition (PLD), we are able to separate the process of crystallization on the substrate from the subsequent surface rearrangement and morphological evolution.

In this report we present *in situ*, time-resolved measurements of homoepitaxial growth of $SrTiO_3$ on $SrTiO_3$ (001) using PLD, submillisecond measurement resolution, and simultaneous monitoring of specular and off-specular crystal truncation rod (CTR) scattering. These measurements span more than seven orders of magnitude in time and represent the first direct x-ray measurements of surface evolution time scales as a function of coverage during epitaxial growth.[1]

Methods and Materials

Experiments were performed at UNICAT (34-ID-D) using 1.24 Å x-rays. The PLD deposition and *in situ* x-ray measurements were carried out in a vacuum chamber integrated with an x-ray diffractometer. A single-crystal $SrTiO_3$ target was ablated by a KrF excimer laser at an energy density of 2 J/cm^2. The substrates were single-crystal $SrTiO_3$ (001) surfaces with TiO_2 termination. Prior to deposition, each substrate was imaged by atomic force microscopy and was found to be atomically smooth. Only steps of single-unit cell height (a = 3.9 Å) were observed, typically separated by more than 1000 Å. During deposition, the substrates were held at temperatures ranging from 310 to 780°C in O_2 pressures ranging from 5×10^{-5} to 10^{-2} torr.

CTR measurements were made at a specular reflection wave vector (in reciprocal lattice units) of $\boldsymbol{Q}$ = (0,0,1/2) and an off-specular wave vector of $\boldsymbol{Q}$ = (0,1,1/2). The reflectivity oscillations that occur for both the specular and off-specular CTRs at these positions correspond to growth of 3.9 Å $SrTiO_3$ bilayers.

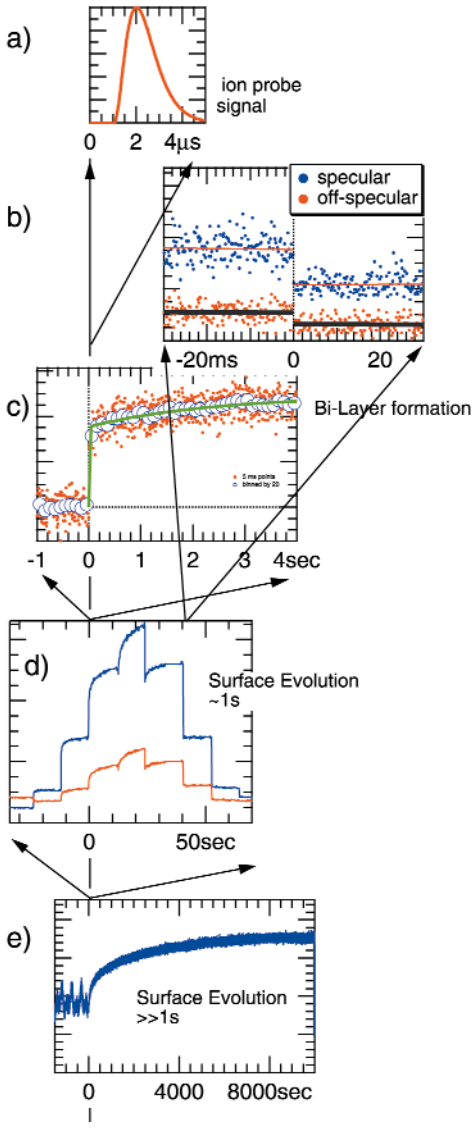

FIG. 1. The surface scattered intensity observed at multiple time scales during crystal growth. (a) The ion signal after the laser pulse. (b) Rapid rise and fall at 200 μs resolution. Higher data points are at (0,0,1/2) and lower at (0,1,1/2). (c) Same as (b), but 5 ms resolution. (d) Growth of one complete monolayer measured at $\boldsymbol{Q}$ *of (0,0,1/2) and (0,1,1/2). (e) Long time relaxation of surface after laser stops.*

Results

Figures 1(a) - (e) show x-ray surface reflectivities for widely differing time scales. Note that ion-probe measurements show that the laser-ablation pulse is deposited on the substrate within a few microseconds [Fig. 1(a)]. Figure 1(b) shows discontinuous changes in intensity observed down to the shortest time slices (200 μs) presently available, where the two curves represent the specular and off-specular intensities measured (simultaneously) at $\boldsymbol{Q}$ = (0,0,1/2) and $\boldsymbol{Q}$ = (0,1,1/2), respectively. The (0,1,1/2) measurements show that in-plane as well as plane-normal ordering occurs on a significantly shorter time scale than the 200 μs time slices. Figures 1(c) and 1(d) show discontinuous reflectivity

changes for time slices of 5 ms, and they further show continuous evolution during the 10 s following laser deposition pulses. The similarity in the shapes of the (0,0,1/2) and (0,1,1/2) reflectivities over the full growth oscillation indicates that in-plane as well as plane-normal ordering is present throughout the 10 s dwell time between laser pulses.

The detailed shape of the reflectivity transients during the 10 s dwell time following deposition pulses in Fig. 1(d) provides a direct measure of interlayer surface evolution as a function of surface coverage. For instance, the intensity transient following the t = 0 pulse in Fig. 1(d) (at approximately ~75% coverage) requires nearly 10 s to reach saturation, while the transient for the succeeding pulse (corresponding to ~90% coverage) is only partially completed after 10 s. On the other hand, no transient is observed for the t = 40 s pulse that corresponds to ~10% coverage. This lack of a transient at 10% coverage indicates the formation of islands on a filled surface layer without significant interlayer surface transport. Quantitative modeling of these processes as a function of temperature and deposition parameters is in progress, and diffuse CTR scattering measurements have been initiated to investigate island sizes as well as interlayer evolution kinetics during PLD epitaxial growth.

Acknowledgments

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Reference

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