



RHEED Intensity Oscillations for the Stoichiometric Growth of SrTiO₃ Thin Films by Reactive Molecular Beam Epitaxy

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Abstract. The growth of high quality multicomponent oxide thin films by reactive molecular beam epitaxy (MBE) requires precise composition control. We report the use of *in situ* reflection high-energy electron diffraction (RHEED) for the stoichiometric deposition of SrTiO₃ (1 0 0) from independent strontium and titanium sources. By monitoring changes in the RHEED intensity oscillations as monolayer doses of strontium and titanium are sequentially deposited, the Sr:Ti ratio can be adjusted to within 1% of stoichiometry. Furthermore, the presence of a beat frequency in the intensity oscillation envelope allows the adjustment of the strontium and titanium fluxes so that a full monolayer of coverage is obtained with each shuttered dose of strontium or titanium. RHEED oscillations have also been employed to determine the doping concentration in barium- and lanthanum-doped SrTiO₃ films.

Keywords: SrTiO₃, RHEED, molecular beam epitaxy (MBE), composition control, sequential deposition

1. Introduction

The primary obstacle in the growth of many oxide thin films by reactive molecular beam epitaxy (MBE) is precise composition control. Often, even 1–2% variation in monolayer doses results in impurity phases or intergrowths [1,2]. High quality films grown by this technique require that both the stoichiometry of the cations is maintained, and that each cation is supplied in a full monolayer dose.

Several *in situ* monitoring techniques have been employed in the growth of multicomponent oxides for composition control with varying degrees of success [3]. Atomic absorption spectroscopy (AA) offers better than 1% composition control of many elements [4–6]. Unfortunately, the absorption of the AA signal for some elements (e.g., titanium) is weak and compositional control of better than 5–10% is not possible using conventional hollow cathode AA sources. Laser atomic absorption offers better sensitivity than traditional AA, but is restricted to elements with absorption in wavelengths achievable with tunable lasers and has not been widely implemented due to its high cost [7,8].

Another *in situ* monitor that has been used for composition control in oxide MBE systems is reflection high-energy electron diffraction (RHEED). RHEED oscillations are routinely used to measure the film growth rate during the growth of either single component materials (e.g., Si, Ge, Fe, Pt) or two-component materials with a volatile constituent (e.g., GaAs, ZnSe, SrO, etc.). However, in multicomponent oxides where two or more components are not growing in an adsorption-controlled regime, measurement of the RHEED oscillation period is insufficient for composition control as there are multiple unknowns. While adjusting the ratio of incident fluxes in response to the appearance of identifiable impurity phase spots in the RHEED pattern has been used for composition control of some multicomponent oxides [9], it lacks the necessary sensitivity for the phase-pure growth of many multicomponent oxide thin films because it only alerts the grower to composition errors after an unwanted impurity phase has been nucleated. In some systems these unwanted impurities can be dissolved, but in others they cannot. Another technique, called RHEED difference, can alert the grower sooner to stoichio-

metry errors, but also is inherently sensitive only after unwanted impurities have been formed and begin to diffract [10].

This work focuses on the development of RHEED oscillations as a highly sensitive composition control method for the growth of multicomponent oxides. Previously, RHEED oscillations have been used during the deposition of the binary oxides CaO and SrO [11], and the co-deposition of multicomponent oxides [12], including SrTiO₃ [10,13,14] to determine when a full monolayer coverage has been obtained. RHEED oscillations have also been observed during the sequential deposition of many oxide films [15], including SrTiO₃ [10,13], but to our knowledge there has been no report of the use of these oscillations for the composition control of multicomponent oxides. We find that composition control based on RHEED oscillations during the shuttered deposition of SrTiO₃ is more accurate than AA to control the titanium flux and ensure that a complete monolayer of each cation is deposited in each shutter cycle.

2. Experimental

All films were grown in an MBE system (EPI 930) designed for and dedicated to the growth of oxides (Fig. 1) [16]. The strontium flux was produced by sublimating elemental strontium contained in an alumina crucible using a low-temperature effusion cell. The strontium flux was monitored by an AA system (Intelligent Sensor Technology model ATOMICAS) with closed-loop real-time feedback to the MBE shutter (WeckTech MicroCrystal software). A Ti-Ball™ titanium sublimation pump powered by a precision power supply (HP model 6673A) was used as a stable ($\pm 2\%$ per hour) alternative to an effusion cell or electron beam source to supply the titanium flux [17]. A RHEED gun (Staib model EK-15-RMG) operated at 10 kV and an incident angle of 1–2° supplied the electron beam to the substrate surface. The RHEED pattern was monitored with a CCD camera and real-time analysis software (k-Space model 400). Molecular beams of strontium and titanium were shuttered in a sequential manner (Fig. 2) to deliver alternating monolayer doses of each cation onto well oriented ($\pm 0.3^\circ$) SrTiO₃ (1 0 0) and (LaAlO₃)_{0.3}–(Sr₂AlTaO₆)_{0.35} LSAT (1 0 0) substrates. Before growth, the SrTiO₃ substrates were etched with a buffered-HF solution to achieve a TiO₂-

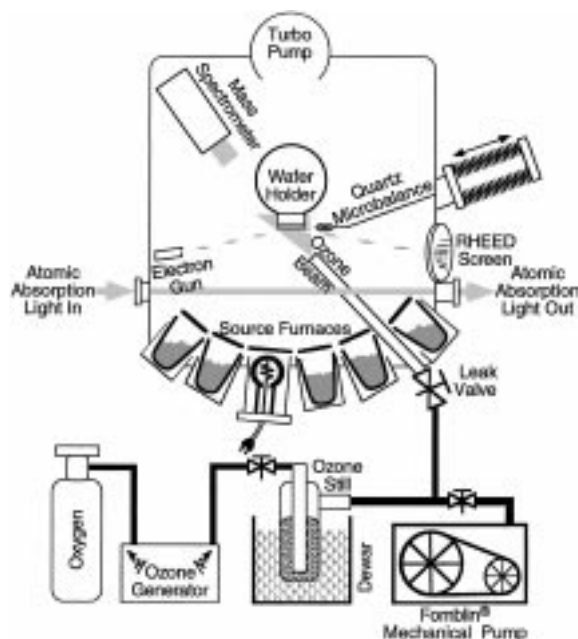


Fig. 1. A schematic diagram of the oxide MBE system used for the deposition of multicomponent oxide thin films.

terminated surface [18]. The average flux at the substrate position of both the strontium and titanium sources was 1.0×10^{14} atoms/cm²·s for all growths. The RHEED intensity oscillations are relatively insensitive to both substrate temperature and background oxygen pressure. During growth, the substrate temperature was typically held at 750°C as measured by an optical pyrometer, although similar results have been obtained for substrate temperatures as low as 550°C. The substrate was immersed in a continuous flux of molecular oxygen, yielding a background pressure of 2×10^{-7} Torr. The oxygen pressure at the substrate surface is about $20 \times$ higher than the measured background pressure [19].

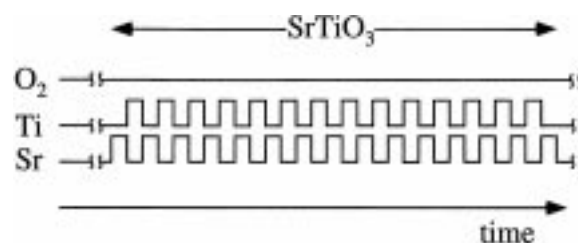


Fig. 2. Timing diagram of the sequential deposition of strontium and titanium atoms during the growth of SrTiO₃. Oxygen is continuously supplied to the substrate during growth.

3. Results and Discussion

3.1. Optimizing the Sr:Ti Ratio

To achieve the optimal ratio of Sr:Ti two complementary techniques are employed. AA has a high sensitivity to the strontium molecular beam and is used to control the deposition of exactly one monolayer during growth. Before growth, a quartz crystal microbalance (QCM) is utilized to calibrate the AA signal. The QCM is located approximately 3 cm directly in front of the substrate, so a correction factor (or tooling factor) is needed to relate the flux measured by the QCM to the flux reaching the substrate. This tooling factor is determined by measuring the periodicity of the specularly-reflected RHEED oscillations as several monolayers of SrO are deposited onto a SrTiO₃ substrate. The period of the RHEED intensity oscillations corresponds to the deposition of one monolayer of SrO [11]. The RHEED oscillations are done on a hot substrate, so in addition to geometric differences, the tooling factor (0.87) also includes sticking coefficient differences between the water-cooled QCM and the hot substrate. Once the AA flux vs. absorption calibration curve is established, the QCM is retracted, allowing strontium to reach the substrate. To deposit one monolayer of strontium, the strontium shutter is opened and the AA signal is converted to a flux using the AA vs. flux calibration curve. This flux is integrated until the desired one monolayer dose is delivered to the substrate at which time the strontium shutter is closed. Using these techniques, a full monolayer of strontium can reproducibly be supplied to the substrate in each shutter cycle.

Although AA provides the required composition control for strontium, it is quite insensitive to the titanium molecular beam and monolayer to monolayer variations in excess of 5% are common. For this reason, we have developed a method based on shuttered RHEED intensity oscillations to determine the correct titanium dose. Figure 3 shows a series of shutter-driven RHEED oscillations that occur during the deposition of homoepitaxial SrTiO₃. The intensity plotted is the average total diffracted intensity of the 00 streak of the zeroth Laue zone with the RHEED beam incident along the SrTiO₃ [011] azimuth. The pattern achieves a maximum intensity following the deposition of one monolayer of SrO and a minimum intensity following the

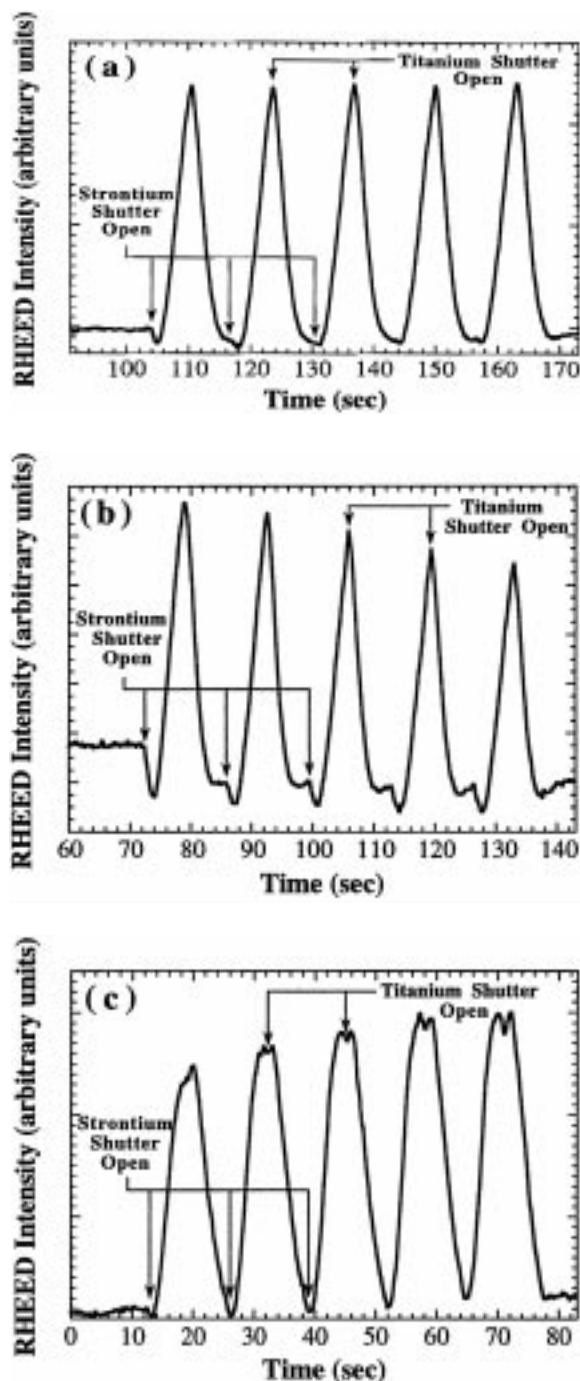


Fig. 3. RHEED intensity oscillations of the entire central diffracted streak (00 rod) as the strontium and titanium are deposited in a sequential manner. (a) Stoichiometric full monolayer of both strontium and titanium deposited. (b) Strontium dose held constant, but titanium dose increased by 3% from a full monolayer. (c) Strontium dose held constant, but titanium dose decreased by 3% from a full monolayer.

deposition of one monolayer of TiO_2 . If a full monolayer of titanium is deposited, the maximum intensity of the pattern remains constant after the deposition of several SrO layers (Fig. 3(a)). However, if excess titanium is deposited, the maximum intensity of the pattern will decrease with each succeeding monolayer (Fig. 3(b)). If an insufficient dose of titanium is deposited, the maximum intensity of the pattern will increase, and often a double peak can be seen (Fig. 3(c)). For clarity, Fig. 3 demonstrates these changes for a 3% change in flux; changes of $<1\%$ are less pronounced, but are noticeable. The fundamental reasons behind this behavior are unclear, but numerous growths of members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series [2], whose phase pure growth is very sensitive to stoichiometry, have confirmed the validity of this growth technique. Section 3.3 also presents evidence confirming the validity of this method.

The behavior of the intensity oscillations of the diffracted portion of the RHEED pattern is more reproducible than those of the specular reflection. The diffracted portion of the 00 and 01 streaks exhibit similar behavior regardless of the incident angle of the RHEED beam and the miscut of the substrate. The oscillations of the specular spot are much less predictable, however. In fact, the two previous studies of shuttered RHEED oscillations report conflicting behavior of the intensity oscillations of the specular spot. Iijima et al. [13] report an increase in the intensity with the deposition of SrO (which matches our results for the diffracted intensity), while Bodin et al. [10] report an increase in intensity during the deposition of TiO_2 . Both of these phenomena have been observed in different growths (or even at different times in the same growth), with the specular beam oscillating in-phase and out-of-phase with the diffracted intensity (Fig. 4(a), 4(b), and 4(c)). This type of behavior has been observed during the MBE growth of GaAs by codeposition where the phase shift is linked to the angle of incidence of the RHEED beam [20]. A direct correlation between the angle of the incident beam and the phase of oscillation of the specular reflection for the growth of SrTiO_3 by sequential deposition has not been established. A “double peak” behavior where an intensity maximum is reached after the deposition of both the SrO and TiO_2 layers has also been observed (Fig. 4(d)). This may

be the result of the sensitivity of the specular reflection to the surface roughness of the film. After the deposition of a complete monolayer of SrO or TiO_2 , the surface is the smoothest and the specularly-reflected intensity is at a maximum. The roughest film surface occurs with the deposition of a half monolayer of each cation, corresponding to the reflected intensity minimum. This behavior has not been observed for all growths and more work must be done to fully understand the relationship between the specular oscillations and variables such as substrate miscut and the angle of incidence of the RHEED beam.

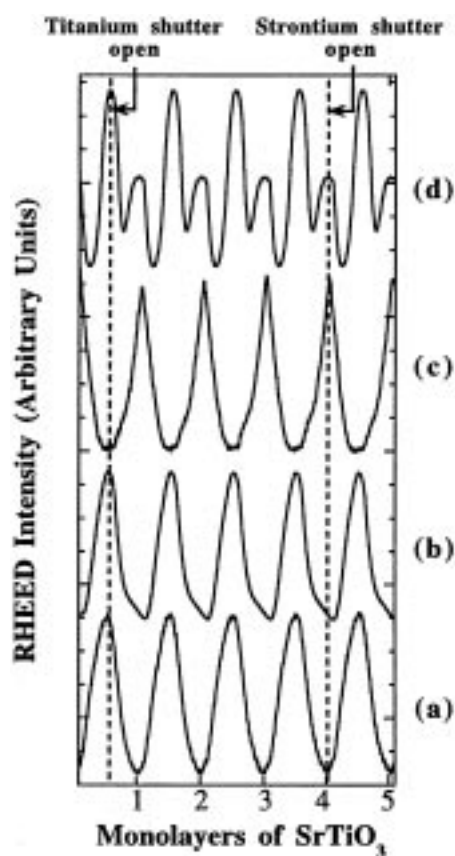


Fig. 4. RHEED intensity oscillations with the RHEED beam incident along the SrTiO_3 [0 1 1] azimuth during different growths of SrTiO_3 by sequential deposition. (a) average diffracted intensity of the 00 streak, (b) specular spot oscillating in-phase with the diffracted intensity, (c) specular spot oscillating 180° out of phase with diffracted intensity, (d) specular spot intensity “double peak” with peaks occurring at the termination of both the SrO and TiO_2 layers.

3.2. Determination of Doping Levels

This technique is also useful when a high level (e.g., 1–20%) of a substitutional dopant or solid solution constituent is desired in a SrTiO_3 film. For instance, we commonly use La-doped SrTiO_3 as a bottom electrode for the growth of overlying epitaxial perovskite films; barium is often added to SrTiO_3 to modify its dielectric properties. Because both of these dopants substitute onto the Sr-site in the lattice, it is common to codeposit the strontium and dopant species. AA is insensitive to the low dopant flux levels desired in these films and it is most common to estimate the doping percentage by extrapolation from an Arrhenius plot of the flux vs. reciprocal temperature of the effusion cell. This is an imprecise method. We have observed up to 50% discrepancy in the calculated doping level and the actual amount of dopant incorporated into the film.

Using RHEED oscillations the doping levels in these films can more accurately be specified. To grow a doped SrTiO_3 film, the correct titanium dose must first be determined using the methods described above. The strontium dose is then decreased by the desired doping level (by proportionally shortening the time that the strontium shutter is open) and both the dopant and strontium are deposited simultaneously. If excess dopant is deposited, the RHEED intensity pattern will increase as in Fig. 3(c). If insufficient dopant is added, the pattern will decrease as in Fig. 3(b). In this manner, the dopant's effusion cell temperature (or codeposition time) is adjusted until a sufficient flux is achieved to compensate for the strontium deficiency, and a stoichiometric RHEED pattern is again reached.

3.3. Incomplete Monolayer Coverage

It is possible to confirm that the methods described above achieve full monolayer coverage of each cation by monitoring the intensity of the RHEED pattern over many supply cycles. If the Sr:Ti ratio is correct and a full monolayer of each cation is being deposited, no fluctuation in the maximum or minimum intensity of the pattern is observed (Fig. 5(c)). However, if the Sr:Ti ratio is maintained constant, but the dose of each is increased or decreased, beat frequencies are observed. Figure 5(c) shows the RHEED intensity oscillations as 20 monolayers of stoichiometric SrTiO_3 are deposited in full monolayer doses. For

the deposition of 1.15 and 0.85 monolayers per dose, there is an overall maximum and minimum intensity in the envelope of the oscillations every 6–7 monolayers (Fig. 5(a) and 5(e)). Similarly, the deposition of 1.1 or 0.9 monolayers results in a beat frequency of 10 monolayers (Fig. 5(d) and 5(b)). This result is identical to results obtained during the shuttered deposition of GaAs films at low temperatures, where fractional coverage resulted in a modulation of the RHEED intensity oscillation

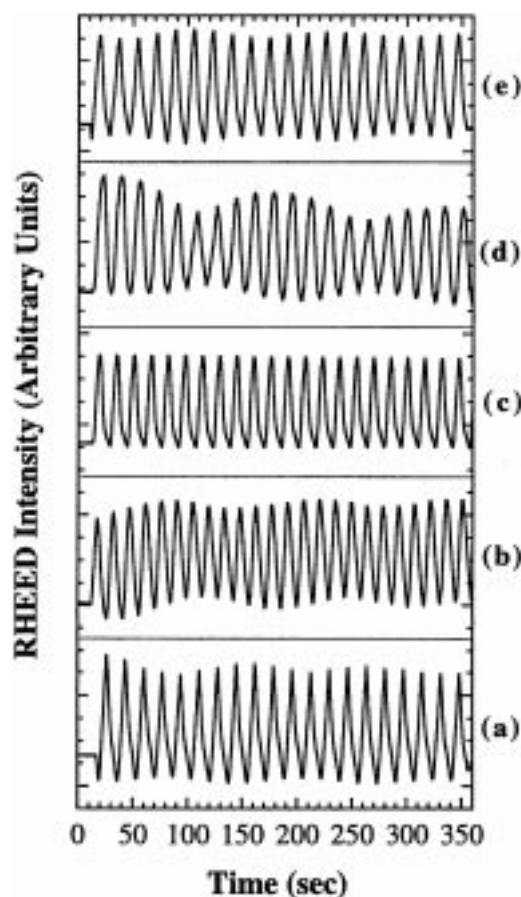


Fig. 5. Beat frequency observed during the deposition of incomplete monolayers of strontium and titanium where the incomplete monolayers contain the correct stoichiometry (i.e., Sr:Ti = 1). (a) 0.85 monolayers of each cation supplied with each shutter cycle; beat frequency = 6–7 oscillations. (b) 0.90 monolayers of each cation supplied with each shutter cycle; beat frequency = 10 oscillations. (c) Complete monolayer of each cation supplied with each shutter cycle; no beat frequency observed. (d) 1.10 monolayers of each cation supplied with each shutter cycle; beat frequency = 10 oscillations. (e) 1.15 monolayers of each cation supplied with each shutter cycle; beat frequency = 6–7 oscillations.

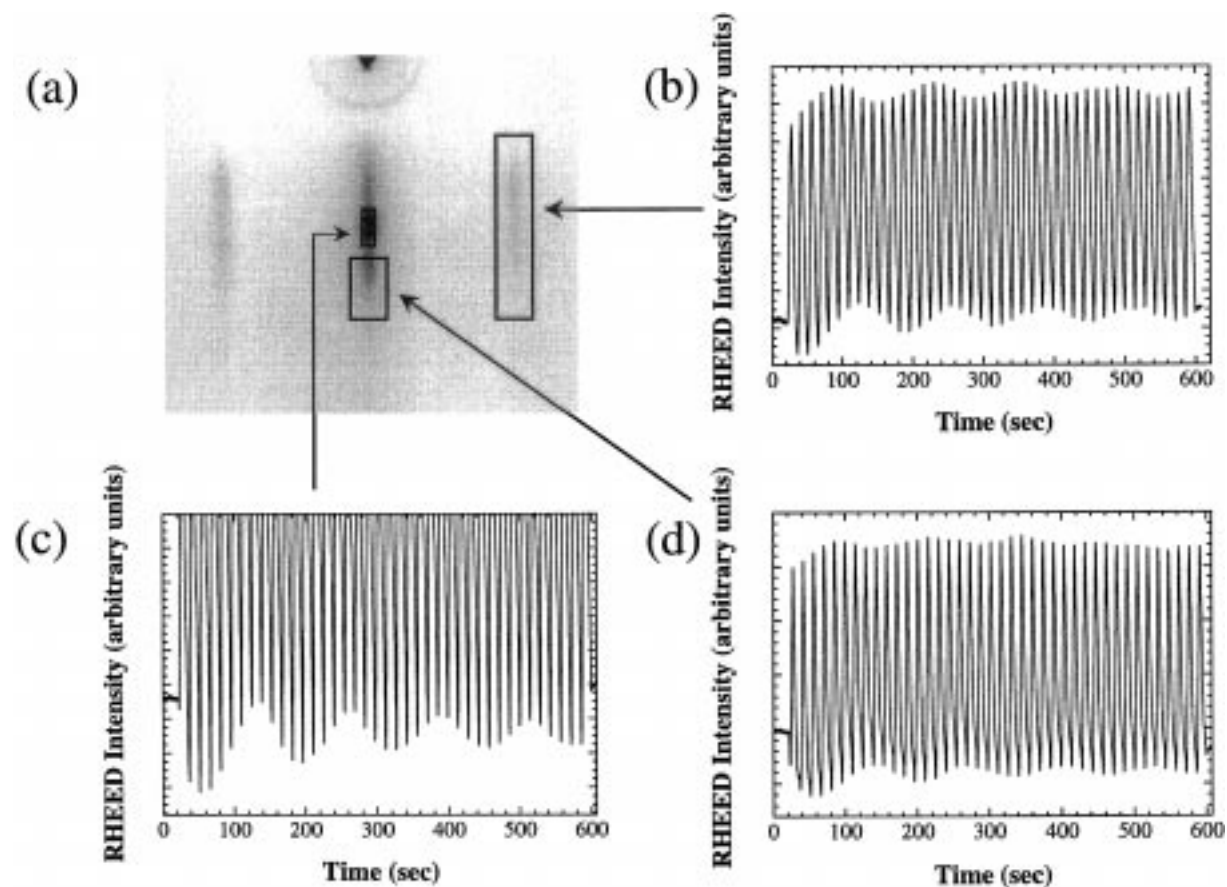


Fig. 6. Beat frequency during the deposition of 0.90 monolayers of each cation with the RHEED beam incident along the [011] azimuth of SrTiO_3 . (a) RHEED pattern of the SrTiO_3 [011] azimuth, (b) average intensity of the entire 10 streak, (c) average intensity of the specular reflection, (d) average intensity of the diffracted portion of the 00 streak.

envelope [21]. This beat frequency is evident in the intensity oscillations of the diffracted 00 streak and 10 streak of the zeroth Laue zone, as well as the reflected specular spot (Fig. 6).

4. Conclusions

The use of shuttered RHEED oscillations in conjunction with AA for the stoichiometric deposition of SrTiO_3 thin films by MBE has been demonstrated. This technique has also been utilized to correctly determine the doping levels in lanthanum and barium doped SrTiO_3 films. The presence of a beat frequency in the RHEED intensity oscillation envelope occurs when incomplete monolayer doses are supplied, providing a confirmation of the effectiveness of this technique, as well as a means to monitor the

deposition of complete monolayers. This technique has enabled the growth of the first five members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper series and provides an effective alternative to other more costly systems for the precise control of titanium.

Acknowledgments

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