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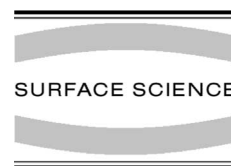

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Annealing characteristics of pulsed laser deposited homoepitaxial $SrTiO_3$ thin films

J.Y. Lee *, J.Y. Juang, K.H. Wu, T.M. Uen, Y.S. Gou

Department of Electrophysics, National Chiao-Tung University, Hsinchu, Taiwan, ROC

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Abstract

The homoepitaxial growth of $SrTiO_3$ (STO) films on as-polished STO(1 0 0) substrates by pulsed laser deposition has been exploited in detail. The intimate correlation between the surface step edge density and reflection high-energy electron diffraction (RHEED) intensity is clearly demonstrated by measuring the relation between the initial RHEED intensity drop and laser repetition rates. Systematic in situ annealing schemes were performed to investigate the film growth mechanisms. The results indicate that the two or three level growth may have occurred during some annealing schemes and can be interpreted by Stoyanov's step edge density model. Complementary atomic force microscopy investigations of the film surfaces further lend direct support to the RHEED intensity observations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Epitaxy; Growth; Reflection high-energy electron diffraction (RHEED); Atomic force microscopy

1. Introduction

Strontium titanate $SrTiO_3$ (STO) is one of the most important materials widely used in today's technologies. The ferroelectricity and low dielectric loss had been the keys to make tunable (frequency and phase agile) microwave devices and many other radio frequency applications [1,2]. Moreover, the STO films are also playing a crucial role in realizing ultrahigh capacity semiconducting memory devices with very low leakage current [3,4]. It is also a nearly perfect template material for growing high temperature superconducting thin films. In every aspect of applications, the capability of manipulating the growth of STO thinfilms down to the atomic level is an obvious prerequisite. However, the understanding of the growth mechanism of oxide materials, unlike metals and semiconductors, is somewhat lacking and, thus, is of fundamental interest.

Pulsed laser deposition (PLD), owing to its explosive nature, has been proved to be a powerful tool for preparing thin films of oxide materials [5,6]. The capability of preserving the target stoichiometry is one of the advantages PLD has to offer for this purpose. The ease of controlling and adjusting the deposition parameters by also makes it a convenient tool for studying the intriguing behaviors involved in growing the multicomponent perovskite oxide thin films. In this report, the homoepitaxial growth of STO films on as-polished STO(1 0 0) substrate is exploited in detail. The

* Corresponding author. Fax: +886-3571-4031.
E-mail address: chaosman@seed.net.tw (J.Y. Lee).

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results not only confirmed our previous conjecture of directly correlating the surface step density to the intensity of the reflection high-energy electron diffraction (RHEED) in a more quantitative fashion [5], but also revealed a number of peculiar features associating the growth kinetics of STO films with thermal annealing. In particular, it is argued that, by monitoring the changes of the RHEED intensity (even after the deposition is stopped) in various annealing temperature ranges, kinetics of different growth modes can be uncovered rather unambiguously.

2. Experiments

A KrF excimer laser with pulse duration of 30 ns, operated primarily at repetition rates of 1–5 Hz, was used for deposition. The target was a single-crystal disk of STO. The typical energy density used was estimated to be about 2 J/cm^2. All films were deposited at an oxygen pressure of 5×10^{-4} Torr. The substrate temperature was controlled by a resistive heater block and was varied from room temperature to 740°C. The energy of electron beam used for in situ RHEED diagnostics was 20 keV. The incident electron beam, with a grazing angle of 0.7°, was directed along [1 0 0] direction of STO substrate. With a de Broglie wavelength of about 0.86 Å, the grazing electron beam is slightly off-Bragg conditions. Under this circumstance the RHEED intensity is expected to be most sensitive to the step edges on the surface [7–9]. The ex situ atomic force microscopy (AFM) investigations were performed to elucidate the results of RHEED oscillation complementarily.

3. Results and discussion

3.1. Step edge density vs. RHEED intensity

Previously, the study of the temperature dependence of RHEED intensity oscillation during deposition of STO has suggested the intimate correlation between the RHEED intensity and the step density of the growing films surface [5]. Here, in order to delineate such correlation in a more quantitative manner, systematic in situ annealing experiments on films deposited on as-polished STO substrates were performed. The experiments were carried out as follows. A typical deposition run was divided into several sections while keep the substrate temperature fixed. In each deposition section, nominally the same amount of STO material (i.e. same number of laser pulses) was deposited onto the substrates at various repetition rates. In between each section, the laser was turned off and the films were annealed at the same temperature for a fixed period of time. During the whole process, the RHEED intensity of the specular reflection [5] was monitored.

Fig. 1(a) shows a typical example of such an experiment performed at 740°C. Each segment in the plot describes the change of RHEED intensity over the period of delivering 240 laser pulses deposit plus 90 s of "annealing" time. As is evident that, although the laser repetition rate has been varied from 1–5 Hz, annealing has effectively recovered the RHEED intensity completely. This is suggestive that each deposition segment is taking place on essentially the same surface condition, regardless of previous deposition events. Nonetheless, a closer examination reveals that, although the film growth behavior at each deposition rate is qualitatively similar, the amount of RHEED intensity drop (ΔI) at the beginning of each deposition is quantitatively different. As shown in Fig. 1(b), ΔI increases monotonically with increasing laser repetition rate. We argue that this is, in fact, a strong evidence for correlating the RHEED intensity to the existing step density on a growing films surface.

Firstly, it is noted that the total number of laser pulses delivered during the period of reaching the first intensity minimum for each case is about the same (14–17 pulses). This implies that about the same amount of STO deposit has been delivered to the substrate before the RHEED intensity hits its minimum. If we further assume that the distribution of the deposit is two-dimensional (there has been much evidence showing that the growth of STO creates predominantly unit-cell height steps on the surface [12,14]), the surface coverage area should be constant for each case at the RHEED intensity minimum. The relation between the aver-

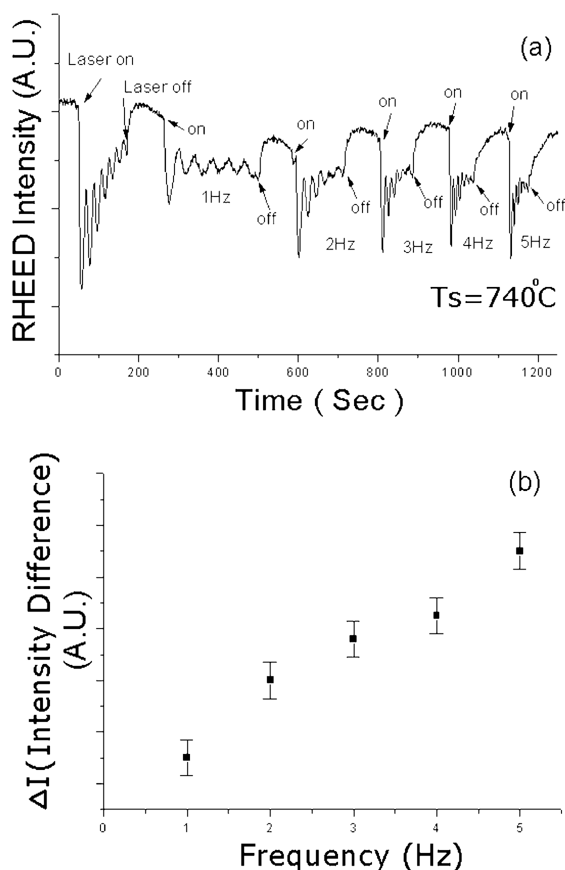

Fig. 1. (a) RHEED oscillations for a film deposited on the same as-polished STO substrate at different laser repetition rates. Each segment of the RHEED intensity corresponds to a number of 240 laser pulses and an annealing time of 90 s. The repetition rate was varied from 1 to 5 Hz. (b) The depth of the initial drop of the RHEED intensity as a function of laser repetition rate extracted from (a).

age size and number of the growing islands can then be expressed as.

$$R_i^2 \times N_i = R_j^2 \times N_j = \text{constant}. \qquad (1)$$

Here R and N are the average size and number density of the growing island, respectively. The subscript indices i and j are the respective laser repetition rates.

Based on the step edge density model, it follows that ΔI should be proportional to the total length of the step edge on the growing surface, thus can be approximated as

$$\Delta I_i : \Delta I_j \cong R_i \times N_i : R_j \times N_j = N_i^{1/2} : N_j^{1/2} = R_j : R_i \qquad (2)$$

Eq. (2) indicates that a larger number of growing islands, and hence smaller average size, on the film surface will lead to a larger ΔI. This, when translated into experimental parameters, implies that a higher laser repetition rate will result in a deeper ΔI with a larger amount of smaller islands on the growing surface. The former feature is immediately evidenced in Fig. 1.

The AFM images of three STO films deposited on the as-polished STO substrates at repetition rates of 1, 2, and 4 Hz are shown in Fig. 2 to reveal the microstructure of the respective film surfaces. The images were obtained by halting deposition at the respective minimum of the RHEED intensity. The images clearly show that the average island size decreases with increasing repetition rate, and is qualitatively consistent with what one would expect. More quantitative results are obtained by image analysis to convert the number of islands on the surface and their area coverage. The results are listed in Table 1. It is interesting to note that the surface coverage at each RHEED intensity minimum ranges from about 0.2 to 0.3 as the laser repetition rate changes from 1 to 4 Hz. The values are much lower than the percolation threshold of 0.5 for a static two-dimensional system [10], suggesting that in situ coalescence during deposition may have occurred. In any case, it seems that the assumption of constant coverage is better justified for cases at higher repetition rates. Also included in Table 1 are the ratios between the island size, number and the corresponding ΔI for films deposited at various laser repetition rates. It is meant to check the validity of Eq. (2) from microstructure measurements. The results, especially for the cases of higher laser repetition rates where the in situ coalescence is less significant, are in good agreement with that predicted by Eq. (2). In summary, the present results are indeed consistent with the conjecture of directly attributing the RHEED intensity oscillation to the variations in surface step density [5].

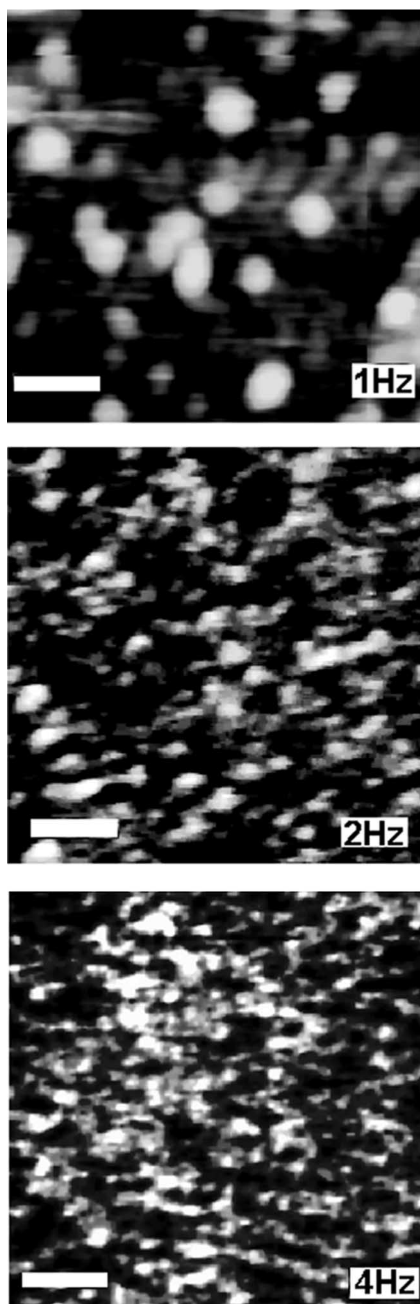

Fig. 2. The AFM images showing the surface morphology of STO films deposited on the as-polished STO substrates at repetition rates of 1, 2, and 4 Hz, respectively. The images were obtained by halting the deposition when the RHEED intensity dropped to their respective minimum. The scale bars represent 100 nm.

3.2. Growth kinetics – effects of in situ annealing

From the studies described in previous section, it is clear that monitoring the RHEED intensity variations not only is useful in characterizing the prevailing film growth mode during deposition, but also can be a powerful tool for extracting rich information about the detailed evolution of a growing surface. In the remaining of the paper, we present the results obtained from a series of in situ annealing studies.

Fig. 3(a) shows a series of in situ annealing studies on homoepitaxial STO films over the temperature range of 500–760°C. In each trace of the figure, the RHEED intensity is plotted as a function of time. The regions showing intensity oscillations represent the periods of deposition. The segments with no intensity oscillation depict periods when deposition is interrupted for in situ annealing. The first feature to be noticed in Fig. 3 is that the recovery of the RHEED intensity during the annealing periods shows very different behaviors at different substrate temperatures. To delineate this feature, windows of the annealing segment are sampled (as indicated in Fig. 3(a)) and enlarged as shown in Fig. 3(b). For temperatures below 600°C, the RHEED intensity shows virtually no changes during the annealing period. While for temperatures above 620°C the RHEED intensity increases exponentially during these annealing periods. Taking the interpretation of RHEED intensity discussed above, these results imply that at temperatures below 600°C annealing does not change the step edge density on the film surface for as long as 90 s, whereas at temperatures slightly above 600°C, the rapid increase of the RHEED intensity reflects a decreasing surface step density and is indicative of a massive surface morphology rearrangement (e.g. coalescence of growing islands on the surface). The fact that the recovery of the intensity follows an exponential-like behavior further suggests that the phenomena are probably associated with thermal activated diffusion processes.

The second feature to be noted in Fig. 3(a) is that, for temperatures below 600°C, when the deposition is resumed, the RHEED intensity picks up the oscillatory traces right from where it was

Table 1
List of the average sizes and numbers obtained from AFM images shown in Fig. 2 for different laser repetition rates by image analysis

Laser repetition rate	Average island size (nm)	Island number	Coverage (%)	Ratio of average island size between different laser repetition rates	Ratio of island number between different laser repetition rates	Ratio of ΔI between different laser deposition rates in Fig. 1(b)
1	$R_1 = 40 \pm 10$	33	21	$R_1/R_2 = 1.89 \pm 0.9$	$N_2^{1/2}/N_1^{1/2} = 1.9$	$\Delta I_2/\Delta I_1 = 2.5 \pm 0.5$
2	$R_2 = 24 \pm 6$	125	30	$R_1/R_4 = 3.1 \pm 1.4$	$N_4^{1/2}/N_1^{1/2} = 3.2$	$\Delta I_4/\Delta I_1 = 3.8 \pm 1$
4	$R_4 = 15 \pm 4$	332	32	$R_2/R_4 = 1.8 \pm 0.9$	$N_4^{1/2}/N_2^{1/2} = 1.6$	$\Delta I_4/\Delta I_2 = 1.5 \pm 0.1$

The surface coverage was estimated by integrating the histogram obtained for each image and then divided by the total area of the respective image. The parameters listed in the last three columns are intended to check the validity of Eq. (2) discussed in the text. Here R and N are the results from the previous columns and ΔIs are sampled from Fig. 1(b). The results are in fair agreement with that predicted by Eq. (2).

stopped for annealing. While at 600°C or higher, the RHEED oscillations always start with an initial drop in intensity. This is indicative that, when the temperature is high enough, significant change of film surface morphology occurred during the in situ annealing period. The questions, however, are how fast does this take place and how does it affect the growth mechanism of these oxide films?

In order to explore these interesting observations in a more quantitative manner, a series of specially designed annealing schemes were performed. The results are illustrated in Fig. 4. Trace (a) shows the RHEED intensity for a deposition-annealing scheme performed at 740°C. In this particular scheme, each annealing period was less than 30 s. More importantly, annealing was engaged at various positions of the oscillating peaks with presumably different extents of surface coverage. For these short periods of annealing, the RHEED intensity oscillations resumed exactly from where it was stopped without damping when deposition was re-engaged. The behavior is very similar to that observed at temperatures lower than 600°C. This implies that short time annealing is inadequate to change the surface morphology of the substrate, and hence the growth mode of the subsequent deposition.

However, as shown in trace (b), at the same annealing temperature of 740°C, the resumed RHEED oscillation behavior as well as its amplitude do exhibit very different characteristics after prolonged annealing. In segment (I) of trace (b), the 20 s annealing shows essentially the same behavior as seen in trace (a). As the annealing period

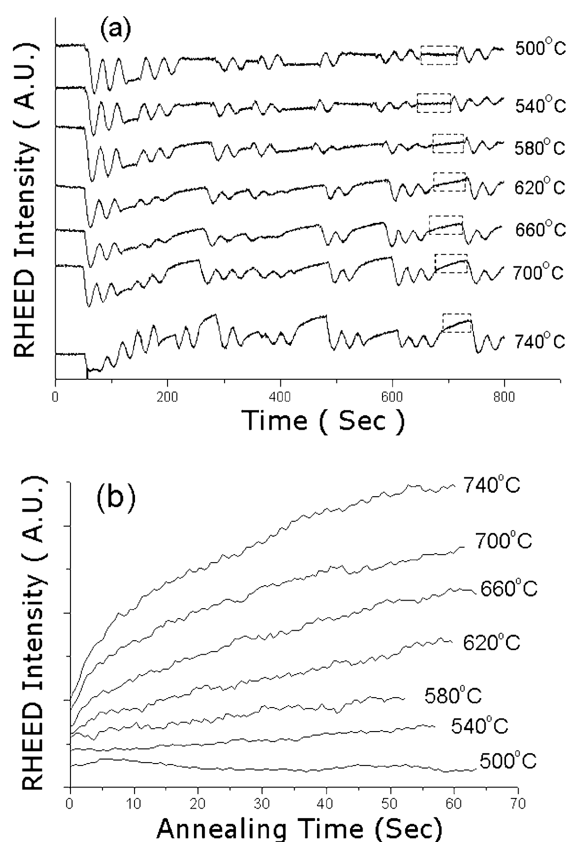

Fig. 3. (a) RHEED intensity as a function of time obtained from a series of in situ annealing schemes performed over the temperature range of 500–760°C. The regions showing intensity oscillations represent the periods of deposition, whereas the regions without oscillation represent the periods of in situ annealing, within which the laser is turned-off. (b) The enlarged version of the annealing segments sampled in the windows indicated as the boxes in each trace of (a). For comparison, the starting time of each trace is reset to zero.

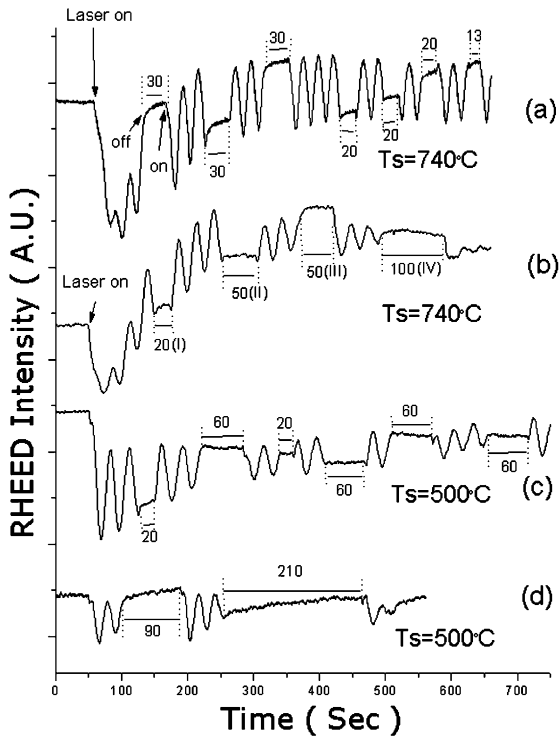

Fig. 4. Series of annealing schemes designed to reveal the film growth kinetics. The numbers displayed between the vertical dotted lines indicate the annealing time of each segment. Please refer to the text for detailed discussions of the obtained results and their physical implications.

was increased to 50 s (segments II and III), the resumed oscillation amplitude shows strong dependence on where the annealing was engaged. For instance, when annealing was engaged at the intensity minimum (segment II), the resumed oscillation amplitude damped by ~40% as compared to the amplitude of preceding oscillation. However, if the annealing was engaged at the maximum of oscillatory peak (segment III), the resumed oscillation amplitude shows only about 10% of damping. For longer annealing period (e.g. 100 s in segment IV), the resumed amplitude of oscillations has damped even more (~45%). Although further extensive investigations are required to delineate the complicated growth dynamics in this system, the present results indicate that at 740°C the characteristic time for island coalescence may locate somewhere between 20 and 50 s. Beyond this period the surface condition prior to annealing appears to affect the subsequently resumed growth drastically (see below).

The other way of elucidating the effects is to change the annealing temperature. Traces (c) and (d) show the results of similar annealing studies performed at 500°C. It is evident that, up to 60 s, the RHEED oscillation characteristics are immediately resumed whenever the deposition is re-engaged, showing no sign of surface rearrangement. Nevertheless, as the annealing time was increased to over 200 s, the resumed RHEED oscillation again exhibited strong damping. It is suggestive that annealing may have resulted in similar surface rearrangement processes in both temperatures. In this simplified thermal activation scenario, the dispersed growing islands are expected to diffuse over the same effective distance to facilitate coalescence, and hence change the RHEED oscillating behaviors. The diffusion distance x can be approximated as $x^2 \approx D\tau$, with D and τ being the effective diffusion constant and characteristic diffusion time at some temperature, respectively. Thus, by taking the characteristic times of $\tau_2 = 30$ s and $\tau_1 = 200$ s for $T_2 = 740°\mathrm{C}$ and $T_1 = 500°\mathrm{C}$, the activation energy Q_a can be estimated by using $Q_a \sim [k_B T_1 T_2/(T_2 - T_1)]\ln(\tau_1/\tau_2) \sim 0.5$ eV for surface diffusion. Here k_B is the Boltzmann constant. The obtained Q_a value, although is much smaller than 3.5 eV obtained by Lippmaa et al. [11] to account for moving a unit cell from a kink site at the edge of the growing islands, may well account for the activation energy for migrating the various atomic species on the flat surface of the growing islands. In any case, it is indicative that the surface morphology changes during the annealing period are directly associated with thermally activated processes and their features are well delineated by monitoring the RHEED intensity in situ. We will next discuss the implications of RHEED intensity damping associated with prevailing surface diffusion under different conditions.

For homoepitaxial growth of STO films on various types of surface-controlled substrates, it has been evidently demonstrated that, under 'normal' deposition conditions, the nearly undamped RHEED oscillations are indeed originated from the atomic-scale surface roughness due to the two-

dimensional layer-by-layer growth [6,12–14]. However, as suggested by Naito et al. [15], the growth mode may switch from a layer-by-layer growth mode to either a Stranski–Krastanov growth mode (SK mode) or a step-flow-like growth as the surface diffusion length varies with growth temperature. Unfortunately, their RHEED oscillation results did not provide sufficient support for these conjectures, presumably due to the limited temperature range investigated. We argue that the damping of the oscillation intensity may be understood as being a consequence of growth mode switching when it is interrupted for annealing at various stages of growth. As was clearly demonstrated in Fig. 4, the RHEED intensity damping is strongly dependent upon the timing, period, and temperature of annealing. This, in turn, implies that the size and distribution of the growing islands on the top layer of the surface must have varied with the annealing processes.

According to Neave and co-workers [8,16], the nucleation rate of new island is zero in the vicinity of the existing steps on the surface. The rate increases with the distance from the step edge toward the terrace center. This is due to that the supersaturation of the adatom is zero at the steps and displays a maximum between them. In principle, nucleation of another monolayer is possible provided that the island size on top surface is large enough to give adequate supersaturation. In this scenario, a second layer can start before the completion of the first growing layer, leading to a SK mode growth and the system becomes a so-called two-level system [17,18]. The concentration of the adatom N_s on the top surface of the growing island can be expressed in term of the island radius ρ and the distance r to its center by the following equation [17,18]:

$$N_s = N_s^e + R(\rho^2 - r^2)/4D_s. \tag{3}$$

Here N_s^e is the equilibrium adatom concentration established between the dilute adlayer and monatomic steps due to flux exchange, D_s is the surface diffusion coefficient, and R is the arriving flux during deposition, respectively. In our case, R can be replaced by the laser repetition rate. Eq. (3) shows that the supersaturation in the adlayer on top of small two-dimensional island is rather low. Therefore, it is very unlikely, though possible, for nucleation event to take place. The film, thus, keeps growing laterally until the two-dimensional islands reach a critical size to initiate nucleation on the top layer, leading to the emergence of the second monolayer. Although the RHEED intensity oscillation is a direct consequence of step edge intensity and may be observed in various growth modes [5,18], one expects that the oscillation amplitude should be suppressed considerably on multilevel surfaces due to the multiple scattering of the electron beams.

In the above situations, when deposition is interrupted at the minimum of the oscillatory RHEED intensity, there will be a larger number of islands existent on the surface. These islands coalesce with each other to form bigger ones during the annealing process. At 740°C, it appeared that the island size reached the critical size required for nucleation of the second layer after ~50 s of annealing. As a result, one starts to see the damping of the oscillation amplitude. To confirm this was indeed the case, ex situ AFM investigations were performed. Fig. 5(a) shows the image of the quenched surface interrupted at the bottom of oscillation amplitude. For comparison, Fig. 5(b) shows the morphology of film surface annealed at the same temperature for 80 s prior to quenching. As shown in Fig. 5(a), the film surface consists of uniformly dispersed isolated islands. The islands appear to have smaller size and distinguishable boundaries. In contrast, Fig. 5(b) features a surface morphology consisting of fewer but bigger islands with irregular boundaries, presumably resulted from annealing-driven coalescences. The apparent differences found here again lend support to our conjectures in interpreting the observed amplitude damping of RHEED oscillations after prolonged annealing.

It is expected that longer annealing time will be required for the growing islands to surmount the critical size at 500°C because of the slower thermal diffusion and less coalescence effect. Consequently, the growth mode picked up after moderate period of annealing time will depend on the average size and detailed distribution of the preceding growing islands. When the growth was stopped at the

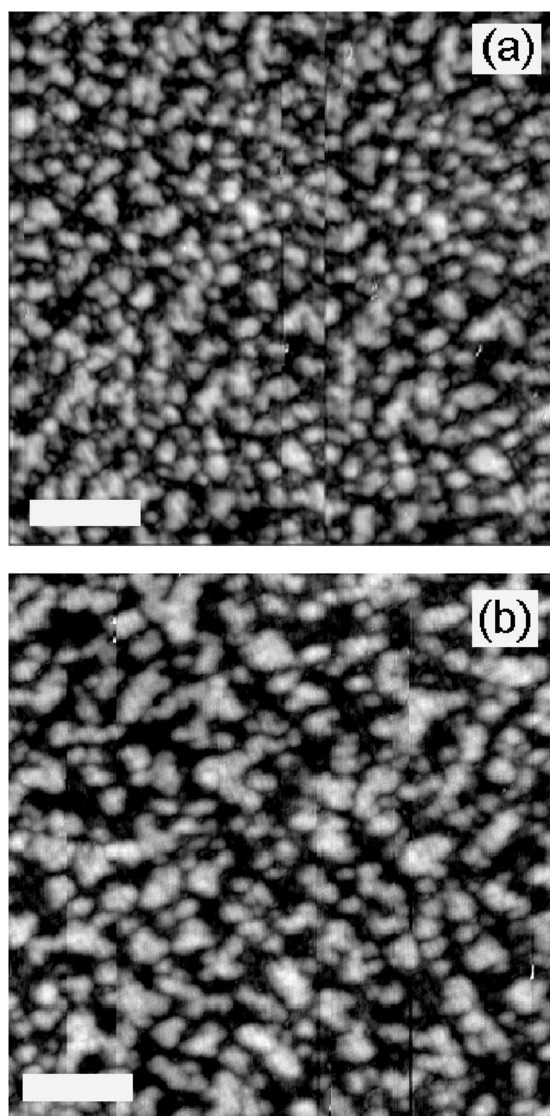

Fig. 5. (a) The AFM image of a growing surface being interrupted and quenched at its minimum of oscillation amplitude. (b) The AFM image of a growing surface subjected to exactly the same conditions as (a), except that it was annealed for 80 s prior to quenching. Both films were deposited at 740°C. The apparent differences in the morphology and size distribution of the growing islands are clearly displayed.

maximum of the oscillation amplitude, the top layer has the smallest step edge density and fewest isolated growing islands. The resumed growth basically starts from the complete coverage situation. As a result, the RHEED oscillation picks up the previous oscillation tendency without damping. On the contrary, the significant damping observed, when annealing was engaged at the bottom and middle position of amplitude, may have been resulted from the fact that some islands were exceeding the critical size and set the stage for a two-level system [17,18] by coalescence effect during annealing and subsequent re-deposition period.

4. Summary

We present a novel method to verify the intimate correspondence between surface step edge density and RHEED intensity by measuring the relation between initial intensity drops of RHEED oscillation and laser repetition rates. The AFM investigations indicate that the correspondent average island size and island density are consistent with the RHEED intensity variations predicted by the step edge density model. A series of specifically designed annealing schemes revealed the important role played by thermally activated diffusion in determining the prevailing mode of film growth. Within the context of the step edge model, it is suggestive that multilevel growth mode may evolve to give rise the amplitude damping of RHEED oscillation, provided that some of the islands exceeded the critical size during deposition. This has been nicely demonstrated by varying the timing as well as the durations of engaging the annealing. Finally, it is noted that by carefully monitoring the RHEED intensity the characteristic features of island nucleation and coalescence at various stages of film growth can be identified.

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