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Temperature dependence of RHEED oscillation in homoepitaxial growth of SrTiO$_3$(100) films on stepped substrates

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Abstract

Homoepitaxial growth of SrTiO$_3$ (STO) films on STO(100) substrates with unit-cell-high steps manifests itself by a marked change in the intensity oscillations of the specular reflectivity of reflection high-energy electron diffraction (RHEED) oscillations with increasing temperature. Atomic force microscopy (AFM) revealed a high density of growing islands distributed all over the edges and terraces of the pre-existing steps at lower deposition temperatures. In response, the RHEED intensity exhibits an 'overdamped' profile with no oscillation. At higher deposition temperatures ($T_s \approx 500°C$), larger (≈ 40 nm) but fewer islands were observed to form preferentially on the step edges with a gradually recovered RHEED intensity, followed by RHEED oscillations after a few monolayers of coverage. At even higher growth temperatures, immediate periodic oscillations in RHEED intensity were observed. However, the temperature dependence of the oscillation period indicates that it may not be directly related to a layer-by-layer growth mode, as is generally believed. © 2000 Elsevier Science B.V. All rights reserved.

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Recently, it has been demonstrated that the surface structure and chemical terminations of SrTiO$_3$ (STO) substrates can be controlled down to the atomic level by treatment with buffered NH$_4$F–HF solution [1,2] and oxygen annealing [3,4]. Such advancement apparently is the key for obtaining reproducible growth conditions, a much-needed prerequisite for fundamental studies of epitaxial growth. It has also provided an opportunity to resolve the outstanding long-term debate about the origin of the intensity oscillations of reflection high-energy electron diffraction (RHEED), a technique used ubiquitously to study epitaxial growth of a variety of materials. For instance, Terashima et al. [5,6], based on the precise correspondence between the oscillation period and the resultant one-unit-cell-height film morphology, concluded that the strong RHEED oscillations were caused by a two-dimensional (2D) layer-by-layer growth in the case of growing YBa$_2$Cu$_3$O$_7$ (YBCO) films on STO(100) substrates. In contrast, Chandrasekhar et al. [7] have attributed the RHEED oscillations to the changing

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surface step densities and distributions. In their studies of YBCO on STO(100), they found that the oscillation period appeared to change with the surface structure (produced by intentional off-axis vicinal cuts) and temperature of the substrates, in contrast to the fixed period expected from a 2D growth.

Although the discrepancies observed may be intrinsic to the complex nature of heteroepitaxy, the vast space of deposition parameters, especially the limited control over the starting conditions of the substrates, could also be crucial. For homoepitaxial growth of STO on these surface-controlled substrates, it has been evidently demonstrated that, under 'normal' deposition conditions, the nearly undamped RHEED oscillations indeed originate from the atomic-scale surface roughness due to the 2D layer-by-layer growth [1–4,8]. However, as

suggested by Naito et al. [3], the growth mode may cross over from layer-by-layer growth to either a Stranski–Krastanov growth 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.

In this letter, we present the effects of substrate temperature on the growth behavior of homoepitaxial STO films by intimately correlating the observed RHEED oscillations to the corresponding surface structures obtained by atomic force microscopy (AFM). The films were grown by a pulsed laser deposition (PLD) system equipped with an in situ RHEED facility. The STO(100) substrates used were obtained from Shinkosha of
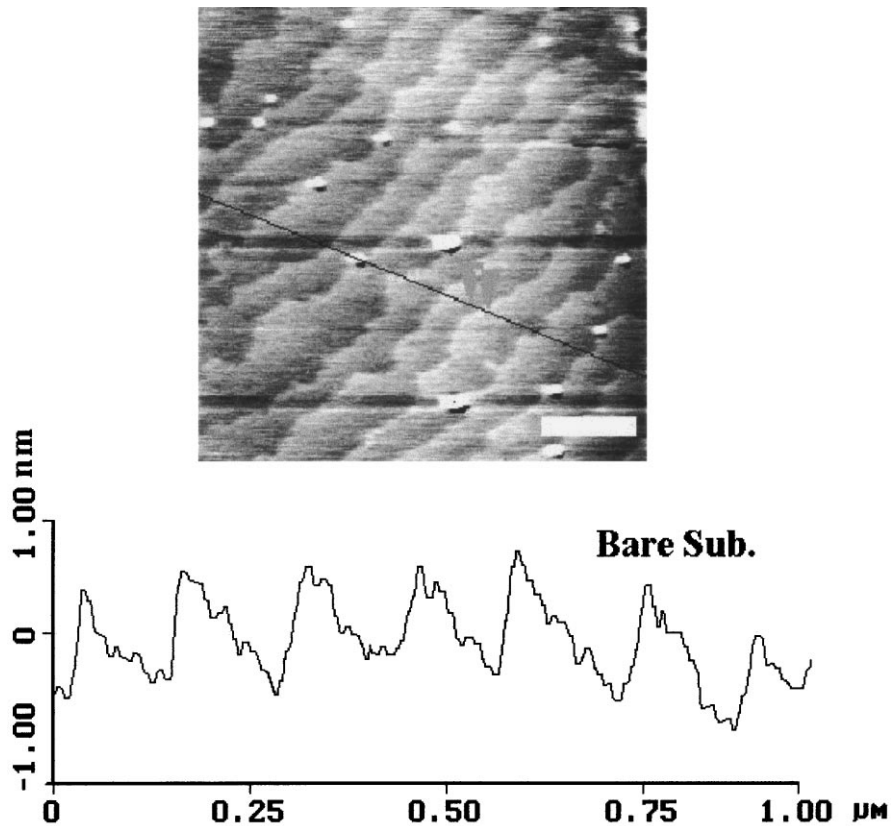

Fig. 1. AFM image showing the surface morphology of the stepped STO(100) substrates after annealing at 790°C for 5 min. The section profile evidently indicates features of unit-cell-height step structure. The scale bar is 250 nm.

Japan. They were all treated with buffered NH_4F–HF solution to produce steps with unit-cell height. Hereafter, this surface will be referred to as stepped STO(100). As confirmed by AFM, the height of the steps and the width of the terraces between steps are about 1–2 unit cells of STO and 110 nm, respectively. In order to simulate the actual surface structure just prior to deposition, the substrate was annealed at 790°C for 5 min under the same deposition environment and then quenched. As shown in Fig. 1, the morphology of the substrate surface remains essentially intact except for a few particles presumably resulting from contamination during the handling processes. Since these particles are relatively far apart (they covered less than 1% of the total substrate area), their presence should not significantly influence the growth behavior prevailing on the otherwise open field of the rest of the substrate area.

KrF excimer laser with a pulse duration of 30 ns, operated primarily at a repetition rate of 1 Hz, was used for deposition. The target used was single-crystal disk of STO. The laser energy was estimated to be about $2\ J\ cm^{-2}$. All the films were deposited at an oxygen pressure of 5×10^{-4} Torr. The substrate temperature was varied from room temperature to 810°C by a resistive heater block. The energy of the electron beam used for in situ RHEED diagnostics was 20 keV with a grazing angle of 0.7°, and was directed along the [100] direction of the 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 edge of surface steps [7,9,10]. The intensity evolution of the specular reflection was obtained by transmitting the diffraction images recorded by a charge-coupled device camera to a frame-grabber board. The image was digitized by a flash analog-to-digital converter and stored in the memory buffer for subsequent display and analyses.

Fig. 2 shows the RHEED intensity oscillations as a function of time for STO films grown on the stepped substrates at various temperatures. It is noted that, due to the explosive nature of the PLD process, the sticking effect should be insensitive to the substrate temperature. Thus, the actual amount
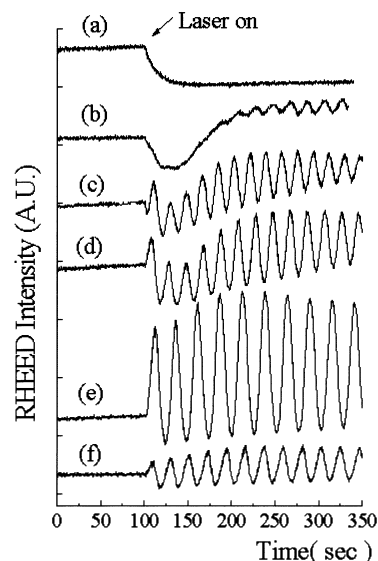

Fig. 2. RHEED intensity oscillations of the homoepitaxial STO films on stepped substrates as a function of growth temperature. Curves a–f are the results for room temperature, 500°C, 720°C, 750°C, 790°C and 810°C, respectively.

of material deposited, and hence the film thickness, is expected to be proportional to the deposition time. In any case, the first feature to be noticed in Fig. 2 is the marked changes of the RHEED intensity oscillations with deposition temperature. It shows an immediate damping with no oscillations at room temperature (curve a). However, at 500°C, the RHEED intensity recovered from its initial drop over some period of time and then started to show small-amplitude oscillations. When the temperature was raised to above 720°C, periodic oscillations in RHEED intensity appeared immediately as the deposition commenced. Nonetheless, as is evident from Fig. 2 (curves c to f), with everything else (including the deposition time) kept the same, both the amplitude and periodicity of the respective RHEED oscillations are changing with deposition temperature. This strongly suggests that the generally accepted notion of attributing the periodic RHEED oscillations to a layer-by-layer growth might not be universally valid [3–5].

Moreover, the periodicity of RHEED oscillations originally increases with substrate temperature and then decreases again (curve f, 820°C).

This behavior is in contrast to that reported by Chandrasekhar et al. [7], where the periodicity was found to increase with reducing substrate temperature. Lastly, we note that there is always an initial non-transient increase in RHEED intensity. Although this has been attributed to the effects of surface reconstruction [5,6] or substrate smoothing [12,13], further confirmation is certainly needed.

In attempt to reconcile the findings described above, Fig. 3 shows several representative AFM images taken after the deposition was interrupted at various conditions. Fig. 3a is the image of an STO film deposited at room temperature for about 250 s. As can be seen, the original stepped structure of the substrate remains essentially intact. Nonetheless, there are numerous of fine particles nucleated homogeneously all over the terraces. On the other hand, for films deposited at 500°C, Fig. 3b clearly shows a significant increase in the average size of particles residing on the substrate terraces. The corresponding profile scans shown in Fig. 3c and d also confirm the features described. According to the kinematics approximation [9,11],
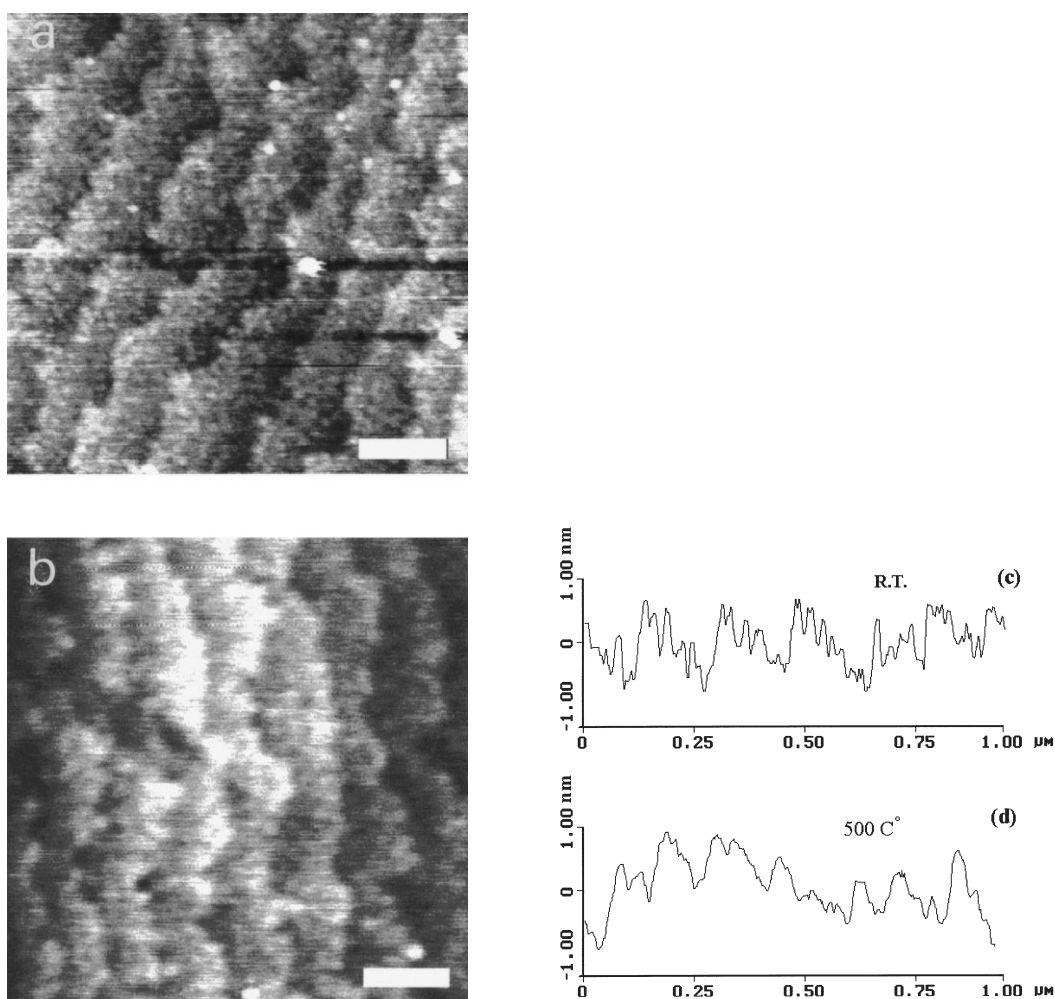

Fig. 3. AFM images (a, b) and their section profiles (c, d) showing the surface morphologies of the STO films grown at (a, c) room temperature and (b, d) 500°C. The length of the scale bars represents 250 nm. Notice that the number of islands growing across a single terrace decreases with increasing temperature.

the undamped oscillations occurred as a result of changing step distribution, while damping was caused by an increasing contribution from a third level; i.e., when the second layer starts to grow before the first is completed. If we adopt this picture of the origin of RHEED oscillations, then the observed results can be understood as follows. At lower deposition temperatures, the islands nucleated homogeneously on the terraces of the stepped substrate resulted immediately in a tremendous increase in step density and hence suppressed the RHEED intensity. The lack of oscillation is believed to result from the limited diffusion at low temperatures, which not only hindered the coalescence of individual particles but also had steps distribute over multiple layers (including the original substrate steps). Such effects were diminished significantly by raising the substrate temperature to 500°C. The higher intensity level and small oscillations seen (curve b in Fig. 2) imply that growth at this temperature prevails on a relatively smooth surface with a moderate variation in step density distributions. As seen in Fig. 3b, the corrugated step edges indeed indicate a modification of step distributions. In both cases, however, the corresponding growth mode cannot be determined by looking solely at the evolution of RHEED intensity. For instance, at room temperature, while the RHEED intensity drops precipitously without oscillations, the AFM image (Fig. 3a) shows that the step structure of the substrate persists with unit-cell-high 2D islands uniformly distributing on the terraces between substrate steps. The other difficulty of attributing the RHEED oscillations to the layer-by-layer growth mode is also apparent in the 500°C case. In that, the initial intensity drop followed by small-amplitude oscillations would imply a reversed Stranski–Krastanov growth mode [i.e., crossover from three-dimensional (3D) island growth to 2D layer-by-layer growth], which is indeed very unlikely.

As noted above for curves c to f of Fig. 2, at even higher growth temperatures the RHEED oscillations varied in both period and amplitude, suggesting that they probably are not due to pure layer-by-layer growth either. Nonetheless, the nearly undamped oscillations in this temperature range indicate that a different surface morphology from the one grown at lower temperatures should be observable. Fig. 4a and b show the surface morphologies of STO films grown at 790°C corresponding to the maximum and minimum RHEED intensity (Fig. 4c), respectively. As is seen in Fig. 4a, even after six cycles of oscillation, at the maximum intensity the film surface shows essentially the same stepped structure as that of the initial substrate. On the other hand, at the intensity minimum of the same cycle, there are numerous islands growing preferentially distributed along the step edges (Fig. 4b). It is evident that the RHEED oscillations are indeed intimately related to the distribution of growing islands, and hence step density distributions, in contrast to the generally accepted notion of attributing them to a layer-by-layer growth.[1] It is noted that similar conclusions have also been reached by Chambliss and Johnson [14] in their study of iron growth on Cu(100) by using in situ medium-energy electron diffraction (MEED) and scanning tunneling microscopy. This is suggestive that present observations may be, in fact, quite universal to epitaxial growth of thin films.

In order to elucidate the above conjecture further, we have performed several in situ annealing experiments on as-polished STO substrates. Preliminary results indicate that, with as short as 20 s of annealing, the RHEED intensity can recover to its original level regardless of the change in repetition rate. For instance, as shown in Fig. 5, each segment of the intensity versus time plot corresponds to the number of 140 laser pulses and an annealing time of 70 s. As can be seen from the results, the annealing recovers the RHEED intensity to its original level completely, regardless of the fact that the repetition rate has been changed from 2 Hz to 10 Hz.

Furthermore, we note that, although the behavior of each deposition segment is qualitatively the same, the depths of initial intensity drop are quantitatively different. As shown in Fig. 6, the initial

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[1] At 790°C, since the growing islands can coalesce very rapidly, it may lead to a circumstance of layer-by-layer growth as seen by many previous work. However, the actual origin of the RHEED oscillations is not because of that particular growth mode.
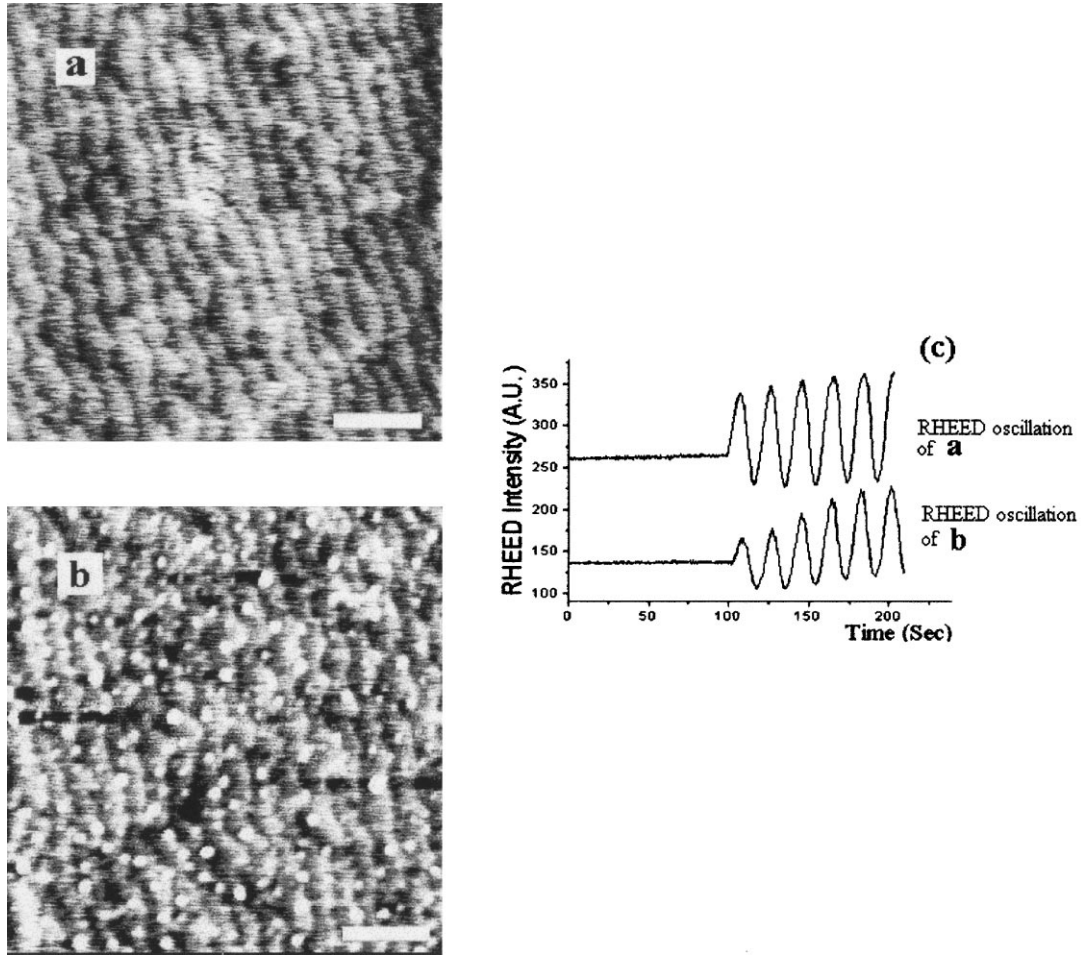
Fig. 4. (a, b) AFM images showing the surface morphologies of films grown at 790°C but stopped at points corresponding to different RHEED intensities, as indicated in (c). The scale bars represent 500 nm.

drop depth, dI, can be fitted fairly well by an empirical equation

$$d_I = A + Bf + Cf^2, \qquad (1)$$

where A, B and C are some constants, and f is the laser repetition rate. If we assume that the minimum intensity of the initial drop corresponds to a surface coverage of 0.5 and the island distribution is two-dimensional, the implication of the present results can be understood as follows. With the 0.5 coverage, the total area of the growing 2D islands is a fixed constant. Under this constraint, one could express the parameters by the following expressions:

$$R_{f1}^2 \times N_{f1} = R_{f2}^2 \times N_{f2}$$

(total constant coverage area),

$$d_{I_{f1}} : d_{I_{f2}} = R_{f1} \times N_{f1} : R_{f2} \times N_{f2}$$

(total step edge length)

and

$$R_{f2} : R_{f1} = N_{f1}^{1/2} : N_{f2}^{1/2},$$

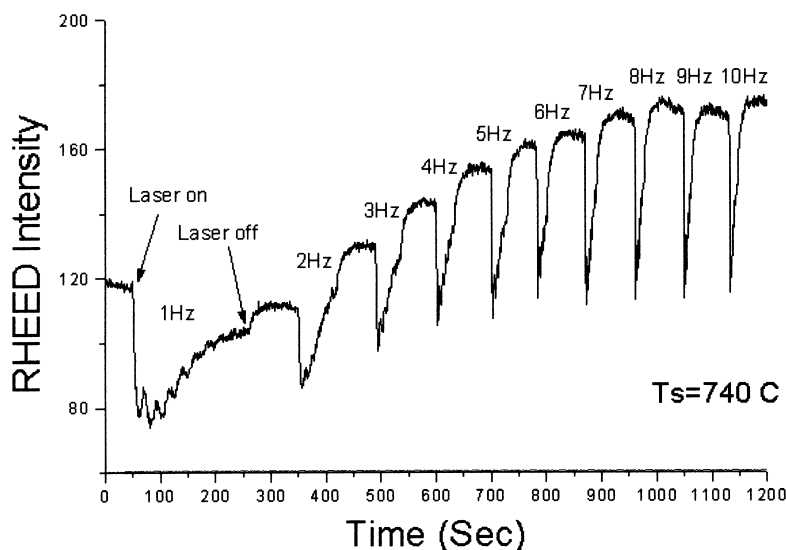where R is the radius of each island and N is the number density of the growing islands.

Fig. 5. RHEED oscillations measured under different laser repetition rates on the same as-polished STO substrate. Each segment of the RHEED intensity corresponds to the number of 140 laser pulses and an annealing time of 70 s. The repetition rate was varied from 2 Hz to 10 Hz.
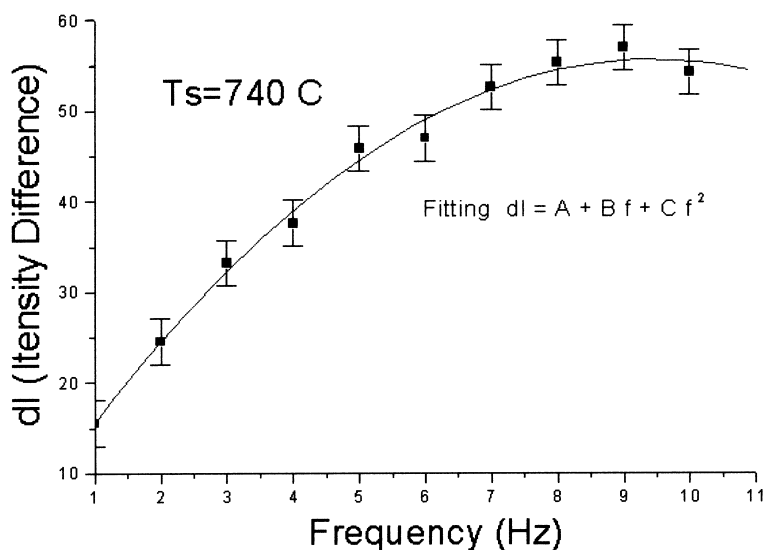

Fig. 6. Depth of the initial drop of the RHEED intensity as a function of laser repetition rate on the same as-polished STO substrate.

In the usual nucleation and growth processes, a faster deposition rate represents a higher degree of supersaturation and a shorter diffusion length, leading to a larger density of smaller growing islands. Within this scenario, the deeper drop in RHEED density observed at higher laser repetition rate naturally translates into smaller island dimension and hence larger total step-edge density. This is consistent with our previous conjecture of attributing the RHEED intensity oscillations to the changing surface step densities. Consequently, the emergence as well as the periodicity and amplitude

of the RHEED oscillations are all determined by the nucleation and coalescence processes prevailing on the substrate. In fact, very similar temperature-dependent behaviors were observed for films grown on as-polished substrates [15].

In summary, we have investigated the homoepitaxial growth of STO(100) films on stepped STO substrates. The in situ RHEED oscillations, including the emergence as well as the periodicity and amplitude, were found to be strongly dependent on the growth temperature. The complementary AFM investigations indicated that the origin of the RHEED oscillations is not directly related to layer-by-layer growth. Rather, it may intimately relate to the variations of step density distribution caused by the detailed nucleation and coalescence processes of the growing islands.

Acknowledgement

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