Invited Paper

In-situ monitoring during pulsed laser deposition of layered oxide materials

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ABSTRACT

Pulsed Laser Deposition (PLD) has developed from a fast but limited preparation tool towards a competitive thin film deposition technique. One of the advantages above other techniques is the possibility to growth at relative high background pressure, with a large freedom in choosing the kind of gas. In a number of applications, the gaseous species in the background pressure even are part of the elements to be grown. An evidence example is oxygen in the case of high Tc superconductors and giant magnetic resistors. However, the benefit of relative high pressures hampers the use of standard diagnostics and monitor techniques, e.g. Reflective High Energy Electron Diffraction (RHEED), used for thin film growth.

With the possibility to use RHEED at standard PLD pressures it became possible to study the growth of oxide materials under different oxygen and temperature conditions. Here, we present the results on applying this technique on $SrTiO_3$, which can be grown in different growth modes, depending on temperature and oxygen pressure, during growth. Applying a modified etch technique to $SrTiO_3$ single crystals, we were able to grow homo-epitaxial $SrTiO_3$ in a real 2D growth mode.

Additional to the usual information obtained with RHEED, another phenomena can be observed. The pulsed way of deposition, characteristic for PLD, leads to relaxations in the intensity of the diffracted pattern. This is caused by the mobility of the deposited material from a disordered distribution till an ordered one. These relaxation times give extra information about relaxation, crystallization, and nucleation of the deposited material.

The results obtained from the intensity oscillations as well as relaxations, has led to a different approach to deposit these complex oxide materials, so-called interval deposition. In this contribution first results on this interval deposition will be presented.

Keywords: Pulsed laser deposition, RHEED, $SrTiO_3$, relaxation, interval deposition

1. INTRODUCTION

Pulsed Laser Deposition has become a unique technique to fabricate various (complex) materials. Especially, the flexibility of a PLD system, i.e. the targets and background pressures can be varied very easily, makes it a powerful tool. For example, the technique has shown its importance in fabricating the high Tc and GMR materials, where the perovskite structures combined with an oxygen environment hinder to some extent the use of other deposition techniques. However, the relative high background pressures during PLD (mostly oxygen, but of course not restricted to that) hamper the monitoring en diagnostic techniques mostly used in thin film techniques. Among the most common technique to monitor and study the growth is *in-situ* Reflective High Energy Electron Diffraction (RHEED).

The intensity of the reflective diffraction pattern varies during thin film growth depending on the growth mode. Layer by layer growth will lead to intensity oscillations. A maximum is reached after completing one mono (unit cell) layer, a minimum is reached when the surface has its highest disorder, typically when half a mono (unit cell) layer is deposited. An increase of the surface roughness, e.g. island formation, will result in an overall decrease in RHEED intensity. Damping of the intensity oscillations reflects a mixture of layer by layer and island growth. Step propagation, or step-flow growth does not change the morphology of the substrate. In this case the diffraction pattern and spot intensity will stay constant during deposition, apart from a decrease in intensity due to surface roughness and/or island formation.

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Since RHEED is very suitable for monitoring the growth of thin films at high vacuum, this diffraction technique is commonly used in standard deposition equipment. Koinuma *et al.*[1] reported RHEED studies on the epitaxial growth of $SrTiO_3$ and $YBa_2Cu_3O_7$ on $SrTiO_3$ by PLD. For that purpose, they operate the PLD system at low pressures. In 1993, Karl and Stritzker [2] reported RHEED studies of $YBa_2Cu_3O_7$ film growth by PLD. A differentially pumped electron gun and integration of the intensity of the diffraction spots were used. They could reach an oxygen pressure of approximately 10^{-2} mbar, which is still more than one order of magnitude lower than standard oxygen pressures during PLD of $YBa_2Cu_3O_7$.

The (oxygen) background pressure, however, is, using the PLD technique, a very important parameter. The pressure influences the shape of the plasma, it will slow down the plasma, and gives its characteristic spheroids profile. For depositing oxides, the oxygen gas reacts with the plasma particles, influencing the film properties. Besides, more general, a different oxygen pressure will lead to another growth regime. If the pressure is too low, the temperature at which one can grow a stable structure has to be lower, reducing the crystallinity of the deposited film, e.g., in the case of $YBa_2Cu_3O_7$ the deposited film decomposes at high temperatures, if the pressure is too low [3].

To overcome these problems a PLD-RHEED system has been developed, which makes it possible to perform RHEED studies during PLD at standard deposition conditions [4]. As a result, additional information about thin film growth with PLD is obtained. In this contribution the details will be presented, applying this technique on homo epitaxial growth of $SrTiO_3$. As a result a new approach of fabricating $SrTiO_3$ thin films by interval depositing will be introduced.

2. EXPERIMENTAL

To apply RHEED at relative high pressures, a standard RHEED system is modified using a two stage differentially pumped electron gun, given a low pressure at the filament of the electron gun ($P < 10^{-7}$ mbar) and a relative high pressure in the chamber ($P \sim 0.5$ mbar). The electron gun, STAIB 20-35KeV, has been extended by a tube that reaches 50 mm from the substrate. A small aperture of 250 μm restricts the connection between the tube (low pressure) and the chamber (high pressure). The diffracted electrons are projected on a phosphor screen. In order to minimize scattering losses of the electrons, the distance between substrate and screen is 50 mm. In this study, the energy of the beam is kept at 20 keV with an angle of incidence of the electron beam of approximately 1degree. Using this setup clear diffraction patterns can been observed up to 0.5 mbar of oxygen.

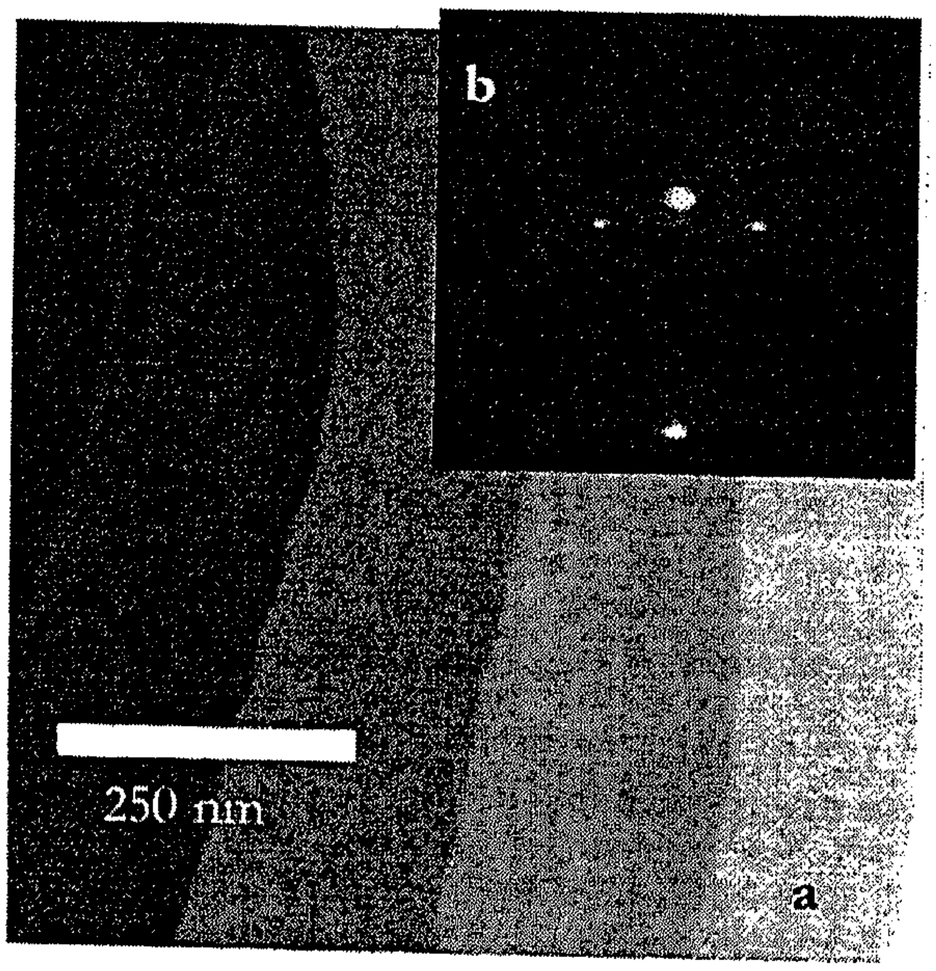

Figure1: *a) AFM micrograph of treated $SrTiO_3$ substrate surface prior to deposition.*
b) RHEED pattern at 750 C at 0.15 mbar oxygen.

The laser used in this study is a KrF (248 nm) excimer laser (Lambda Physik). The laser beam is focussed on the target using standard mirror and lenses. The projection of the beam can be adjusted, keeping the energy density at 1.35 J/cm^2, to change the deposition rate. Typical value for the spot size is 2.3 mm^2 in the case of $SrTiO_3$. The laser reputation rate is usually 0.5-1 Hz and oxygen pressure during deposition is 15 Pa, unless otherwise noted.

To perform initial growth and relaxation studies, the surface of the single crystal substrate surface is of the utmost importance. Here, we used nearly perfect single terminated $SrTiO_3$ surfaces. These surfaces are obtained performing a two-step procedure. First, hydroxylation of the SrO followed by its dissolving in BHF. The first step enhances the selectivity in solubility by the formation of a Sr-hydroxide complex and is confined to the topmost SrO-layer. This pre-treatment makes the p$\mathcal{H}$-value of the BHF-solution and etch-time become much less critical. Because of the possibility to reduce the etch-time, formation of etch-pits and holes due to prolonged etching is prevented. After annealing (mostly at deposition temperatures), the surface shows straight single terminated terraces with only one unit cell steps [5].

The surface morphology of the substrates and thin films are characterized using a Nanoscope IIIa atomic force microscope (AFM) in contact mode in air. Rectangular tapping mode tips with

spring constant k = 20-100 N/m are utilized in an attractive mode. In figure 1 an example is given of an AFM picture (1a), including the RHEED pattern (1b) at high temperatures (650 C) and high pressure (15 Pa), of a high quality, single terminated, single crystal, $SrTiO_3$ substrate as used in this study.

3. RESULTS AND DISCUSSION

3.1 Intensity oscillations depositing $SrTiO_3$ on $SrTiO_3$

The applicability of the presented high pressure PLD-RHEED system is demonstrated by studying the growth behaviour of $SrTiO_3$ on the special treated single terminated $SrTiO_3$ single crystal surface. Figure 2 shows the normalized RHEED intensity during the deposition at 750°C, at an oxygen pressure of 0.05 and 0.15 mbar. The RHEED intensity of the specular reflection is given during the deposition of the first two unit cell layers. The difference in growth behavior at different oxygen pressures is clear visible. At higher pressure (0.15 mbar) the intensity has decreased significantly after the deposition of two unit cells, indicating the formation of islands at the surface (3D growth). The height of the maximum of the intensity at 0.05 mbar of oxygen stays constant, indicating layer by layer growth, without the formation of islands. The data obtained at this low pressure could be fitted with the 2-level growth model, presented by Lagally *et al.* [6]. The proposed model describes the shape and amplitude of the intensity oscillation if the deposition remains a two-level system and the effect of kinetic roughening or stress relaxation, so-called transition to a multilevel system. The dotted lines are the fitted data with this 2-level model. Moreover, figure 3 shows the intensity oscillation during deposition of 4 unit cells of $SrTiO_3$ at 850 °C, using an oxygen pressure of 0.05 mbar. The data fit excellent with the above mentioned model, indicating that $SrTiO_3$ can be grown in a true 2D mode in this temperature and pressure regime. For the fit we used an incident angle of 0.8 degree and a period of 27 sec. The RHEED signal deviates only at the beginning of the $SrTiO_3$ deposition. A possible explanation can be the stress, during the growth of the first unit cell, although we must not exclude the surface quality of the $SrTiO_3$ target during the first shots. However, the latter effect should be very small, because prior to the deposition we clean the target by ablating it during several pulses.

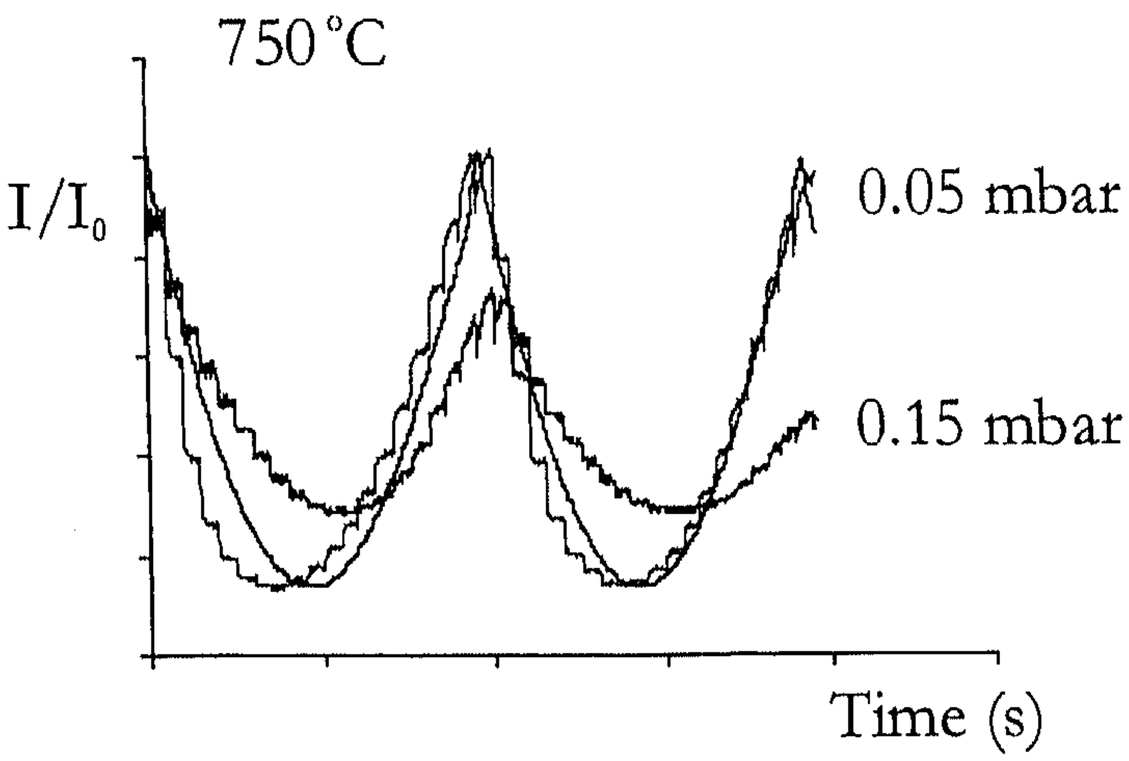

Figure 2: *Normalized RHEED intensity during deposition of $SrTiO_3$ at 750 °C at an oxygen pressures of 0.05 mbar and 0.15 mbar. The dotted line is a fit with the 2-level model [6].*

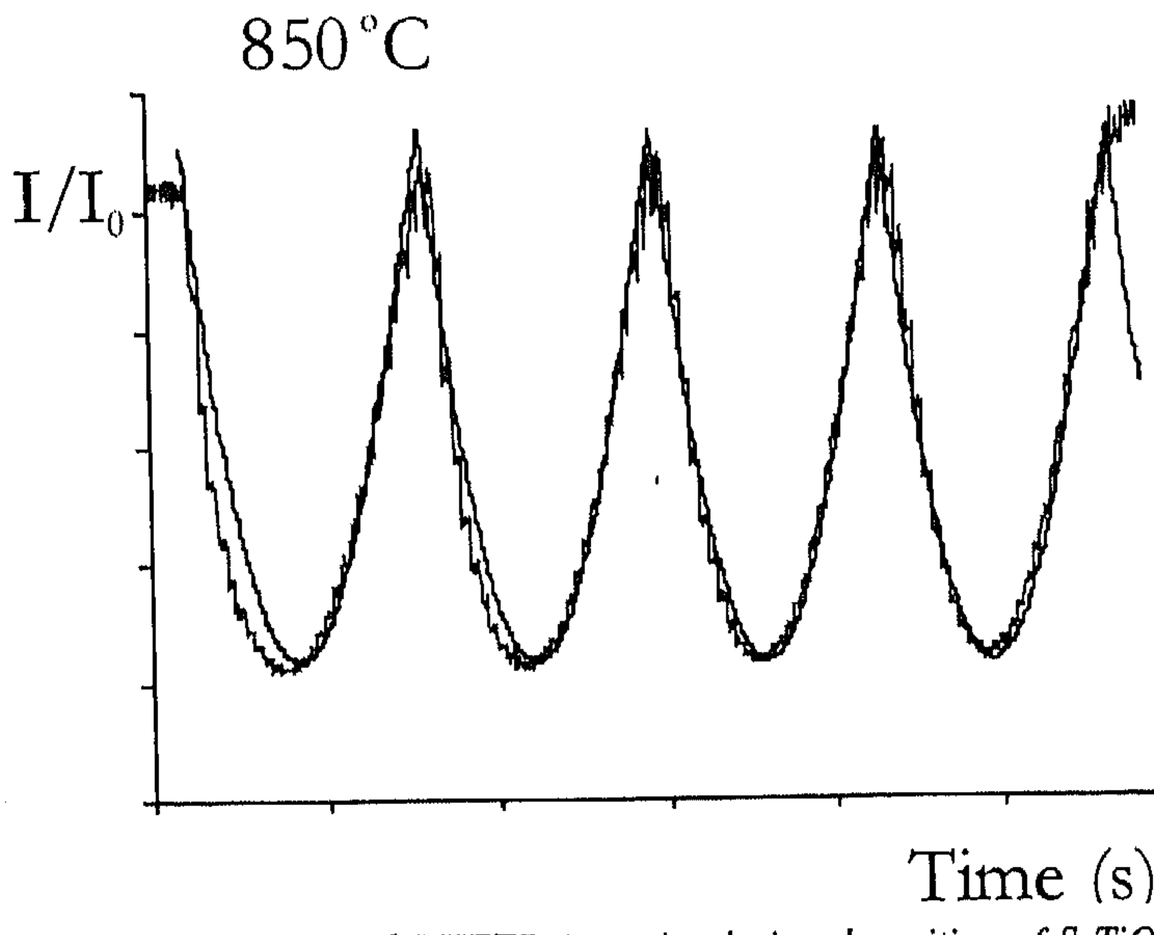

Figure 3: *Normalized RHEED intensity during deposition of $SrTiO_3$ at 850 °C and 0.05 mbar O_2. The dotted line is a fit with the 2-level model of Lagally et al. [6], with incident angle of 0.8 degree and period of 27 sec.*

The surface morphology of the sample presented in figure 3 has been analyzed with AFM. The surface shows only unit cell high islands at the surface. Their number and size depend on the amount material deposited. The surface morphology of a sample deposited at higher pressures (0.15 mbar) shows, after depositing

several unit cells, clear islands growth, see figure 6. Although the terraces caused by the miscut angle of the $SrTiO_3$ substrate is still clearly visible, multiple stacks of $SrTiO_3$ islands can be observed. This explains the decrease in the RHEED intensity oscillations as shown in figure 2. Subsequent we will show that we can prevent the formation of these islands by interval deposition.

3.2 Intensity relaxations

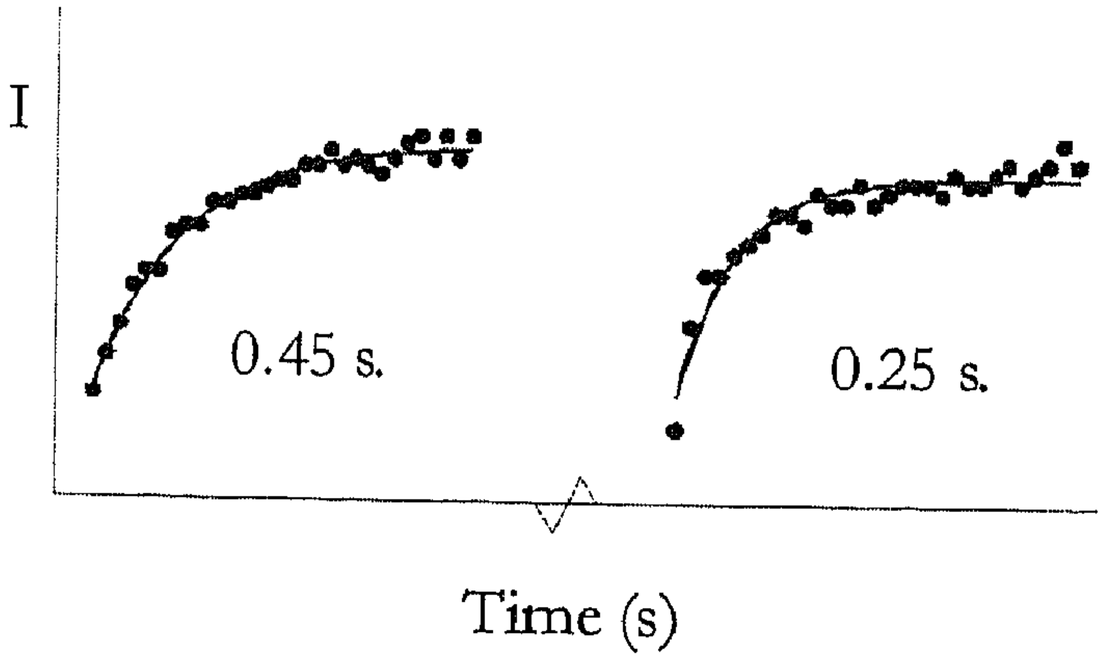

Figure 4: *Relaxation of RHEED intensity after laser pulse, both recorded at 750 °C and 0.05 mbar. The recovery is shown at θ=0.95 and θ=0.9, with θ the 2D-coverage ratio*

From the previous experiments we can 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, explained by the fact that decreasing the oxygen pressure means increasing of the mobility of the ad atoms. This is also confirmed by the observed intensity relaxation times, originated from the pulsed deposition. In figure 2 and 3 one can observe these relaxations; it gives the intensity oscillations a stepped shape. Each laser pulse produces a relatively large amount of material within several microseconds resulting in a high degree of disorder at the surface. The material will either nucleate on terraces or be adsorbed at step edges. This relaxation is seen superimposed on the RHEED oscillations. The relaxation time and amplitude depends on the position of the RHEED intensity oscillation. Figure 4 shows two examples of relaxation pulses; both recorded at 750 °C and an oxygen pressure of 0.05 mbar. The recovery after the laser pulse is shown at θ=0.95 and θ=0.9, where θ is the 2D coverage ratio (θ=1 for complete coverage). The recovery has an exponential rise, characterized by a specific relaxation time constant. This constant depends on substrate temperature, surface condition, deposited material and background pressure. Karl and Stritzker noticed already in their first RHEED oscillations during the pulsed laser deposition of $YBa_2Cu_3O_7$ this relaxation behaviour [2].

In first approximation this intensity relaxation can be represented by the following expression:

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

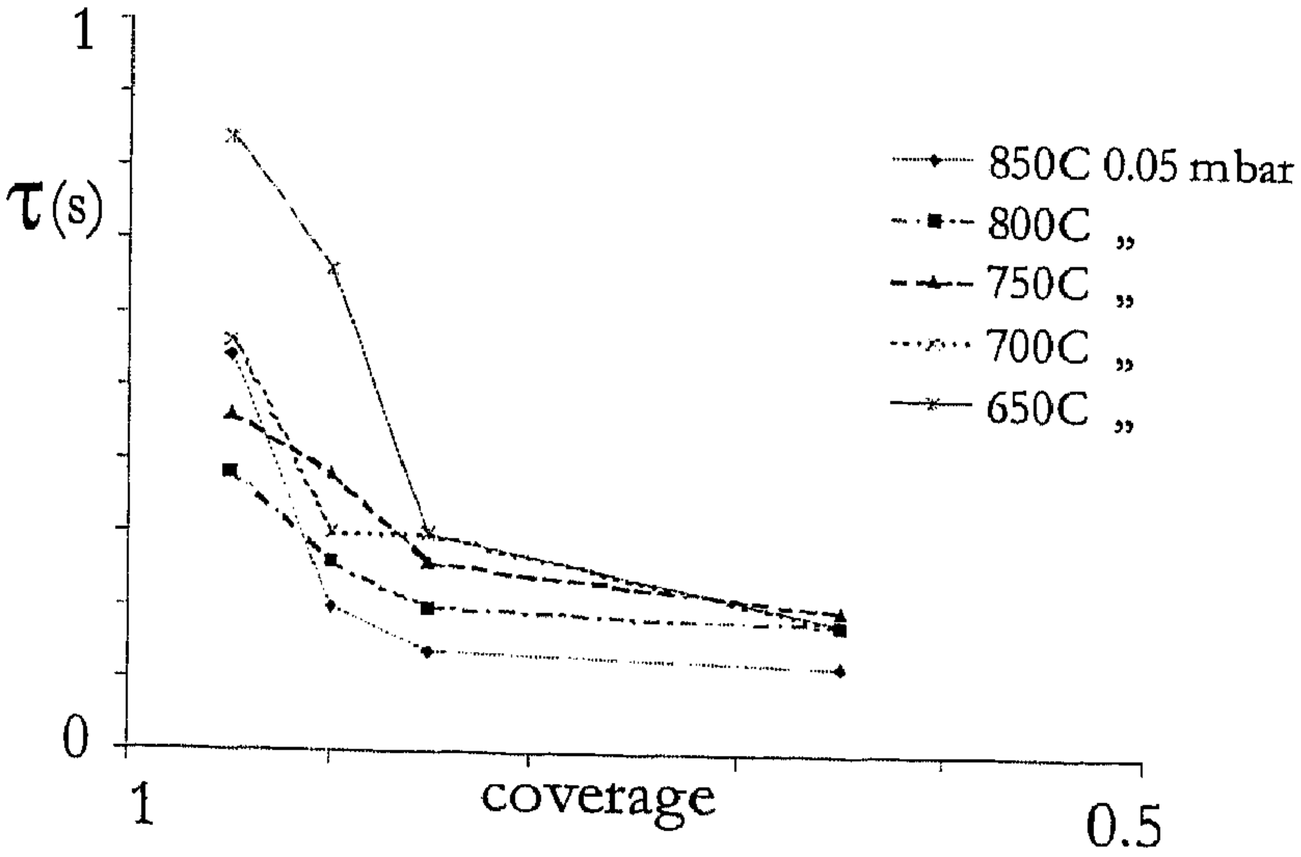

Figure 5: *Relaxation times determined using equation (1) for different temperatures at oxygen pressure of 0.05 mbar as a function of the 2D-coverage ratio θ.*

with, τ the characteristic time of the diffusion of ad atoms on the terraces. An exponential time constant is chosen, assuming an initial random distribution of material and nucleation sites. Random diffusion across the surface gives rise to an overall exponential time constant for the nucleation process. This time constant τ depends on the density of nucleation sites, the mobility and the diffusion velocity. Here, we neglect the relaxation of the intensity due to migration of surface steps. Using expression (1) characteristic time constants are calculated for different $SrTiO_3$ deposition conditions. Figure 5 shows the different time constants as a function of the 2D-coverage θ. The time constants vary between of 0.6 s (θ=0.95) and 0.1 s (θ=0.75). For smaller θ the accuracy becomes too

small, due to the increased overall intensity of the oscillation.

The characteristic times shown in figure 5 depend on, both, temperature and pressure during PLD. The deposition rate has kept constant, although small variations cannot be avoided. Variations in deposition rate will change the number of pulses needed to complete one unit cell. Another important parameter is the surface morphology prior deposition. In all cases the $SrTiO_3$ surface has been treated as described in the experimental section. Nevertheless, variations in miscut angle can influence the relaxation time significantly, especially at $\theta>0.95$. From figure 5 we observe the following characteristics. At higher temperatures shorter relaxation times have been found, whereas longer times are measured for higher pressure. This is in agreement with the results obtained from the RHEED intensity oscillations as discussed above. The coverage, however, has a much stronger effect on the relaxation time. When it is near unity, that is, a unit cell layer has nearly become completely filled, the relaxation times become very sensitive for temperature, compared to those values found at a coverage of half a unit cell layer. This can be explained by the fact that at the latter 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. As mentioned before, one has to keep in mind that the results near unity will be influenced by the miscut angle of the substrates, which determines the terrace step density.

The characteristic times depositing $SrTiO_3$ with a background pressure of 0.15 mbar are less dependent on the coverage (data not included in figure 5). This is in agreement with the results obtained from the intensity oscillations. Since we no longer deal with a 2D system there will be less variation in step density during deposition.

3.3 Interval deposition

A consequence of the results described in the previous sections is the fact that a high oxygen pressure (~0.15 mbar) introduces surface roughness and the occurrence of island (or 3D growth). Figure 6 shows the decrease of RHEED oscillation intensity through the increase of surface roughness during deposition of $SrTiO_3$ at 800 C at 0.15 mbar oxygen pressure. In the correspondent AFM image the islands are clearly visible. Besides the terraces due to the miscut angle of the $SrTiO_3$ substrate (still visible after depositing 35 nm $SrTiO_3$), 3D features can be seen. Each height difference is one unit cell of $SrTiO_3$.

Growth interruption, allowing surface reconstruction, could be an alternative to smoothen the film again. This effect can be observed by RHEED, by an increase of intensity after the deposition has been stopped. Growth interruption usually has been applied at growth temperature, but mobility at these temperatures is slow. A higher temperature can increase the mobility. In a previous paper we showed that the RHEED intensity after deposition of several unit cells of $SrTiO_3$ can be recovered after an *in-situ* annealing of 5 min. at 850 °C [4]. This is a direct consequence of the surface smoothening during the annealing step. The recovery of the oscillations can be repeated several times.

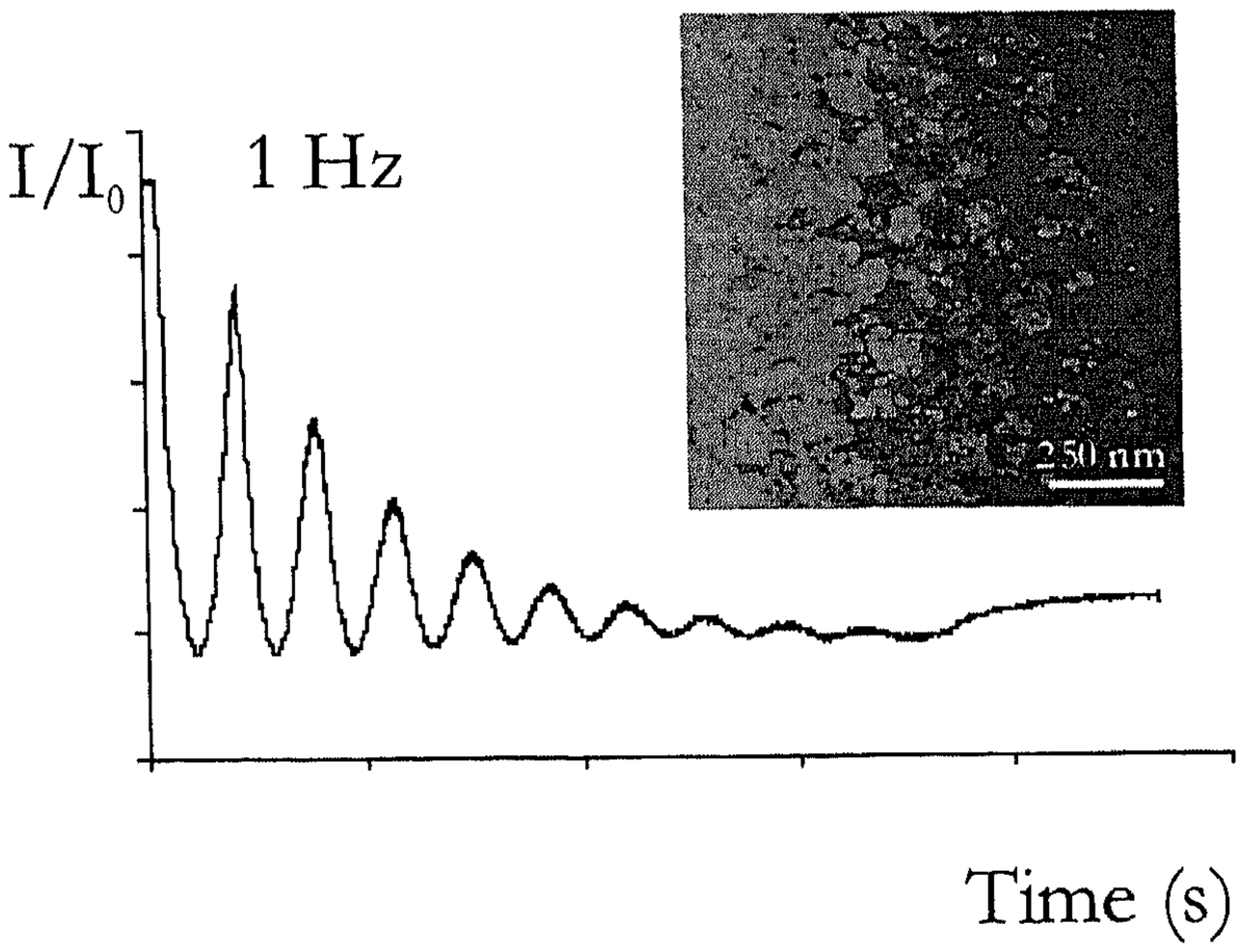

Figure 6: *RHEED oscillations, depositing $SrTiO_3$ at 800 C in 0.15 mbar oxygen pressure at laser frequency of 1 Hz. AFM image after depositing 35 nm $SrTiO_3$.*

An alternative solution is interval deposition. The idea finds its origin from the relaxation times and RHEED intensity oscillations, as reported in the previous sections. At higher oxygen pressures, the time constant becomes smaller indicating a smaller diffusion length of the ad- atoms. By depositing one unit cell layer, using a very high laser pulse frequency, followed by a period with no deposition, the material has the possibility to form one complete unit cell layer. By repeating this procedure, it is possible to grow $SrTiO_3$ in a 2D mode at higher pressures (0.15 mbar). Figure 7 shows the RHEED intensity, applying this method of

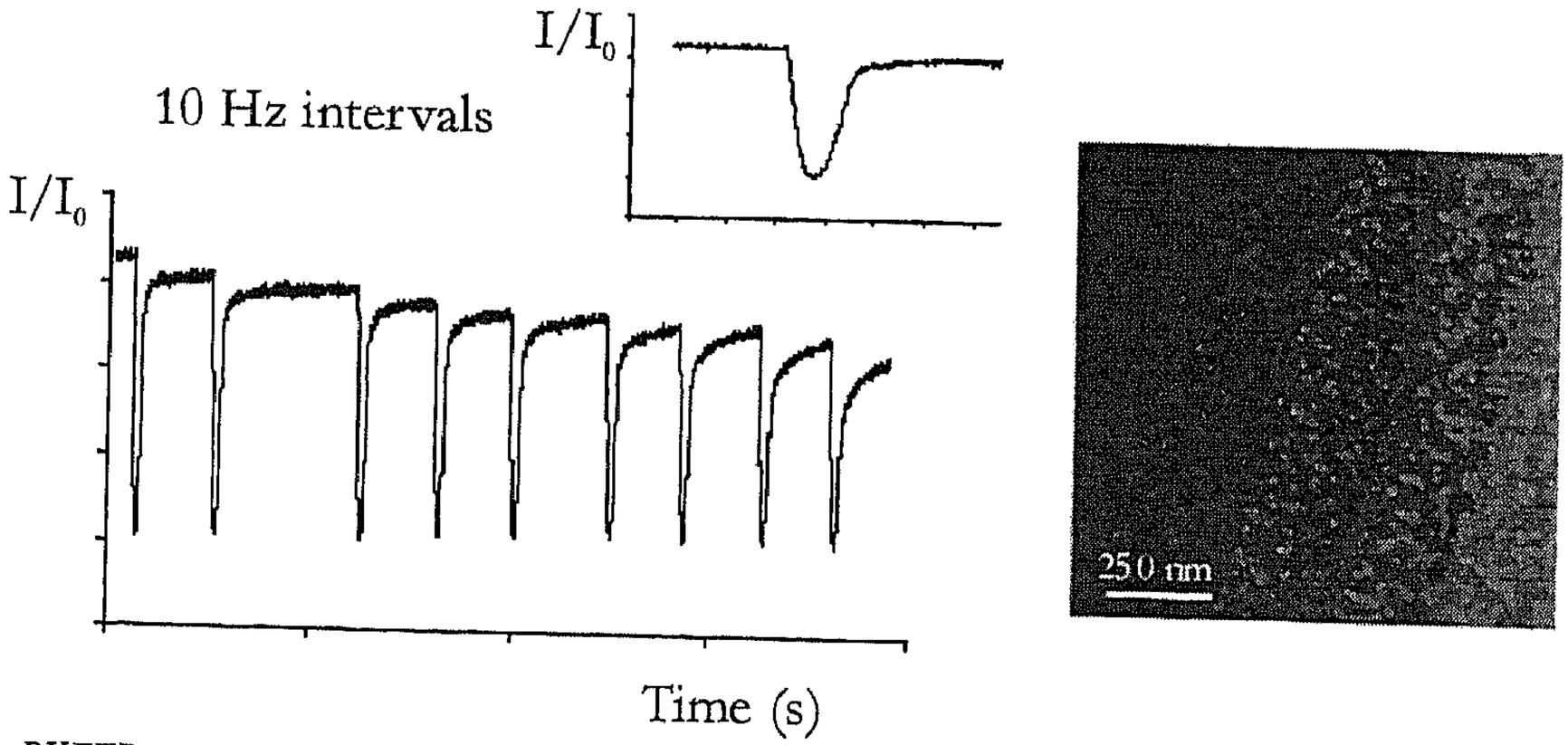

Figure 7: *RHEED intensity during interval deposition. Inset is deposition of one unit cell with laser frequency of 10 Hz. AFM image is taken after deposition of 35 nm $SrTiO_3$ with interval deposition, using a laser frequency of 100 Hz.*

interval deposition. The pulse frequency is 10 Hz. After depositing exact the amount material to form one unit cell of $SrTiO_3$, the deposition has been stopped for 0.5 sec. This has been repeated several times. The decrease of RHEED intensity is very small, indicating a smooth surface or layer by layer growth. Note that the intensity has been dropped almost completely after completing 10 unit cell layers if the interval deposition not has been used, see figure 6. Using the interval deposition, the intensity drop is less then 20%. This interval procedure has also been applied, using a laser pulse frequency of 100Hz. The AFM image in figure 7 shows the result. Clearly visible are the terraces, initiated by the miscut angle of the $SrTiO_3$ substrate. Only island with heights of one unit cell of $SrTiO_3$ could be find. This way of interval deposition opens the way of depositing infinite layer compounds at high oxygen pressures in a layer by layer fashion.

Finally, during the interval deposition experiments we observed the following. A decrease of the RHEED intensity is predominantly due to a not complete deposition of one unit cell. Adjusting the amount material during deposition (i.e. the number of laser pulses can compensate this effect). An example of real time monitoring with RHEED during the growth layered material.

4. CONCLUSIONS

Although scattering of electrons in high oxygen pressure decreases the intensity of the electron beam, we have shown that growth monitoring of complex oxides at high oxygen pressures is feasible using RHEED. With this system we have monitored the growth of $SrTiO_3$ using PLD up to 0.15 mbar of oxygen. Clear oscillations of the diffracted intensity could be obtained. This has led to true 2D growth of $SrTiO_3$, deposited at 850 C in 0.05 mbar of oxygen background pressure.

The relaxation times, due to the pulsed deposition, have been measured for different deposition temperatures. In the case of $SrTiO_3$, the measured characteristic times depend both on temperature and deposition pressure, but most of all on the coverage ratio.

In-situ anneal steps between deposition runs improve the smoothness of the $SrTiO_3$ surface, as indicated by the RHEED patterns. Applying this phenomena in so-called interval deposition leads to layer by layer (or 2D) growth of $SrTiO_3$ at much higher oxygen pressure (typically 0.15 mbar). For the interval deposition we used a laser frequency of 10 and 100 Hz, respectively. Especially the films deposited with the higher frequency have very smooth surfaces. This method can be applied to almost all layered materials.

5. ACKNOWLEDGEMENTS

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