Fundamental Investigation of Epitaxial Thin-film Growth by Pulsed-Laser Deposition

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Introduction

Epitaxial growth is the dominant method for stabilizing nonequilibrium materials in the form of thin films and artificial structures. The method of choice for epitaxial growth of complex materials is laser-molecular beam epitaxy (MBE) [1]. Laser-MBE combines the advantages of conventional MBE and the broad applicability of pulsed laser deposition (PLD) into a versatile film growth method with atomic-layer control capabilities, so that metastable and artificial phases can be synthesized in a reactive gaseous environment. The focus for this project is pulsed-deposition growth of complex oxide thin films, a class of materials that exhibit correlated electron and novel magnetic phenomena that give rise to an extraordinarily rich variety of properties of interest for a wide range of technological applications, including colossal magnetoresistance, high-temperature superconductivity, and spintronics applications.

Remarkable advances have been made in pulsed-laser MBE growth of oxide thin films and other materials. However, the range of structural complexity and the complicated multicomponent chemistry of the complex oxides that drive their electronic and magnetic properties make the control of epitaxial growth a challenge [1, 2]. Progress in understanding the deposition, aggregation, and surface evolution associated with epitaxy has been hampered significantly by a lack of direct measurements of growth kinetic processes that govern single-layer growth and interface formation. However, with the high intensities of undulator beamlines at synchrotron sources, time-resolved surface x-ray diffraction (SXRD) measurements at (anti-Bragg) crystal truncation rod (CTR) positions now provide a real-time monitor of surface layer morphology and formation kinetics [3]. Accordingly, SXRD and laser-MBE have been combined to obtain fundamental information on the mechanisms of surface structure, morphology, and evolution during epitaxial growth of $SrTiO_3$ (STO).

Methods and Materials

Pulsed-KrF laser deposition was performed in a roll-in film growth chamber specially designed for SXRD and based on the so-called 2+2 diffraction geometry [4]. The samples were 001-oriented, TiO_2-terminated STO in a vacuum of $<10^{-7}$ Torr. Sample heating was accomplished by radiative heating from a pyrolytic boron-nitride-encapsulated, graphite-filament heating element. The background oxygen pressure during STO PLD ranged from 10^{-5} Torr to a few milli-Torr. PLD was performed by ablating a single-crystal STO target with a laser pulse energy density of ~3 J/cm^2 and with a typical laser pulse repetition rate of 0.1 Hz. Measurements of the diffracted intensity reported here were performed on the (0 0 1/2) surface truncation rod positions of STO at a temperature ot 650°C by using 10-keV x-rays and a scintillation detector at the UNI-CAT undulator beamline at the APS.

Results and Discussion

Figure 1 shows a single oscillation of the (0 0 1/2) CTR for homoepitaxial growth of STO by using PLD. These data differ from the data that result from conventional MBE epitaxial film-growth investigations by reflection high energy electron diffraction (RHEED), which produce the well-known (smooth) sinusoidal RHEED oscillations, denoting a single layer of growth for each oscillation. As inferred above, the pulsed nature of PLD modifies the continuous sinusoidal oscillation form to a series of steplike structures with an average sinusoidal form, as shown in Fig. 1.

These steps are the signature of the inherent separation of the deposition and surface aggregation/evolution processes by PLD; hence, an analysis of the step structure provides fundamental information at the submonolayer (sub-unit-cell) level that is not available in steady-state growth modes. The direct correspondence between x-ray

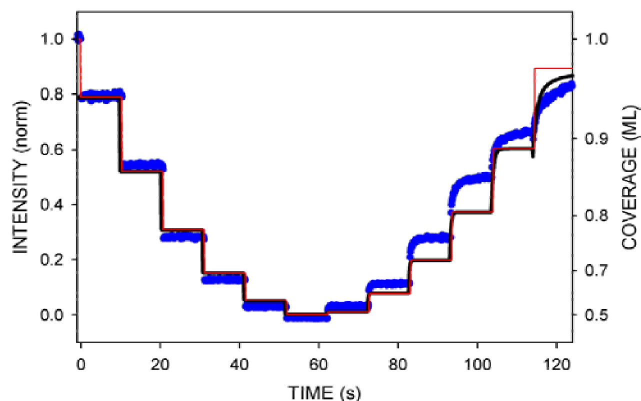

FIG. 1. Normalized CTR intensity measurements on STO as a function of time during homo-epitaxial PLD growth of STO. The solid blue markers represent the measurements, the red line denotes model calculations with instantaneous interlayer transfer, and the black line denotes model calculations with a finite interlayer time.

CTR scattering and surface coverage facilitates quantitative investigations of PLD growth mechanisms and evaluation of theoretical film growth models. We discuss these results with a particularly instructive model of Cohen [5] for studying the effects of interlayer transport on growth mode evolution and surface roughening. Cohen's model consists of a system of coupled rate equations that describe deposition and subsequent diffusion of atoms from the top of islands into the growing layer in terms of layer coverages. According to this model, a departure from layer-by-layer (LBL) growth to 3-D island-on-island structures is caused by hindered interlayer transport [5].

Without discussing the details, the analysis of the CTR transients using the rate equation model reveals that the epitaxial growth mode can be extracted from single PLD pulses by treating pulsed deposition as a series of growth interruptions to conventional continuous growth techniques. The model shows that a finite rate of interlayer transport from the top of islands to the growing layer imposes a characteristic asymmetry in the time-resolved diffraction response when referenced to half coverage, where half coverage is denoted by the minimum in the intensity in Fig. 1 at ~55 seconds. These trends are illustrated in Fig. 1 for experimental data (blue), finite interlayer transport (black), and infinite interlayer transport (red). For infinite interlayer transport, the recovery is instantaneous, and the asymmetry is not present. For example, the time-dependent CTR intensity response is different at 0.4 coverage than at 0.6 coverage (i.e., ~30 and 80 seconds). The rate equation model shows that the measurement is most sensitive to the interlayer transport rate near full coverage. A finite or sluggish rate of interlayer transport causes the deposited species to search longer for holes in the growing layer, which results in a time-dependent recovery transient in the scattered intensity following each laser pulse.

The shape of the measured transients for $SrTiO_3$ with the simple adaptation of Cohen's model to pulsed deposition growth is reproduced rather well for less than half coverage (<55 seconds), but it does not explain the measured CTR transients for greater than half coverage in the ranges of 70-90 seconds. The magnitude of the abrupt intensity changes in the measurements are larger than those predicted by the simple model for greater than half coverage, and the shape of the slugggish transient is correct only near full coverage. These represent serious deficiencies, indicating both short-time-scale (millisecond) and long-time-scale (seconds) inconsistencies. Therefore, we conclude that simply interrupting conventional, continuous deposition MBE film-growth does not provide the essence of PLD growth, and we further conclude that the success of PLD for growing complex oxides and compound materials is not simply due to the deposition of short pulses at high instantaneous rates. Quantitative fits to the measured transients are presently being made, with the incorporation of growth aspects specific to the pulsed-laser ablation process.

Acknowledgments

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