Complex oxide growth using simultaneous in situ RHEED and x-ray reflectivity: 
When is one layer complete?

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During layer-by-layer homoepitaxial growth, both the Reflection High-Energy Electron Diffraction (RHEED) intensity and the x-ray reflection intensity will oscillate, and each complete oscillation indicates the addition of one monolayer of material. However, it is well documented, but not well understood, that the phase of the RHEED oscillations is not constant and thus the maxima in the RHEED intensity oscillations do not necessarily occur at the completion of a layer. We demonstrate this using simultaneous in situ x-ray reflectivity and RHEED during layer-by-layer growth of SrTiO3.

Many of the models, especially the simpler step density model and the kinematic approximation, share similar traits. Chief among those traits is the prediction that the specular RHEED intensity decreases as the surface becomes rougher. For example, in the step density model, as the step density increases the likelihood of diffuse scattering increases, thus the specular intensity decreases. As the layer reaches completion, the number of steps decreases, and thus the specular intensity recovers – ideally returning to its original value. The prediction is the same for the kinematic approximation: we expect the RHEED intensity to oscillate exactly out of phase with the surface roughness.

In practice, RHEED oscillations are often more complex: the RHEED intensity can increase at the start of the growth, or decrease and then recover to an intensity greater than the intensity before growth. The RHEED intensity can (of course) oscillate exactly out of phase with the roughness. Even identical RHEED and growth conditions can yield RHEED oscillations that are surprisingly 180° out-of-phase with previous oscillations.

RHEED oscillations during PLD have an added layer of complexity due to the movement of adatoms between laser pulses. During PLD, each laser pulse ablates a large amount of material from the target. This material is deposited randomly on the surface of the substrate, creating a sharp decrease in intensity after each laser pulse. Be-
tween laser pulses, the adatoms diffuse on the surface, falling into pits and attaching to step edges and islands, and thus the surface “heals” and becomes smoother. As the surface heals between laser pulses, the RHEED intensity increases. This behavior agrees with the simple RHEED oscillation models – despite the fact that the overall growth oscillation is not necessarily out of phase with the roughness. This can be a major drawback when using RHEED – it is not always obvious when a layer is complete.

In order to quantify the RHEED oscillations, researchers have defined the phase of the RHEED intensity oscillations. The period \( T \) of the oscillations is easy to define based on the maxima or minima of the intensity oscillations. Following previous work, we assume the growth begins at \( t = 0 \) and look for the minimum of the RHEED intensity that occurs between \( t = T \) and \( t = 2T \) and label this time as \( t_{3/2} \). Then the phase of the RHEED oscillations is defined as:

\[
\phi = 2\pi(t_{3/2}/T - 1.5).
\]  

Using the simple models we expect \( t_{3/2} = 1.5T \) (RHEED intensity is a minimum when the surface is roughest), so \( \phi = 0 \), indicating that the RHEED intensity is in phase with the smoothness of the substrate and exactly out of phase with the roughness.

Despite the proliferation of RHEED systems, it is not the only \textit{in situ} growth diagnostic tool. With a suitably chosen scattering geometry (typically at incident angles smaller than that of the first Bragg peak), x-ray scattering is highly surface sensitive and can also yield information about growth dynamics. X-ray reflectivity (XRR) probes much deeper than RHEED and contains additional information about layers below the topmost layer. As a result, XRR intensity at angles below the first Bragg peak will oscillate not only with roughness but also due to thin-film interference. However, in the case of homoepitaxy, there is no thin-film interference, and therefore the XRR intensity oscillates due to roughness only. Because x-rays are weakly interacting, the kinematic scattering approximation describes XRR intensity oscillations very accurately. As a result, we can use Eq. 1 to find \( \phi = 0 \) always for homoepitaxial XRR intensity oscillations.

In addition, the intensity lost from the XRR specular reflection can be seen directly in the XRR diffuse scattering (something that is very difficult to capture with RHEED). In fact, the diffuse scattering can be used to determine the distance between islands on the surface of the substrate. However, at these angles far from a Bragg peak, nearly complete destructive interference means that very bright synchrotron x-ray sources are required to be able to see XRR intensity oscillations, which is why XRR continues to be less common than RHEED.

In this article we discuss direct, simultaneous comparison of RHEED and XRR during homoepitaxial growth of SrTiO\(_3\) (STO) via pulsed laser deposition onto STO (001) substrates. We used a KrF eximer laser (\( \lambda = 248 \) nm) with a fluence of \( \approx 2 \) J/cm\(^2\), with a spot size on the target of 3.7 mm\(^2\), yielding approximately 10 laser pulses per monolayer. Depositions occurred at 900 °C and an O\(_2\) pressure of \( 1.3 \times 10^{-5} \) mbar. Before deposition, the substrates are etched in HF and annealed to produce an atomically smooth TiO\(_2\) terminated surface. Further experimental details can be found in Ref. [51].

The x-ray and RHEED measurements were performed using a custom PLD/x-ray diffraction system installed in the G3 hutch at the Cornell High Energy Synchrotron Source. X-ray measurements were taken at the “anti-Bragg” or “quarter-Bragg” positions (the (00 \( \frac{1}{2} \)) or the (00 \( \frac{1}{4} \))) in reciprocal space and images collected using a Pilatus 100K detector. The RHEED system is attached to the chamber at 45° to the x-ray beam. For our substrates, the miscut ran parallel to the (110) direction, usually to within \( \pm 5^\circ \), so we were able to align the incident x-ray beam perpendicular to the miscut and the RHEED beam along the (100) axis. We used the average intensity of the specular reflection for our RHEED oscillations, and the incident angle of the electron beam varied from 0.8° to 1.5°.

Two typical growths of STO on STO (001) via pulsed laser deposition are presented in Fig. 1. XRR data was taken at the quarter-Bragg position, (00 \( \frac{1}{2} \)) and RHEED beam was parallel to the (100) axis. Each individual laser pulse is obvious, marked by the sharp decrease in intensity both in RHEED and XRR, followed by the exponential recovery between pulses. The number of pulses per layer is \( \approx 11.3 \) and \( \approx 10.2 \) for Fig. 1(a) and (b), respectively.

The growth conditions of these two films were nearly the same (deposition temperatures of 915 °C and 890 °C for Figs. 1(a) and 1(b), respectively). For both growths, the XRR intensity oscillation remains out of phase with the roughness (x-ray diffuse scattering), so \( \phi = 0 \). However, in Fig. 1(a), the RHEED intensity oscillation is nearly in phase with the XRR oscillation (\( \phi \approx 0.05\pi \)), and in Fig. 1(b), the RHEED intensity oscillation is nearly out of phase with the XRR oscillation (\( \phi \approx 0.81\pi \)). Other researchers have presented similar growths of STO on STO (001) that appear to have \( \phi \approx -0.62\pi \) (69°). In our experiments, we can repeatedly adjust the phase not via growth conditions but rather via substrate annealing conditions. If the substrate is annealed just before growth in high vacuum, the RHEED oscillations are very nearly in phase; if the substrate is annealed in high O\(_2\) pressure, the oscillations are very nearly out of phase. The substrate in Fig. 1(a) was annealed for one hour in 2.7 \( \times 10^{-6} \) mbar, the substrate in Fig. 1(b) was annealed for 20 minutes in 1.7 \( \times 10^{-3} \) mbar. Our experiments show that the annealing condition dictates the RHEED oscillation phase for a wide variety of different growth conditions!
φ created oscillations very nearly out of phase (Fig. 2c) has pinholes covering 15% ± 2% of its surface. These pinholes are expected for layer-by-layer growth and are why the XRR intensity does not recover to its initial maximum. Here the RHEED intensity is close to its minimum, yet the surface is very smooth.

Most growth systems do not have the capability to measure both RHEED and XRR simultaneously, so the question is: using only RHEED, is there any way to know when a layer is complete? The answer is simple: yes. As discussed above, determining the growth period \( T \) is straightforward. If it is true 2D growth and the starting surface is smooth, then each new monolayer is complete at times \( t = 2T, 3T, 4T, \ldots \). This is true independent of RHEED oscillation phase, and can be seen in Figs. 1(a) and (b) as well as Fig. 2(a) and (d).

For 2D growth, it is still possible to determine when a layer is complete using RHEED – even if the starting surface is not smooth. Returning our attention to the intensity as measured between pulses, each laser pulse causes a sharp decrease in intensity followed by an exponential recovery as the adatoms move on the surface and the surface heals. The step density model predicts a recovery of the form:

\[
I \approx I_0 \left( 1 - e^{(t - t_{\text{pulse}})/\tau} \right),
\]

where \( \tau \) is the relaxation time. When the surface is rough, the relaxation time \( \tau \) is short, as it takes very little time for the adatoms to diffuse the short distance required to find a hole, step edge, or island. On the other hand, when the sample is very smooth, this relaxation time is long, as it takes adatoms a long time before finding one of the few islands or holes on the surface.

An increase in relaxation time between laser pulses indicating the completion of a layer has also been seen explicitly in XRR. Increasing relaxation times as layers reach completion has also been seen in RHEED when the phase \( \phi = 0 \). Though it is counterintuitive, the recovery between pulses can be fit using the step density model even when the overall RHEED oscillation is more complex than this simple model. Thus, we can use the relaxation time after each laser pulse to characterize the layer coverage, as the relaxation times per pulse will still reach a maximum when the layer is complete, independent of the RHEED oscillation phase.

Using Eq. 2 we fit the recovery after each laser pulse for the growth shown in Fig. 1(b), where \( \phi \approx 0.81 \pi \). In Fig. 3, the blue dashed curve represents the relaxation times per pulse as measured by XRR and the green solid line represents the relaxation times as measured by RHEED. As expected, the XRR relaxation times are 11 maxima when the layer is complete, roughly every 11
FIG. 2. (Color online) Atomic force microscope images of two growths. All AFM images are approximately 1 µm × 1 µm. (a) and (d) show the simultaneous RHEED and XRR intensity oscillations, both nearly exactly out of phase. XRR is measured along (0 0 1)2 in (a), along (0 0 1)4 in (b). The first growth (a) was interrupted at the minimum of the XRR oscillations and near the maximum of the RHEED oscillations, the second growth (d) was interrupted after three complete monolayers, putting it near the minimum of the RHEED oscillations. Pre-growth AFM images are shown for both substrates in (b) and (e). In (c), we see the surface of (a) post growth, where ≈50% of the surface is covered with islands. The post growth surface of (f) has pinholes over 15% ± 2% of its surface. For both growths, the maximum of the XRR corresponds to a complete layer, whereas the RHEED intensity cannot be used to determine layer completion.

FIG. 3. (Color online) Recovery times per laser pulse for XRR (blue dashed) and RHEED (green solid). Error bars (not shown for clarity) are on average ±5%. These relaxation times are from the growth in Fig. 1(b). Clear oscillations in the relaxation times can be seen, with maxima occurring approximately every 11 laser pulses. Here, the maxima in the relaxation times from RHEED and x-ray occur after the same number of laser pulses and occur at the completion of the layer, thus a maximum in the RHEED relaxation time signals the completion of a layer.

laser pulses. Since the XRR intensity is at its maximum when the layer is complete, the oscillations of the XRR relaxation times are roughly in phase with the XRR intensity oscillations. Remarkably, the maxima in the relaxation times in the RHEED data occur at the same laser pulse as the XRR relaxation times, that is to say the relaxation times measured by both techniques are a maxima at \( t = T, 2T, 3T, \ldots \). Thus, the RHEED relaxation times are a maximum when the layer is complete – despite the fact that the RHEED intensity oscillation phase is nearly 180°!

Similar behavior has been seen at other RHEED intensity oscillation phases. Khodan et al. grew STO on STO (0 0 1) via PLD and used substrates etched using a similar HF etch. Assuming a smooth starting surface, their data present an oscillation phase of \( \phi \approx -0.62\pi \) (69°) with RHEED relaxation times that are a maxima at \( t = T, 2T, 3T, \ldots \), again as expected.

In conclusion, we have studied the homoepitaxial growth of STO on STO (0 0 1) via simultaneous in situ RHEED and XRR. We have shown that the RHEED intensity oscillation phase \( \phi \) can change even for identical growth conditions, and that in contrast the XRR intensity oscillations are always at a maximum when the layer is complete (\( \phi = 0 \) for XRR). From post-growth AFM images, we have shown that the substrate surface can be
rough even when the RHEED intensity oscillation is near a maximum and smooth when the RHEED oscillation is near a minimum.

Finally, the main point of this article is to provide a tool to the oxide growth community to determine when a layer is complete, a tool that does not depend on the magnitude of the RHEED intensity oscillation. For PLD, the RHEED and XRR intensities increase after each laser pulse as the adatoms diffuse and the surface heals. The characteristic relaxation time between each laser pulse is a maximum when the surface is least rough, and can be used to determine when a layer is complete. We have shown in our own results that this relaxation time is a maximum at layer completion for various phases of RHEED growth.

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To determine the coverage in Fig. 2(f), we masked any area more than 2 Å below the level of the terrace and compared the masked area to the total area. We measured this ratio for two \( \approx 100 \text{ nm}^2 \) areas per terrace.