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ABSTRACT

We perform in situ synchrotron x-ray diffraction (SXRD)/reflection high energy electron diffraction (RHEED) studies on the growth of complex oxide thin films by molecular beam epitaxy. The unique deposition chamber, located at the Advanced Photon Source, allows the preparation of complex oxide samples with monolayer precision and facilitates the formation of direct correlations between in situ x-ray studies and the more prevalent RHEED investigations. Importantly, because SXRD and RHEED probe different atomic-scale processes during thin film synthesis, their concomitant use enables the extraction of details concerning growth behavior that one cannot determine from either probe alone. We describe the results of such in situ studies on the epitaxial growth of perovskite LaNiO$_3$ on (La$_{0.18}$Sr$_{0.82}$)(Al$_{0.59}$Ta$_{0.41}$)O$_3$ (001).

We find that during the earliest stages of growth, the RHEED and x-ray signals do not agree with each other, demonstrating that while regular RHEED oscillations may imply high quality growth, the film–substrate interface can undergo significant changes during deposition due to the occurrence of interdiffusion at the growth temperature.

Molecular beam epitaxy (MBE) allows the growth of a single crystalline film one monolayer at a time. It is typically conducted in ultrahigh vacuum leading to high purity, and the slow growth rate and elevated temperatures generally result in excellent crystal quality. For these reasons, MBE is a paragon of thin film synthesis, and the samples grown by this method can exhibit unrivaled material properties. While the technique was first developed for III–V semiconductors, it was later adapted for the growth of other complex materials such as the multicomponent oxides, where synthesis is conducted in a background of oxygen or ozone. More recently, researchers combined MBE with methods known from metal–organic chemical vapor deposition and developed the hybrid MBE growth technique, which allows for greatly improved stoichiometric control.

The thickness of the growing film can be monitored with a quartz crystal microbalance, but such techniques are not sensitive to the deposition of individual monolayers. Many MBE researchers therefore employ reflection high energy electron diffraction (RHEED), where a focused beam of high energy electrons (10–30 keV) is aimed toward the sample and scattered by the surface of the growing film. When RHEED is conducted during MBE deposition, the scattered intensity oscillates between high and low values. The period of an oscillation typically corresponds to the growth of a single monolayer or unit cell, as will be discussed further below.

Another method for monitoring thickness during thin film growth is surface x-ray diffraction (SXRD). Here, one also monitors the intensity of a spot in reciprocal space that oscillates during deposition. The position of the spot must be sensitive to the structure of the surface, similar to RHEED. However, since the interaction between the incoming photons and electrons in the sample is much weaker than that between incoming electrons and sample
As shown, the system is mounted on a six-circle diffractometer, allowing rotation of the entire chamber about a vertical rotation axis. The position of the sample is indicated by the asterisk lying at the intersection of the vertical rotation axis and horizontal rotation axis (parallel to the transfer arm), with the surface normal (\( \hat{n} \)) aligned to point along the horizontal axis. The x rays (15.5 keV) enter the chamber through a beryllium window (dark blue line), scattering off the sample and into an area detector, allowing both in-plane and out-of-plane diffraction. RHEED (10 keV, incidence angle \( \sim 1.5^\circ \)) is performed using the electron gun (top) and RHEED camera (bottom).

In SXRD, a smooth surface leads to the formation of crystal truncation rods (CTRs) in reciprocal space. These rods are evident in Fig. 2. The large Ewald sphere for electron scattering is shown in light blue, while the small one for x-ray scattering is shown in gray (neither to scale). The incoming and outgoing vectors for electrons and x rays are labeled \( k_i \) and \( k_f \), respectively. The specular rod for a (001)-oriented crystal is also shown (also called the 00\(L\) rod), and the intersections of the rod with the electron and x-ray Ewald spheres are projected onto their corresponding detectors (RHEED screen or x-ray detector). We do not depict the array of rods parallel to the 00\(L\), e.g., 10\(L\) or 1\(L\); in the case of electron diffraction, these rods are very close together, and their intersections with the large Ewald sphere are shown as the elongated green spots on the RHEED screen.

In SXRD, a smooth surface leads to the formation of crystal truncation rods (CTRs) in reciprocal space. These rods are evident
at every Bragg reflection and extend along the surface normal, as depicted in the reciprocal space geometry shown in Fig. 2. We show the Ewald sphere construction for x rays (small gray sphere) in which scattering takes place at an “anti-Bragg” position, i.e., midway between Bragg reflections. For an (001)-oriented crystal substrate, such positions would correspond to the 00½, 00½, . . . positions along the specular rod in reciprocal lattice units. Lying away from the Bragg reflections, these regions are particularly sensitive to the surface, and we and others have shown that the associated scattered intensity oscillates with film thickness during step flow or layer-by-layer growth.\textsuperscript{25}

Surface reconstructions also lead to rods in reciprocal space that are unaffiliated with Bragg reflections; these can be measured with our system and modeled quantitatively\textsuperscript{26} for understanding the behavior of surfaces under different environmental conditions. Unlike RHEED, high vacuum is not necessary for x-ray scattering, allowing one to monitor growth in moderate to high pressure environments.\textsuperscript{27} Furthermore, grazing incident angles are unnecessary for surface sensitivity: with 8 keV x rays and a LSAT (001) crystalline substrate, the surface sensitive 00½ position corresponds to incoming and outgoing angles of \(-11°\) with respect to the surface.

We also show the Ewald sphere for high energy electron diffraction in Fig. 2 (large blue sphere). The Ewald sphere is relatively large due to the small electron wavelength. The rods due to electron scattering are narrowly spaced, and the intersections between the rods and the Ewald sphere reside on circles called Laue zones; we show the 0th and first zones in the figure.\textsuperscript{7} An example image from the RHEED camera is shown in Fig. 3(a). The rod from the 000, or the 00 rod, is shown at the center, with the 10 and 10 rods adjacent to it. Oscillations during growth may be observed at any of these features, and Haeni et al.\textsuperscript{8} have shown that the behavior of the oscillations can differ depending on which feature is monitored.

Scattering from RHEED is sensitive only to the topmost atomic planes due to the strong interaction between the incoming electrons and the electrons within the sample.\textsuperscript{11} During step-flow growth, the intensity stays constant, as the average surface roughness and crystallinity do not change. However, the surface roughens and smooths during layer-by-layer growth, producing one RHEED oscillation per layer completion.\textsuperscript{6,23} This is reflected by the following simplified equation for the intensity of the specular reflection:\textsuperscript{24}

\[
I_{\text{RHEED}}(\theta, \beta, S_0, q_s, d) = \frac{\beta}{2} + (1 - \beta S_0)^2 (1 - \theta)^2 + 2 \theta (1 - \theta) \cos(q_s d) (1 - \beta S_0),
\]

where \(\theta\) is the fractional layer coverage, \(\beta\) is the characteristic length of electron scattering by step edges, \(S_0\) is the step density, and \(q_s\) and \(d\) are the scattering vector and layer spacing along the surface normal, respectively.

In contrast, the x-ray intensity at the 00½ is sensitive not only to the evolving surface but also to the structure of the film and interface beneath, given the large penetration depth of hard x rays. Here, the scattered intensity at the 00½ as a function of film thickness \(N\) can be described by

\[
\frac{1}{2} \frac{I_{\text{RHEED}}}{I_{\text{RHEED}}^\text{half}}(N, \sigma_f, \sigma_s, \sigma_i, \sigma_r) = \left( \frac{F_f (1 - e^{-i\pi N \sigma_f})}{1 - e^{-i\pi \sigma_f}} + \frac{e^{-i\pi (N - 1) \sigma_f}}{1 - e^{-i\pi \sigma_f}} \right)^2 + \frac{F_s (1 - e^{-i\pi N \sigma_s})}{1 - e^{-i\pi \sigma_s}} \]

\[
\times \frac{F_s (1 - e^{-i\pi N \sigma_s})}{1 - e^{-i\pi \sigma_s}} \frac{1}{1 - e^{-i\pi \sigma_r}},
\]

where \(F_f\) and \(F_s\) are the structure factors for the film and substrate, \(\sigma_f\) and \(\sigma_s\) are roughness functions for the film and substrate, and \(\sigma_i\), \(\sigma_r\), and \(\sigma_s\) are the out-of-plane lattice parameters for the film, interface, and substrate, respectively.\textsuperscript{25} Although both intensities from Eqs. (1) and (2) exhibit oscillations during layer-by-layer growth, only Eq. (2) oscillates in the step-flow growth mode (with twice the period) due to interference between the surface and interface. In the case of homoepitaxial growth, however, the intensity at the 00½ is mainly sensitive to changes in surface roughness, much like RHEED.
Below, we present results for the case of an epitaxial LaNiO$_3$ film grown on LSAT (001). The as-received substrate was prepared by ultrasonic cleaning in acetone, isopropanol, and deionized water before entry into the MBE system. Prior to deposition, the substrate was heated to 570 °C in 10$^{-6}$ mbar of O$_3$. Growth was conducted using the shuttered growth technique, i.e., alternating between the La and Ni sources. The shutters were controlled with a program using a fixed deposition time (735 s per LaNiO$_3$ unit cell) as calibrated with a crystal thickness monitor prior to growth.

In Fig. 3(a), we show an image of the RHEED screen from the LSAT substrate prior to deposition. The intensity along the green line (through the 00 rod) is plotted in Fig. 3(b) as the green curve [rotated such that the vertical axis in (a) is now along the horizontal axis in (b)]. The time dependence of the 00 intensity profile during the growth of ten unit cells of LaNiO$_3$ is shown in Fig. 3(c).

In Fig. 4(a), we present the RHEED intensity integrated over pixels 60–66 in Fig. 3(c). In general, the RHEED oscillations reach a maximum with every complete NiO$_2$ deposition (smooth surface) and a minimum with every complete LaO deposition (rough surface), although the asymmetry in the RHEED profile indicates some degree of off-stoichiometry.

In Figs. 4(b) and 4(c), we show the results of simultaneous surface x-ray scattering taken at the 00$^1/2$ for two distinct regions on the area detector [Fig. 4(e)]. After close examination of the separate regions, we find that they arise from two distinct but nearly parallel 00L rods, with the intensity from region 1 stronger than the one from region 2. The growth mode is mostly layer-by-layer, producing a peak for every unit cell due to the oscillatory nature of surface roughness. However, some step-flow is evident, in agreement with the general lack of diffuse scatter adjacent to the rod. Step-flow growth causes a beating in intensity at $L = 1/2$ due to the oscillatory nature in structure factor discussed below. For example, the fourth and sixth maxima in region 1 are less intense than the fifth and seventh. This is illustrated by the schematic diagram shown in Fig. 4(f). We depict the surface during growth for step-flow layer-by-layer and mixed—where both step-flow and layer-by-layer modes are active. Here, adatoms near the step edges have sufficiently mobility to reach them and attach; those farther away form their own islands.

According to kinematical scattering, the scattered intensity at 00$^1/2$ should indeed be larger for $N = 1, 3, 5, 7, \ldots$, where $N$ is the unit cell film thickness. Interestingly, the behavior of the maxima in region 2 is generally out-of-phase with respect to region 1 and RHEED at the start of growth [Fig. 4(g)]. The underlying reasons for this are not only due to crystal miscut and mosaic, as both the (00$^1/2$)$_{000}$ and (00$^1/2$)$_{001}$ should behave similarly (using the nomenclature of Ref. 27 for describing the 00$^1/2$ stemming from either the 000 or 001 rod). However, the LSAT substrate can exhibit both A-site and B-site terminations over large portions of the crystal, with reference to the ABO$_3$ perovskite unit cell. Therefore, intensities from two slightly different rods can exist at the 00$^1/2$ position: (00$^1/2$)$_{A\text{-site}}$ and (00$^1/2$)$_{B\text{-site}}$, the former referring to the (La, Sr)O-terminated surface and the latter referring to the (Al, Ta)O$_2$-terminated surface.

![Fig. 4](image-url)
During initial deposition, growth may take place differently on the two surfaces, leading to a difference in the rod intensities. We deposit one monolayer of LaO first (blue shading), and as shown in Figs. 4(a)–4(c), both the RHEED and x-ray intensities initially rise before decreasing, when the La shutter is closed and the Ni shutter is open (green shading), the RHEED intensity increases sharply, but there is only a slight increase in the intensities of regions 1 and 2. We observe that the intensity maxima for RHEED, x-ray region 1, and x-ray region 2 do not align until roughly five unit cells; thereafter, it appears that the completion of NiO deposition consistently leads to the smoothest surface, while the completion of LaO leads to the roughest, based primarily on the behavior of the RHEED signal.

The behavior of the maxima in x-ray region 1 is consistent with growth on a (Al, Ta)O$_2$-terminated surface. (The greater intensity from this surface is consistent with the findings of Ohnishi et al. The unit cell film thickness for LaNiO$_3$, N, produces greater intensity at the 002 for N = 1, 3, 5, 7, . . . , as would be expected for this termination. When LaNiO$_3$ is grown on a (La, Sr)O-terminated surface, the results are shifted by a 1/2 unit cell. At it depends very sensitively on the interfacial structure between the LSAT substrate and the LaNiO$_3$ film, however, this cannot currently be proven. For example, after growth, it is unclear whether the topmost (La, Sr)O monolayer of the substrate can continue to be described as part of the substrate or be incorporated into the structure of the film. The time-dependent behavior of the x-ray signal in regions 1 and 2 suggests that significant rearrangement of the deposited species takes place at the surface during the deposition process itself. Indeed, diffusion in steep concentration gradients at elevated temperatures is very likely, as demonstrated by Chambers et al. who employed scanning transmission electron microscopy and other techniques for the study of intermixing at LaAlO$_3$/SrTiO$_3$ heterojunctions. More detailed in situ studies are needed to distinguish between the different scenarios.

Scans along the specular rod are shown in Fig. 5 for both the initial LSAT substrate and the complete LaNiO$_3$/LSAT heterostructure. The specular rod exhibits high intensities and well-defined thickness fringes even at the mid-zones near L = n/2 with n = 1, 3, 5, . . . . As the thickness fringes originate from the interference between the film surface and substrate interface, our results suggest that regardless of the initial substrate termination, the final interfaces are extremely smooth.

We describe early studies of oxide MBE growth utilizing both SXRD and RHEED as in situ probes. Due to the relatively strong interaction between matter and electrons and weak interaction between matter and x rays, RHEED and x rays sample very different aspects of the growth process. We employ both of these probes for the study of LaNiO$_3$ growth on LSAT (001). We find that while the behavior of the growth oscillations observed by RHEED and x rays generally agree after the deposition of approximately five unit cells, they are initially are out of phase with respect to each other. This is likely due to the several factors including a changing definition of the interface between the film and substrate and the occurrence of diffusion between the interface and surface during the deposition process. We also observe the presence of two specular rods on the LSAT substrate that differ in behavior during growth, presumably due to two distinct surface terminations. The oscillatory behavior of these rods suggests that significant atomic rearrangement takes place at the film–substrate interface under deposition conditions.

**AUTHORS’ CONTRIBUTIONS**

X.Y. and F.W. contributed equally this work.

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**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**REFERENCES**