In Situ X-ray Scattering Study of $PbTiO_3$ Homoepitaxy by Metal-Organic Chemical Vapor Deposition

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Introduction

In this report, we discuss grazing incidence x-ray scattering (GIXS) studies of growth and processing by metal-organic chemical vapor deposition (MOCVD). Although most *in situ* studies of surface structure and morphology during crystal growth have been performed in vacuum environments, chemical interactions between the vapor-phase environment and surface play a critical role during MOCVD growth. It is clear that synthesis mechanisms and growth morphology will be affected by the surface chemistry and dynamics as determined by a gas composition, flow rate, pressure, substrate temperature, and impurity levels. However, there have been few *in situ* measurements of atomic-scale surface structure during MOCVD growth because few surface analysis techniques are compatible with this vapor phase environment.

X-ray scattering is the most direct atomic-scale structural probe compatible with the near-atmospheric-pressure, reactive environment of MOCVD. The features in the scattering pattern known as crystal truncation rods (CTRs) are very sensitive to the atomic-scale surface morphology. The evolution of the CTR intensity with time during growth can be used to identify the homoepitaxial growth mode of the crystal. The competition among deposition rate, surface mobility, and propagation of atomic steps on the surface determines which of three homoepitaxial growth modes are favored: step-flow, layer-by-layer, or 3-D. For step-flow mode, in which atoms arriving on the surface attach at existing step edges, the surface morphology is in steady state and the CTR intensity remains constant. For layer-by-layer mode, in which islands are nucleated on the terraces between steps and subsequently coalesce, the CTR intensity oscillates in time with each layer of growth as a result of the cyclic changes in the occupations of neighboring layers. For 3-D mode, in which deposited atoms typically remain on the layer where they arrive, the surface roughens rapidly and the CTR intensity decays monotonically.

In situ x-ray scattering has previously been used to study the MOCVD of III-V semiconductors [1, 2]. This activity report summarizes highlights of the results [3] of a study of homoepitaxial growth of $PbTiO_3$ by an MOCVD process based on the precursors tetraethyl lead (TEL) and titanium isopropoxide (TIP). This work is part of a program to understand and control the synthesis of complex oxides at the same level that is currently achieved for semiconductors.

Methods and Materials

Experiments were conducted at the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) undulator station 12-ID-D of the APS by using a vertical-flow MOCVD chamber mounted on a "z-axis" surface diffractometer designed for *in situ* GIXS studies [4, 5]. X-rays of 24-keV energy were used to penetrate the 2-mm-thick quartz walls of the chamber. The x-ray incidence angle was near the critical angle (0.13^o) to increase surface sensitivity.

Homoepitaxial growth was investigated. Polished, etched $SrTiO_3$(001) single crystals with an initial thin film of $PbTiO_3$ were used as substrates. The single-crystal $PbTiO_3$ film replicated the substrate crystal quality (mosaic width 0.05^o), and epitaxial strain was fully relaxed. For further details on the samples or growth conditions, see Ref. 3.

Results

Because this is an *in situ* method, the growth mode behavior can be rapidly mapped under different conditions by using a single sample. Repeated cycles of growth and recovery were performed. For each cycle, a growth pulse was initiated by adding the TIP into the cation precursor flow, with TEL flow already established. The duration of growth pulses presented here corresponds to ~4 unit cells (16 Å). Growth halts when the TIP flow is diverted from the sample chamber. After each growth pulse, the surface gradually recovered its initial smoothness. All results reported here are from the same sample and were reproducible. Identical growth rates and similar growth mode behaviors were observed on other samples.

Figure 1 shows the evolution of the 20*L* CTR intensity at $L = 0.5$ during deposition at various temperatures in the range of 650–730°C, with fixed TIP and TEL flow. Strong intensity oscillations indicate that layer-by-layer growth is observed at all temperatures. The reduced depth of the oscillations at higher temperatures indicates a gradual tendency toward step-flow growth, consistent with an expected increase in surface mobility. At the lowest temperatures, the relatively rapid decay in the oscillations indicates a tendency toward 3-D growth. By comparison with growth rates obtained optically under selected conditions, we verified that the layer-by-layer period corresponded to the growth of single-unit-cell layers. As shown in the inset of Fig. 1, the growth rate is almost independent of temperature.

Figure 2 shows the CTR intensity during deposition at various TEL flow rates, with TIP flow during growth fixed at 0.26 µmol/min. The inset shows that the growth rate is independent of TEL flow. However, the growth mode varies significantly, tending toward step flow at low TEL flows. This indicates either that the surface mobility increases or that island nucleation or step attachment kinetics change. The recovery behavior gives additional information about the mechanism. Following each growth, reducing the TEL flow facilitated recovery of a smooth surface. This is consistent with a higher surface mobility at lower TEL flows.

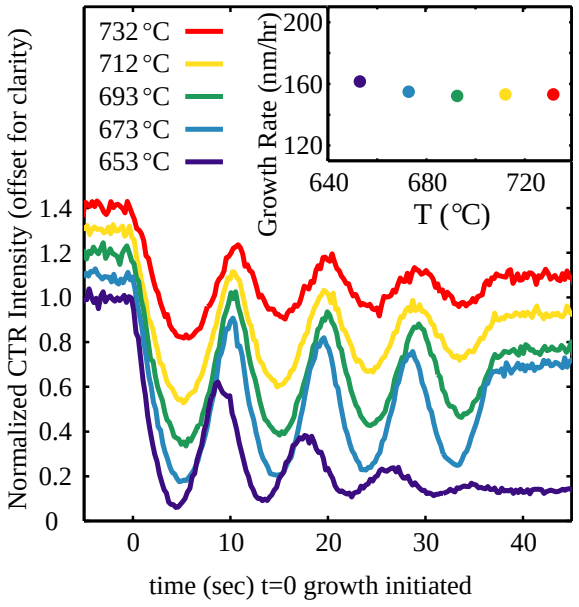

FIG. 1. Evolution of CTR intensity before, during, and after growth of approximately 16 Å (4 unit cells) of $PbTiO_3$ at various temperatures using fixed TIP and TEL flows. Inset: Growth rate is independent of temperature for fixed flows.

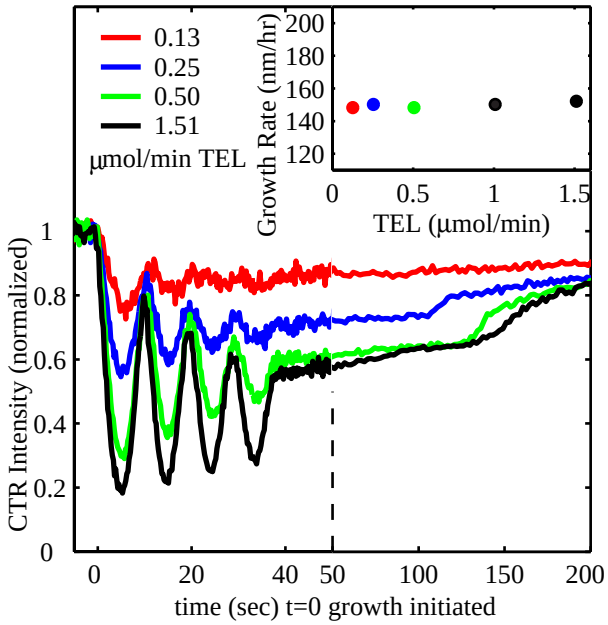

FIG. 2. Evolution of CTR intensity before, during, and after growth of approximately 16 Å of $PbTiO_3$ at various TEL flow rates, using a fixed TIP flow. Following growth, TEL flow was reduced, and surface recovery is shown. Inset: Growth rate is independent of TEL flow.

Discussion

An overall picture of the MOCVD growth mechanism emerges from this study. Within the range of conditions studied, the rate of growth is limited only by Ti transport and is independent of temperature, TEL flow, and P_{O_2}. The lack of temperature dependence is in agreement with previous *ex situ* studies, as is the linear dependence on TIP flow. It is noteworthy that Ti transport remains rate-limiting even for TIP/TEL ratios higher than unity. This indicates that the reactions converting TIP to adsorbed cations are less efficient than those for TEL.

In summary, an *in situ*, real-time x-ray scattering investigation of MOCVD of the prototypical Pb-based perovskite $PbTiO_3$ has been performed [3]. The evolution of surface structure and morphology was measured in real time by using GIXS. In particular, these experiments determined the influence of substrate temperature *T* and delivery rates of TIP and TEL on the homoepitaxial growth mode and rate.

Acknowledgments

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