RHEED in-situ Monitored Step Edge Diffusion During Interrupted Laser Ablation Epitaxy Growth of $SrTiO_3$

T. C. Wang, J. Y. Lee, C. C. Hsieh, J. Y. Juang, K. H. Wu, T. M. Uen, and Y. S. Gou

Department of Electrophysics, National Chiao-Tung University, Hsinchu, Taiwan 300, R.O.C.

(Received July 10, 2003)

A series of investigations on the interrupted deposition of laser ablation strontium titanate epitaxy growth were conducted. RHEED intensity recovery curves at various temperatures show a near-quadratic power law dependence on annealing time. Combined with the evidence showing the intimate correlation between the step edge density and the RHEED intensity, a diffusion Arrhenius plot with the activation energy of 1.0 eV was obtained for the kinetics of step edge migration.

PACS numbers: 61.14.Hg, 68.55.Jk, 81.15.Fg

I. INTRODUCTION

Since the discovery two decades ago, reflection high energy electron diffraction (RHEED) has proved to be one of the most valuable tools for monitoring, analyzing and even controling MBE thin film growth [1–3]. Due to the high energy and the ultra-low angle of the glancing electron beam, which is almost in the direction perpendicular to the depositing source materials, RHEED is well known for its capability of in-situ resolving the surface condition at the atomic level of the topmost few layers. During the layer by layer growth condition, the RHEED intensity was found to oscillate with a period synchronized with the number of growing layers [2]. This feature has long been used to symbolize the well-controlled layer growth condition.

Although the application of RHEED in epitaxy growth has been shown to be successful, the identification of the detailed diffraction mechanism has not been conclusive. In principle the higher intensity represents a smoother plane and the lower intensity symbolizes a rougher surface; there are still two theories under debate. According to a two-layer interference picture, the topmost surface coverage can be equated to the RHEED diffraction intensity [4]. Another diffraction mechanism attributed the RHEED intensity to the density of step edges [5]. From the evidence currently available, neither theory can be regarded as a complete solution for all the material conditions. For example, the step edge density theory encountered challenges especially in the high density regime in which the RHEED intensity even evolves proportionally to the edge density [6, 7].

© 2004 THE PHYSICAL SOCIETY OF THE REPUBLIC OF CHINA

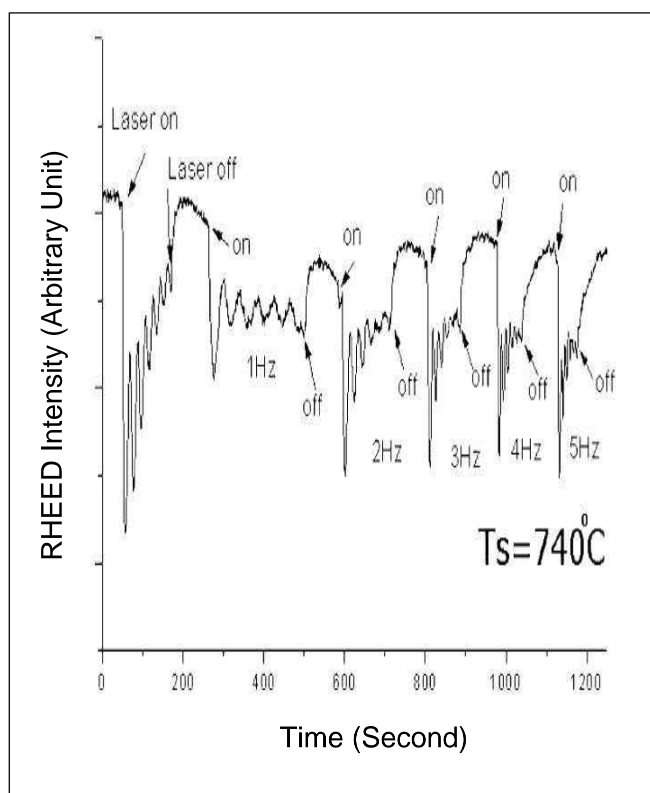

FIG. 1: A series of deposition-annealing RHEED monitoring was conducted for laser repetition rates from 1 Hz to 5 Hz. The deposited amounts of STO were supposed to be the same for each drop with $14 \sim 17$ pulses Sudden drops of the RHEED intensity can be seen at all the laser turn-on points after each annealing period.

II. STEP-EDGE INTERPRETATION FOR THE RHEED INTENSITY

In order to clarify the essential difference between these two pictures, an investigation on the RHEED evolution during the interrupted laser deposition for $SrTiO_3$ film growth was conducted [8, 9]. The most evident result for the step edge density interpretation for the RHEED intensity came from a series of deposition and annealing treatment, as discussed in the following.

The as-polished STO sample was deposited by laser ablation with various repetition rates, but with the same count of pulses during which the RHEED intensity oscillates to show layer growth. It was noted that the RHEED intensity experienced a sudden drop each time the laser was turned on again, after the same amount of deposition was interrupted and the sample was annealed for the same period, as shown in Fig. 1. Since the laser count was kept at $14 \sim 17$ pulses for each drop, the same for all repetition rates from 1Hz to 5 Hz, the amount of materials deposited or the coverage of the surface should be quite

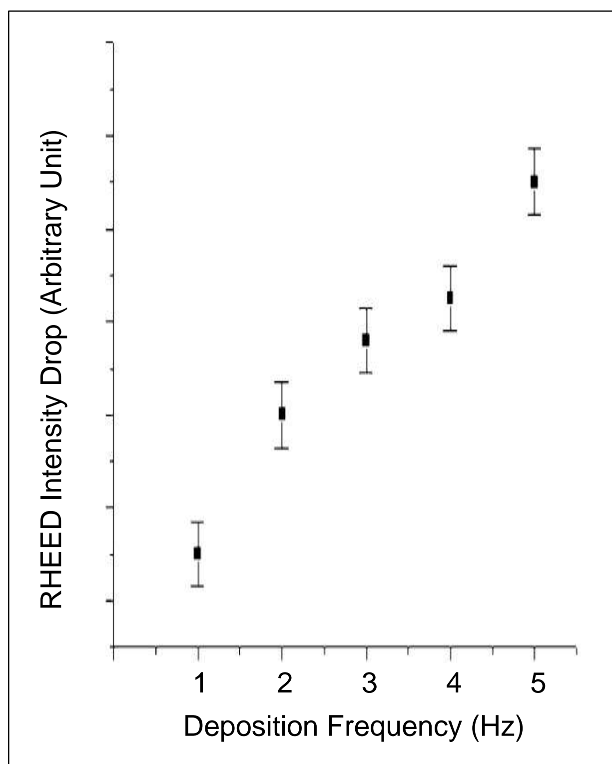

FIG. 2: The RHEED intensity drops in Fig. 1 were found to increase with an increased laser repetition rate, suggesting that step edge density accounts for the RHEED diffraction instead of topmost layer coverage, which was kept unchanged for all 5 repetition rates by having the same total pulses.

the same. However from the RHEED intensity drop data, as shown in Fig. 2, the drop depth was proportional to the repetition rate. Which means, as the step edge density was increased by increasing the deposition rate, as well as the number of islands formed under the assumption of monolayer deposition [10, 11], the RHEED intensity dropped more.

III. DIFFUSION KINETICS EXTRACTED FROM RHEED INTENSITY

The step edge model can provide not only a geometric measure of the surface morphology but also kinetic information, such as diffusion characteristics. In our investigation on the in-situ RHEED monitoring the interrupted deposition recovery, we found that, at least for a smoother surface, the deposition-interrupted time-annealing curves possess observable temperature dependent features. As shown in Fig. 3, for the near-peak-interrupted oscillating RHEED intensity, the annealing data in the insets showed a clear temperature dependence, as enlarged in Fig. 4. The most intriguing fact to be noted is the monotonic

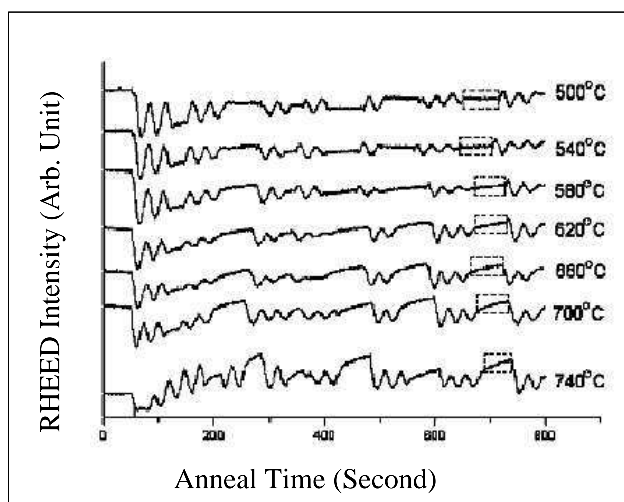

FIG. 3: Time evolution of the RHEED intensity from 500C to 740C. Layer growth can be confirmed from the oscillation for all curves. The insets show recovery from near-peak positions of oscillations.

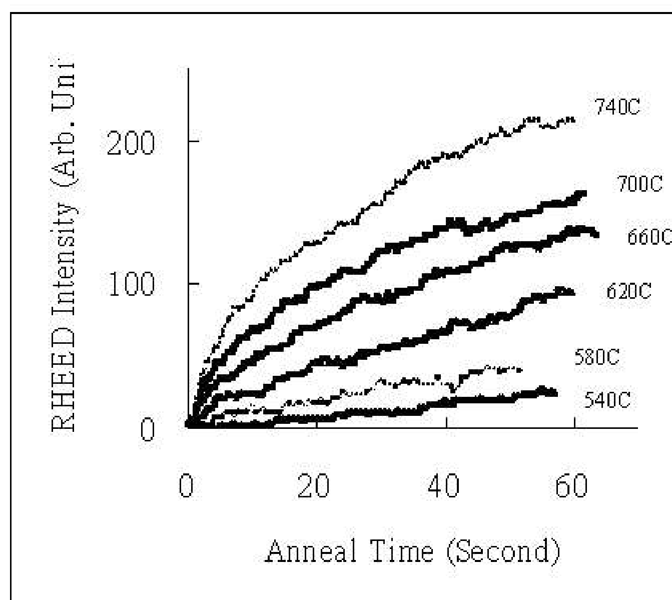

FIG. 4: Enlarged time curves of the RHEED intensity dring the annealing after the interrupted depositions in Fig. 3. The curvatures show a monotonic increasing dependence on temperature.

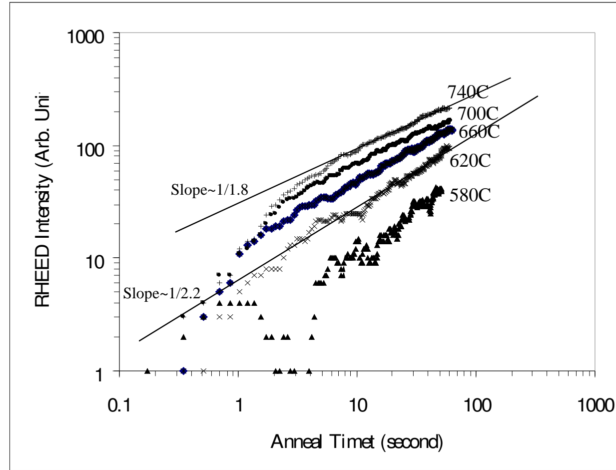

FIG. 5: Double logarithmic plot of RHEED intensity v.s annealing time for various temperature. Except for the first few seconds, all curves display a clear linearity with a slope of 2 ± 0.2 during most of the annealing time.

trend of the curvatures. Double-logarithmic plots were checked for these curves, as shown in Fig. 5. From the apparent linearity observed in these curves, one immediately realized that there is a power law embedded in the time annealing RHEED intensity. Although in earlier papers the temporal behavior of the annealing recovery curves were analyzed using exponential functions with corresponding time constants [12], we noticed that a power law, especially a quadratic power time dependence as fitted in Fig. 6, can provide straightforward kinetic information for the interpretation of RHEED intensity.

In an early RHEED intensity analysis done for GaAs, Neave *et al.* [13] developed a method for deciding the diffusion properties from the Einstein relation:

$$\langle x^2 \rangle = 2Dt \,, \tag{1}$$

where $\langle x^2 \rangle$ represents the mean square displacement of adatom diffusion with the hopping time t, and D is the diffusion coefficient. The displacement was determined by the step separation of the epitaxy film. Diffusion time was calculated from the deposition rate. Also the activation energy was obtained from the Arrhenius plot, by taking the temperature thresholds of layer growth to step flow transition for various deposition rates. In such a kinetic study, the RHEED intensity provided a qualitative criterion to determine another quantity, namely the temperature thresholds of different growth mechanisms.

For our film deposition research, however, the time evolution of the annealed RHEED intensity was found to show a quantitative dependence relation on temperature. If the complete condensation assumption is made, the RHEED intensity would be directly proportional to the migration velocity of the step edges [11]. Based on this scenario, we drew the Arrhenius plot for the RHEED intensity. The result was obtained with an activation energy of 1.0 eV, which corresponds to the order of the activation energy of atomistic diffusion

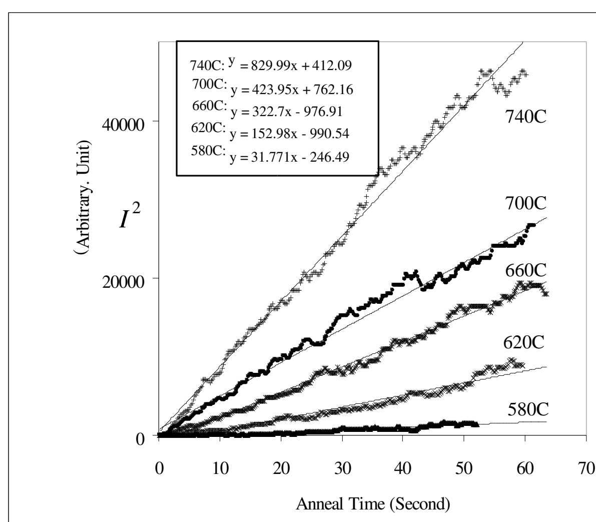

FIG. 6: RHEED intensity square vs. annealing time for various temperatures. The inset shows perfect linear fittings for the curves. A monotonic dependence can be clearly seen.

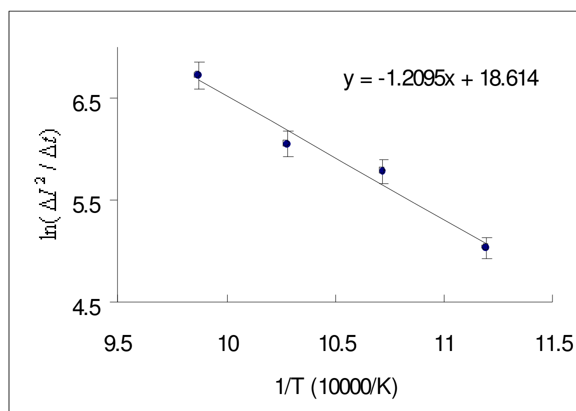

FIG. 7: Diffusion Arrhenius plot of $\ln(\Delta I^2/t)$ vs. $1/T$. An activation energy of 1.0 eV can be obtained. Combined with the step migration assumption, this energy level strongly suggests that certain atomistic barrier-crossing mechanisms can be revealed directly from RHEED monitoring.

of the crystal surface, as shown in Fig. 7. Although, due to the undefined proportionality factor between the step edge density and the RHEED intensity, the diffusion coefficients of corresponding temperatures can not be explicitly obtained, the activation energy of the order of the atomistic barriers suggests that, under well-controlled diffraction conditions and a proper film environment, the RHEED intensity can provide useful information for kinetic analysis. Starting from the diffusion characteristics directly provided by the RHEED

intensity, we are constructing a model of the dynamics for the step edge migration, the result is expected to be published in the near future.

In summary, following the step edge model, we conducted a series of in-situ RHEED intensity investigations on the interrupted deposition of STO epitaxy film. The RHEED intensity can provide kinetic information for the step edge diffusion, for which an activation energy of 1.0 eV was obtained from the diffusion Arrhenius plot, with the diffusion length assumed to be proportional to the RHEED intensity.

Acknowledgments

This work was partly supported by the National Science Council of Taiwan under grants NSC91-2112-M009-049.

References

[1] J. J. Harris, B. A. Joyce, and P. J. Dobson, Surf. Sci. **103**, L90 (1981); ibid. **108**, L444 (1981); C. E. C. Wood, ibid. **108**, L441 (1981).
[2] J. H. Neave et al., Appl. Phys. A**31**, 1 (1983).
[3] *RHEED and Reflection Imaging of Surfaces*, edited by P. K. Larsen and P. J. Dobson (Plenum, New York, 1988), p. 427.
[4] C. S. Lent and P. I. Cohen, Surf. Sci. **139**, 121 (1985).
[5] J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, Appl. Phys. A**31** (1983); S. Stoyanov: Surface Sci. **199**, 226 (1988).
[6] U. Korte and P. A. Maksym, Phys. Rev. Lett. **78**, 2381 (1997).
[7] Z. Mitura, S. L. Dudarev, and M. J. Whelan, Phys. Rev. B. **57**, 6309 (1998).
[8] J. Y. Lee, J. Y. Juang, K. H. Wu, T. M. Uen, and Y. S. Guo, Surface Sci. **488**, 277 (2001).
[9] J. Y. Lee, T. C. Wang, S. F. Chen, J. Y. Juang, J. Y. Lin, K. H. Wu, T. M. Uen, and Y. S. Gou, Chinese Journal of Physics **39**, L299 (2001).
[10] J. Y. Lee *et al.*, Physica B **284-288**, 2099 (2000).
[11] S. Stoyanov and M. Michai1ov, Surf. Sci. **202**, 109 (1988).
[12] T. Franke, P. Kreutzer, Th. Zacher, W. Naumann, and R. Anton, J. Crystal Growth **193**, 451 (1998).
[13] J. H. Neave, P. J. Dobson, B. A. Joyce, and Jing Zhang, Appl. Phys. Lett. **47**, 100 (1985).