# *IN SITU* INITIAL GROWTH STUDIES OF $SrTiO_3$ ON $SrTiO_3$ BY TIME RESOLVED HIGH PRESSURE RHEED.

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## ABSTRACT

The initial growth of pulsed laser deposited $SrTiO_3$ on $SrTiO_3$ has been studied using high pressure Reflection High Energy Electron Diffraction (RHEED) and Atomic Force Microscopy (AFM). For this, we developed a Pulsed Laser Deposition (PLD)-RHEED system, with the possibility to study the growth and to monitor the growth rates, *in situ*, at typical PLD pressures (10-50 Pa). Using perfect single crystal $SrTiO_3$ substrate surfaces, we observe true 2D intensity oscillations at different temperatures. Simultaneously, information on the diffusion of the deposited material on the surface could be extracted from the relaxation of the intensity after each laser pulse. The characteristic times depend on pressure and temperature as well as the 2D coverage during growth.

## INTRODUCTION

Pulsed Laser Deposition (PLD) is very suitable for the deposition of thin films made of complex oxides like high-Tc superconductors, e.g., $REBa_2Cu_3O_{7-\delta}$ and dielectrics, e.g., MgO and $SrTiO_3$. This technique uses mostly a focused beam of an excimer laser to evaporate material from a stoichiometric target. Especially in PLD, the deposition pressure is an important parameter because it influences the size and shape of the plasma and, therefore, the deposition rate and the homogeneity of the thin film. The deposition of oxides takes place in a well-controlled oxygen atmosphere, allowing oxygen incorporation in the as-grown film. The substrate temperature is elevated (typically up to 850 °C) in order to obtain epitaxial growth.

Reflection High Energy Electron Diffraction (RHEED) is often used for the analysis and monitoring of thin film growth in Ultra-High Vacuum (UHV) deposition systems [1]. Because the electron beam strikes the surface under a grazing angle this technique is very surface sensitive. Two-dimensional layer-by-layer growth is indicated by RHEED as intensity oscillations of the diffracted intensity. In PLD the diagnostics of the growing film surfaces by *in-situ* RHEED is hampered by the relatively high oxygen pressure. Nevertheless, several groups have monitored the growth of complex oxides with RHEED and have shown intensity oscillations, by depositing under pressures compatible with their RHEED setup. To incorporate oxygen in the as-grown films, different alternatives were used, e.g., low pressures ($10^{-4}$-1 Pa) of molecular oxygen [2, 3], $NO_2$ [4, 5], or $O_3$ [6], and alternatively pulsed oxygen sources [7].

A low deposition pressure during PLD, however, can lead to stress, usually compressive, in the film [8]. This is caused by the bombardment of the film during the deposition by high energetic particles, originating from the plasma. In general the oxygen pressure is an important parameter in the oxidation process of the deposited film. The oxidation power is higher at higher pressures, which allows us to grow at higher deposition temperatures. This improves crystallinity of the deposited films. Furthermore, some complex oxides, like high-Tc superconductors, are not stable in low oxygen pressure at high temperature and, therefore, must be deposited at high oxygen pressures of up to 30 Pa to avoid decomposition of the film. By


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using a 2-stage differentially pumped system Rijnders *et al.* are able to use RHEED in combination with PLD under standard deposition conditions [9].

As mentioned above RHEED intensity oscillations indicate layer-by-layer growth. For true 2D growth, Lagally *et al.* [10] proposed a model with which the intensity as a function of the 2D coverage θ can be described. This model holds only in the case where the surface during deposition remains a two-level system. Transition to a multilevel system, e.g., due to kinetic roughening or stress relaxation, will affect the shape and amplitude of the oscillations [10,11]. To be able to observe ideal 2D growth, one needs a perfect starting surface, which is atomically flat and in the case of $SrTiO_3$ single terminated. Several methods to obtain such a surface have been proposed by others [12], however true 2D oscillations have never been reported on these surfaces.

In this paper, we will study, using high pressure RHEED in combination with PLD, the deposition of $SrTiO_3$ on $SrTiO_3$ substrates which were treated with a new method proposed by G. Koster *et al.* [13] and observe for the first time true 2D oscillations. In addition, characteristic diffusion times are determined by recording the relaxation of the RHEED intensity after each laser pulse [2,14].

## EXPERIMENTAL

$SrTiO_3$ is deposited on single crystal (001) $SrTiO_3$ substrates by PLD. The as received substrates were subjected to a chemical treatment described elsewhere [13] followed by annealing in a tube oven at a constant oxygen flow at 950 °C. The obtained surfaces are free of contaminants and are uniquely terminated by the $TiO_2$ plane of $SrTiO_3$, as confirmed by the existence of only unit cell steps and straight terraces, see Fig. 1a.

We use a single crystal target on which the laser energy density is kept at 1.35 J/cm$^2$. The spot size on the target was 2.30 mm$^2$ and we use a frequency of 0.5 Hz to be able to monitor the relaxation of the RHEED intensity after each laser pulse, given the speed of the detector.

In this study the temperature ranged from 650 °C - 850 °C, and we used pressures of 0.05-0.15 mbar $O_2$. The energy of the electrons was 20 KeV, and incident angle was typically 1°.

*Ex situ* analysis was performed on a NanoscopeIII AFM, using a $Si_3N_4$ contact mode tip. Measurements were performed immediately after taking out of the vacuum or the tube oven to minimize the amount of ambient contaminants.

## RESULTS AND DISCUSSION

The RHEED pattern obtained prior to deposition is depicted in Fig. 1b. Extremely sharp Bragg reflections lying on the first Laue circle indicate an well-ordered crystalline surface. We use low miscut substrates (typically $< 0.1°$) or, if possible, the electron beam was directed parallel to the vicinal terraces, both to prevent splitting of the Bragg reflections due to these terraces.

In Fig. 2a, the RHEED intensity of the specular reflection is given during deposition of two unit cell layers of $SrTiO_3$ at 750 °C and 760 °C using an oxygen pressure of 0.05 mbar and 0.15 mbar respectively. Although the deposition temperature used were practically identical, we detect a difference in initial growth behavior due to the difference in oxygen pressure. At the higher pressure, the intensity of the maxima decreases significantly, indicating a transition from 2D to 3D growth. On the other hand, at the lower pressure, the intensity of the maxima remains constant. The shape of the latter intensity curve is explained by fitting with the 2-level growth model mentioned earlier. The intensity curve at a higher pressure initially has a similar shape,

but within one unit cell layer, this shape is destroyed due to the occurrence of multiple levels due to kinetic roughening.

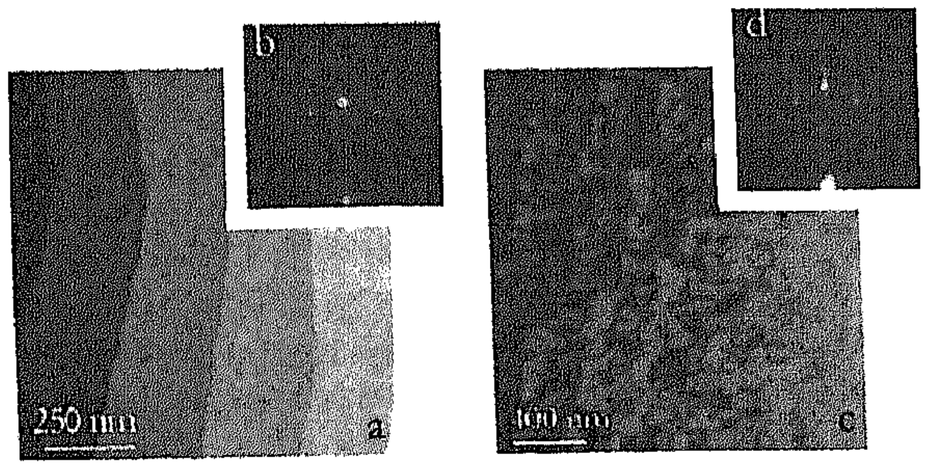


*Figure 1: AFM Micrograph of a) $SrTiO_3$ surface prior to deposition and c) after deposition of 1.5 unit cell layer (deposited at 800 °C and 0.05 mbar $O_2$), b) and d) are the corresponding RHEED patterns, respectively.*

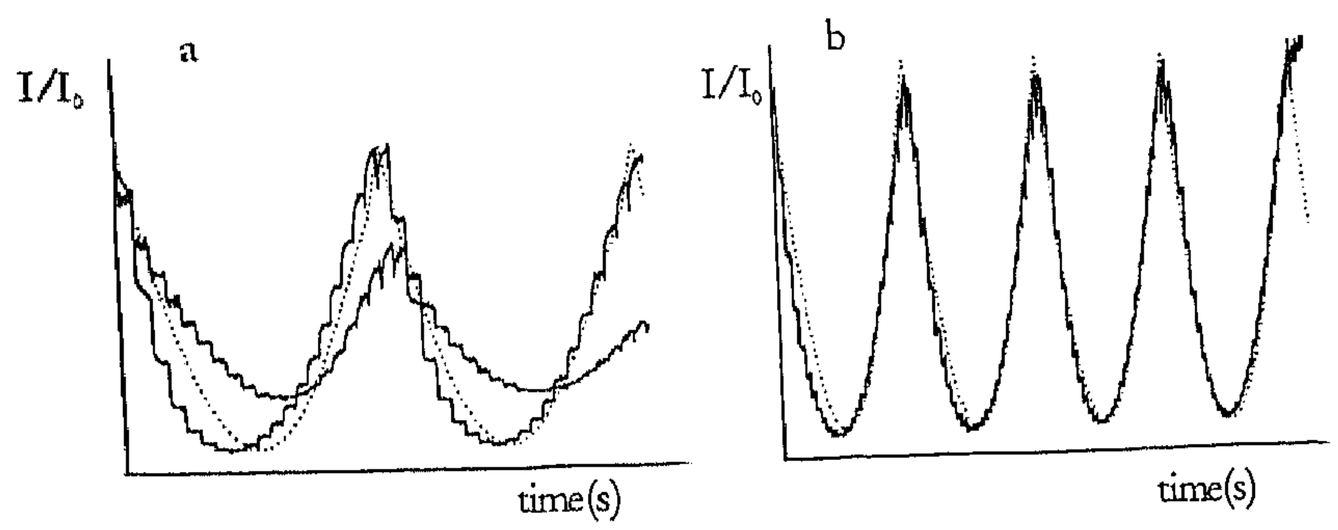


*Figure 2: a) Normalized RHEED intensity during deposition of $SrTiO_3$ at 750 °C at different oxygen pressures (black, 0.05 mbar, gray 0.15 mbar), b) Normalized RHEED intensity during deposition of $SrTiO_3$ at 850 °C and 0.05 mbar $O_2$. The dotted lines are a fit with the 2-level model.*

During deposition of $SrTiO_3$ at a range of temperatures between 650 °C and 850 °C, using the lower oxygen pressure, we observed similar shaped intensity oscillations. In Fig. 2b, perfect 2D intensity oscillations, fitted with the 2D model, are shown when depositing 4 unit cell layers of $SrTiO_3$ at 850 °C. After deposition of 1.5 unit cell layers at 800 °C, AFM revealed the existence of only unit cell high islands lying on terraces, see Fig. 1c. As expected, the corresponding RHEED pattern in Fig. 1d shows broadened reflections due to the augmentation of disorder.

From the above, we conclude that within the covered temperature range the oxygen pressure during deposition of $SrTiO_3$ on perfect $TiO_2$ terminated surfaces, determines the initial growth mode. This can be explained by the fact that decreasing the oxygen pressure means increasing of the mobility of the ad atoms. This is also confirmed by the shorter relaxation times at low pressures, which will be described below. Dam *et al.* [15] ascribe this effect to a higher energy of the arriving ad atoms at low oxygen pressure.

Another feature of the RHEED intensity curves during PLD is the relaxation of the intensity after each laser pulse. Arriving ad atoms on the surface momentarily destroy the order on the surface, causing the intensity to drop. Subsequent migration of the ad atoms on the surface can be monitored through the relaxation of the intensity. In first approximation the intensity as function of time is given through:

$$I = I_0\left[1 - \exp\left(\frac{t}{\tau}\right)\right] \qquad (1)$$

Here $\tau$ is the characteristic time of the diffusion of ad atoms given the temperature, pressure and as will become clear, the surface morphology. Here, we neglect the relaxation of the intensity due to migration of surface steps. We expect its characteristic time to exceed former relaxation times (typical values are of the order of minutes to hours, which we estimate from anneal experiments).

As an example two relaxation pulses for $\theta$=0.95 and $\theta$=0.9 are shown in the inset of Fig. 3. Both were measured at 750 °C and 0.05 mbar. From the fit with (1) we derive characteristic times of 0.45 seconds and 0.25 seconds, respectively. In Fig. 3, the characteristic times for different temperatures are given as a function of the 2D coverage $\theta$ during deposition.

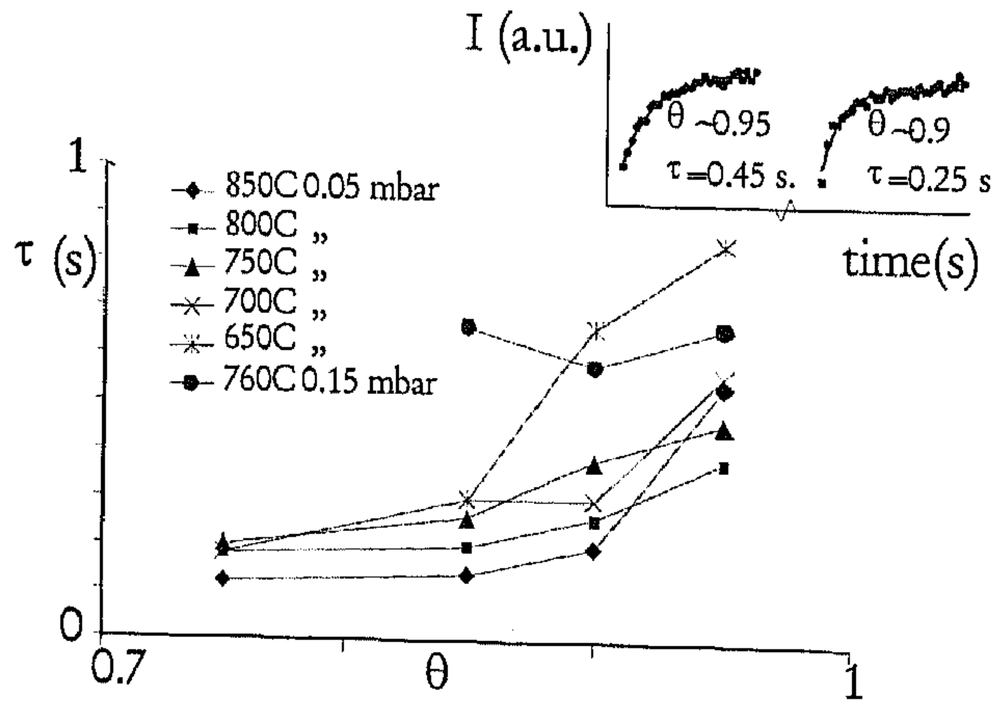


*Figure 3: Relaxation times determined from a fit with (1) for different temperatures and oxygen pressures as a function of the 2D coverage $\theta$. In the inset, two examples of relaxation of the intensity after a laser pulse are given (at 750 °C and 0.05 mbar)*

We conclude from Fig. 3 that the characteristic times depend on both temperature and pressure during PLD. At higher temperatures we typically measure shorter times, whereas longer times are measured for higher pressure, which is consistent with the results, mentioned above. However, it is clear that the characteristic times heavily depend on the coverage. When the coverage is near unity, that is, a unit cell layer has nearly become completely filled, the relaxation times vary much more with temperature, relative to the values found at a coverage of half a unit cell layer. This can be explained by the fact that at this coverage, the step density on the surface is much higher and thus the characteristic diffusion length at a given temperature

exceeds the mean distance between steps. At coverage near unity, we measured an unexpected characteristic time at 850 °C. We think that this is due to a difference in miscut angle of the substrates used, which determines the terrace step density at this coverage.

In contrast, the characteristic times found for 0.15 mbar seem to be less dependent on the coverage. This is also consistent with the results mentioned above, since we no longer deal with a 2D system and there will be less variation in step density during deposition.

In conclusion, using high quality $SrTiO_3$ substrate surfaces we observe true 2D homo epitaxial growth as indicated by the specific shape of the RHEED intensity oscillations. Furthermore, from the relaxation of the diffracted intensity after each laser pulse we extract diffusion properties of the deposited ad atoms. The characteristic times depend on temperature and deposition pressure as well as the step density during growth of one unit cell layer.

REFERENCES


1. I. Bozovic and J.N. Eckstein, MRS Bulletin **20**, 32 (1995).

2. H. Karl and B. Stritzker, Phys. Rev. Lett. **69** 2939 (1992).

3. M. Yoshimoto, H. Ohkubo, N. Kanda, H. Koinuma, K. Horiguchi, M. Kumagai and K. Hirai, Appl. Phys. Lett. **61**, 2659 (1992).

4. Z. Liu, T. Hanada, R. Sekine, M. Kawai and H. Koinuma, Appl. Phys. Lett. **65**, 1717 (1994).

5. M. Kanai, T. Kawai and S. Kawai, Appl. Phys. Lett. **58**, 771 (1991).

6. T. Terashima, Y. Bando, K. Iijima, K. Yamamoto, K. Hirata, K. Hayashi, K. Kamigaki and H. Terauchi, Phys. Rev. Lett. **65** 2684 (1990).

7. T.M. Shaw, A. Gupta, M.Y. Chern, P.E. Batson, R.B. Laibowitz and B.A. Scott, J. Mater. Res. **9** 2566 (1994).

8. E.J. Tarsa, E.A. Hachfeld, F.T. Quinlan, J.S. Speck and M.Eddy, Appl. Phys. Lett. **68** 490 (1996).

9. A.J.H.M.Rijnders, G.Koster, D.H.A.Blank and H.Rogalla, Appl.Phys. Lett. **70**, 1888 (1997) V.S. Achutharaman, N, Chandrasekhar, O.T. Valls and A.M. Goldman, Phys. Rev. B **50** 8122 (1994).

10. M.G. Lagally, D.E. Savage and M.C. Tringides, NATO series B: Physics Vol. **188**, 139 (1987).

11. G. Koster, J. Heutink, B.L. Kropman, A.J.H.M. Rijnders, D.H.A. Blank and H. Rogalla, EUCAS '97 Proceedings, Inst. Phys. Conf. Ser. No 158, 181 (1997).

12. M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto and H. Koinuma, Science **266** 1540 (1994).

13. G.Koster, B.L.Kropman, A.J.H.M.Rijnders, D.H.A.Blank and H.Rogalla, Submitted to Applied Physics Letters.

14. R. Sum, H.P. Lang and H.-J. Güntherodt, *Physica C* **242**, 174 (1995).

15. B. Dam and B. Stäuble-Pümpin, submitted to the journal of Materials Science.