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A New Approach in Layer-by-layer Growth of Oxide Materials by Pulsed Laser Deposition

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Abstract. Pulsed laser deposition (PLD) has become thin film deposition technique with increasing prominence. One of the advantages above other techniques is the possibility to growth at relative high background pressures, with a large freedom in choosing the kind of gas. An example is oxygen in the case of high T_c superconductors and giant magnetic resistors. However, the advantage of relative high pressures hinders the use of a number of diagnostics and monitor techniques, like reflective high energy electron diffraction (RHEED).

With the introduction of 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. In this paper we employed this technique on $SrTiO_3$, which can be grown in different growth modes depending on growth temperature and oxygen pressure during deposition. Applying a modified etch treatment on $SrTiO_3$ single crystals, a real 2D growth mode could be observed by the homo-epitaxial growth of $SrTiO_3$, as indicated by RHEED oscillations.

In addition to the RHEED oscillations another phenomenon is observed, typical for PLD. The pulsed way of deposition leads to discontinuities 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 and leads to a characteristic exponential slope with characteristic relaxation time constants. These time constants give extra information about relaxation, crystallization, and nucleation of the deposited material during growth.

Finally, a new approach to deposit these complex oxide materials will be introduced. This, so-called interval deposition, is based upon the results obtained from the intensity oscillations as well as relaxations. The basic idea is to deposit an equivalent of one unit cell of material in such a short time that no coalescence in larger islands can occur, followed by a relaxation time before the next unit cell layer is deposited. This interval deposition leads to an imposed layer by layer growth.

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

Introduction

In recent years pulsed laser deposition (PLD) has become a common technique to fabricate various (complex) materials. Especially the versatility 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 depositing the high T_c superconductors and giant magnetic resistance (GMR) materials. The relative high oxygen pressure needed during the deposition of perovskite structures hinders to some extent the use of other deposition techniques, making PLD such a preference technique as it is up-to-date. However, this relative high background pressure during PLD (mostly oxygen, but of course not restricted to that) hampers monitoring and diagnostic techniques 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).

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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.

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] published 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, e.g., $YBa_2Cu_3O_7$.

The (oxygen) background pressure during deposition is a very important parameter. The pressure influences the shape of the plasma; it will slow down the species inside the plasma, given it the characteristic spheroids profile. Moreover, 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 we have developed a PLD-RHEED system, which makes it possible to perform growth studies during PLD at standard deposition conditions [4]. From these growth studies, additional information about the mobility of the deposited material during one laser pulse could be obtained. As a result a new approach of fabricating oxide thin films will be introduced.

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 20–35 KeV, 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 one degree. Using this setup clear diffraction patterns can been observed up to 0.5 mbar of oxygen.

The lasers used in this study are a KrF (248 nm) and XeCl excimer laser (both 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. The laser reputation rate during continuous deposition is typically 0.5–1 Hz and oxygen pressure during deposition is 0.15 mbar, unless otherwise noted. Using interval deposition the reputation rate must be as high as possible (10–100 Hz).

One of the most important issues in initial growth and relaxation studies is the quality of the surface of the single crystal substrate. In this study we used nearly perfect single (Ti) terminated $SrTiO_3$ surfaces. These surfaces are obtained performing a two-step procedure. This treatment finds its basic in the buffered HF etch processing, as published by Kawasaki et al. [5]. The outcome of this treatment is (in our case) very sensitive to the quality of the as-received substrates. For that reason, in addition to the aimed preparation, we propose a hydroxylation of the SrO followed by its dissolving in BHF. The thorough

procedure has been published elsewhere [6]. In brief, 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 $p\mathscr{H}$-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.

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 $k = 20\text{-}100$ N/m are utilized in an attractive mode. In Fig. 1 an example is given of an AFM picture (1a), including the RHEED pattern (1b) at high temperatures (650°C) and high pressure (0.15 mbar), of a high quality, single terminated, single crystal, $SrTiO_3$ substrate treated with the above described method and used in this study.

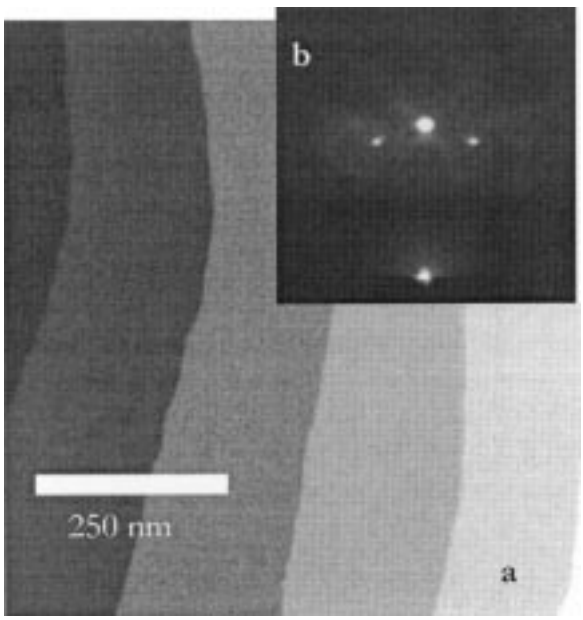

Fig. 1. (a) AFM micrograph of treated $SrTiO_3$ substrate surface prior to deposition. (b) RHEED pattern at 750°C at 0.15 mbar oxygen.

Results and Discussion

Intensity Oscillations

It is well known that $SrTiO_3$ can be grown in different growth modes, ranging from 2D layer by layer till step flow. For this we used homoepitaxial growth of $SrTiO_3$ on the special treated single terminated $SrTiO_3$ single crystal surface to study the applicability of the presented high pressure PLD-RHEED system. Figure 2 shows the normalized RHEED intensity during the deposition at 750°C, in an oxygen background pressure of 0.05 and 0.15 mbar, respectively. The RHEED intensity of the specular reflection is given during the deposition of the first two unit cell layers. The effect of the oxygen pressure on the growth behavior is clear visible. At higher pressure (0.15 mbar) the intensity already reduces significantly after the deposition of two unit cells, indicating a surface roughness, thus the formation of islands at the surface (3D growth). Though, the height of the maximum of the intensity for $SrTiO_3$ deposited with 0.05 mbar of oxygen stays constant, indicating an extremely flat surface without the formation of islands. Such an oscillation pattern can only be obtained if the material grows in a true 2D layer by layer growth mode. The data obtained at this low pressure could be fitted with the 2-level growth model, as presented by Lagally et al. [7]. 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

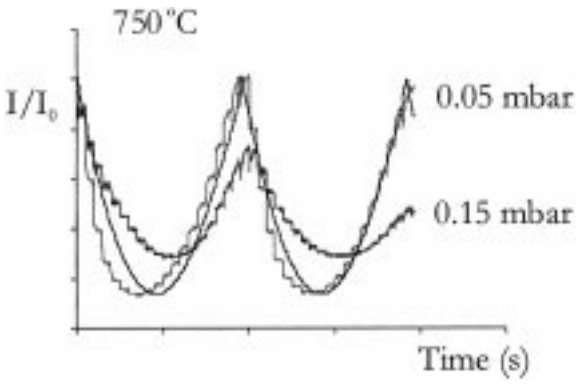

Fig. 2. Normalized RHEED intensity during deposition of $SrTiO_3$ at 750°C at an oxygen pressures of 0.05 mbar and 0.15 mbar. The dotted line is a fit with the 2-level model.

or stress relaxation, so-called transition to a multilevel system, does not occur. The dotted lines are the fitted data with this 2-level model. Moreover, Fig. 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 could be fit 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.

Figure 4 shows the surface morphology of a 35 nm $SrTiO_3$ thin film deposited at 850°C, using an oxygen pressure of 0.05 mbar. The AFM data show a very smooth surface with only islands with one unit cell height. Their number and size depend on the time at which the deposition has been stopped during the formation of one unit cell. The surface morphology of a sample deposited at higher pressures (0.15 mbar) shows, after depositing 35 nm $SrTiO_3$, clear islands growth, see Fig. 5. 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 Fig. 5. From the 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. Subsequent we will show that we can prevent the formation of these islands by interval deposition.

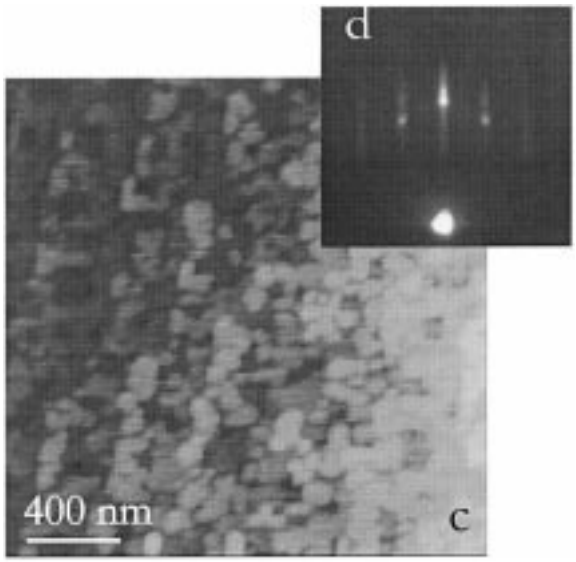

Fig. 4. AFM image of 35 nm $SrTiO_3$ deposit at 850°C in 0.05 mbar oxygen (c), with corresponding RHEED pattern (d).

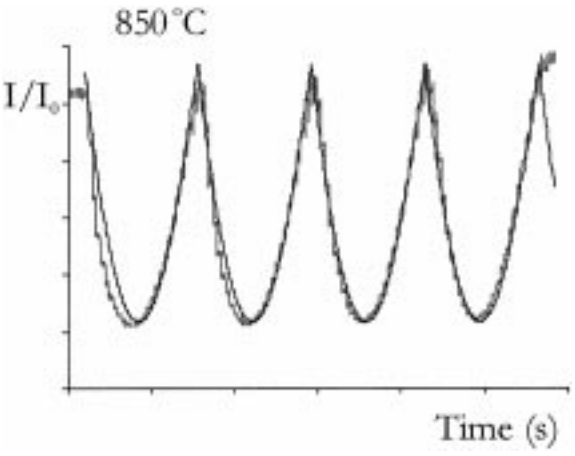

Fig. 3. Normalized RHEED intensity during deposition of $SrTiO_3$ at 850°C and 0.05 mbar O_2. The dotted line is a fit with the 2-level model of Lagally et al. [7], with incident angle of 0.8° and period of 27 sec.

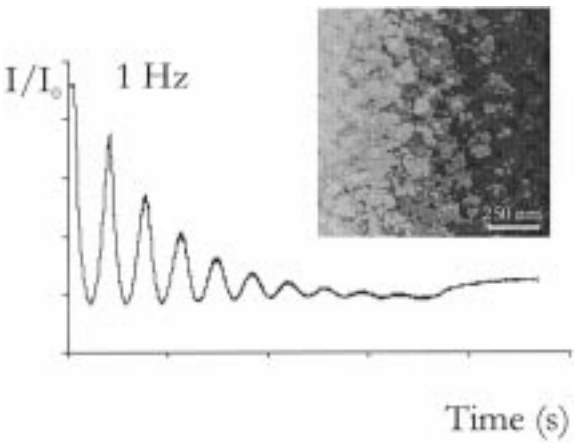

Fig. 5. RHEED oscillations, depositing $SrTiO_3$ at 800°C in 0.15 mbar oxygen pressure at laser frequency of 1 Hz. AFM image after depositing 35 nm $SrTiO_3$.

Intensity Relaxations

From the intensity oscillations as given in Fig. 2 and 3 one can observe discontinuities, originated from the pulsed way of deposition: 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. A closer look shows that this relaxation time and amplitude depends on the position of the RHEED intensity oscillation or in other words if the surface is smooth (full coverage) or rough (half coverage or half unit cell layer). Figure 6 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 $\theta = 0.95$ and $\theta = 0.9$, where θ is the 2D coverage ratio ($\theta = 1$ 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.

Assuming an initial random distribution of material and nucleation and neglecting the relaxation of the intensity due to migration of surface steps this intensity relaxation can be represented by the following expression:

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

with, τ the characteristic time of the diffusion of ad atoms on the terraces. Here, an exponential time constant is chosen (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. Using expression (1) characteristic time constants are calculated for different deposition conditions. Figure 7 shows the different time constants as a function of the 2D-coverage θ. The time constants vary between of 0.6 s ($\theta = 0.95$) and 0.1 s ($\theta = 0.75$). For smaller θ the accuracy becomes too small, due to the lower overall oscillation intensity.

The characteristic times shown in Fig. 7 depend on, both, temperature and background pressure during PLD. The deposition rate has kept constant, although small variations cannot be avoided. Variations in deposition rate, e.g., a change in the amount of ablated material, change in plasma formation, or temperature dependent sticking coefficient, will change the number of pulses needed to complete one unit cell and thus the period of the oscillation. 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 $\theta > 0.95$.

The shorter relaxation times at higher temperatures, whereas for higher pressure longer times are found, 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

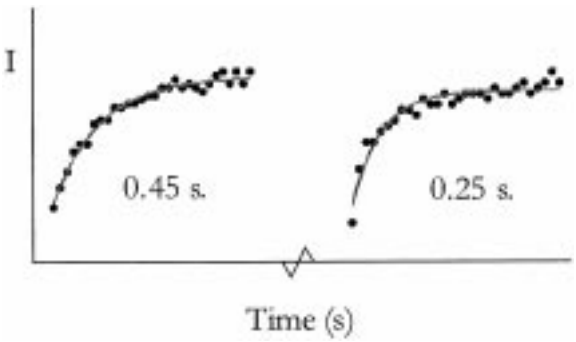

Fig. 6. Relaxation of RHEED intensity after laser pulse, both recorded at 750°C and 0.05 mbar. The recovery is shown at $\theta = 0.95$ and $\theta = 0.9$, with θ the 2D-coverage ratio.

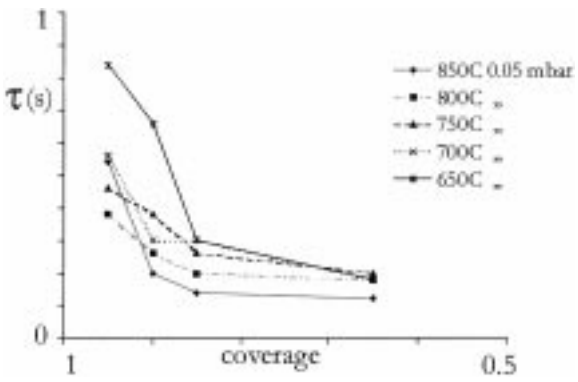

Fig. 7. Relaxation times determined using Eq. (1) for different temperatures at oxygen pressure of 0.05 mbar as a function of the 2D-coverage ratio θ.

cell layer has nearly become completely filled, the relaxation times become very deposition temperature dependent, compared to those values found at a coverage of half a unit cell layer. 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. On has to beware that the results near unity will be influenced by the terrace step density or miscut angle of the substrates.

The characteristic relaxation times depositing $SrTiO_3$ with a higher background pressure of 0.15 mbar are less dependent on the coverage. This is in agreement with the results obtained from the RHEED intensity oscillations, as given in Fig. 5. Because of an increase of 3-D islands, and thus no perfect 2D layer by layer growth, the variation in the number of nuclei will be less during the deposition of one unit cell layer.

Interval Deposition

Because of the observed relaxation times, as shown in Fig. 7, the deposition conditions, like temperature and pressure, are critical in obtaining 2D growth. Depositing $SrTiO_3$ at high oxygen pressure one can clearly see a surface roughness and the occurrence of island (or 3D growth). The difference in RHEED oscillation intensities in Fig. 2 and 5 emphasize this behavior.

A possibility to correct for this increase in surface roughness is by interrupting the growth, allowing the surface to reconstruct. This reconstruction can be observed by RHEED through 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 $SrTiO_3$ and $YBa_2Cu_3O_7$ 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.

Here, we present a different approach to obtain smooth films by imposing layer by layer growth. Usually, in *continuous* deposition, the islands are allowed to coalesce and thus forming larger islands on

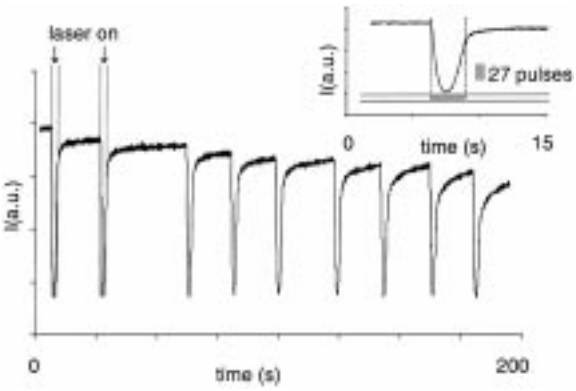

Fig. 8. RHEED intensity during interval deposition. Inset is deposition of one unit cell with laser frequency of 10 Hz.

the surface between the laser pulses. On top of these larger islands smaller islands will be formed during subsequent deposition, resulting in the formation of so-called pyramid growth. This will lead to roughening of the surface and an exponential decay of the RHEED specular spot intensity, see Fig. 5. With this new approach a complete mono- or unit cell layer is deposit in a short period of time, using a high laser pulse frequency (typically 10–100 Hz). The small islands that are formed on the surface during this short deposition period do not have time to coalesce. The surface becomes very rough and the RHEED intensity

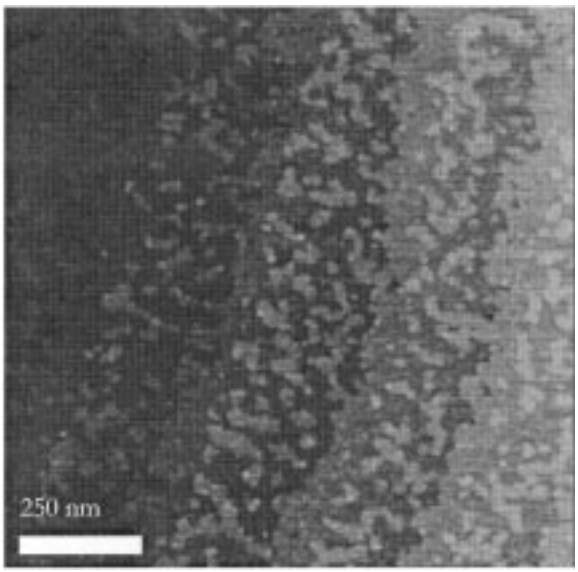

Fig. 9. AFM image after deposition of 35 nm $SrTiO_3$ with interval deposition, using a laser frequency of 100 Hz.

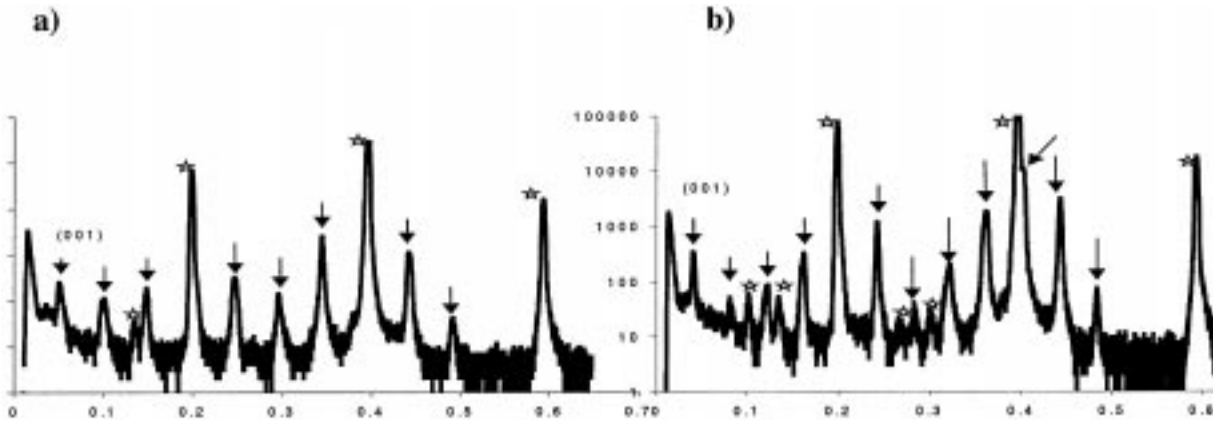

Fig. 10. Two examples of X-ray diffraction intensity profiles of superlattices fabricated with pulsed laser interval deposition. (a) $2xBaCuO_2/2xSrCuO_2$, (b) $2xBaCuO_2/3xSrCuO_2$; arrows indicate the (0 0 l) reflections of the film, stars are the reflections of the substrate.

drops, because of a great number of small islands at the time one stops to deposit material. At this point in time, the surface will immediately start to relax and form a complete mono- or unit cell layer. The next layer will be deposited after this layer is completed. Due to the formation of a completely closed layer, prior to the next deposition interval, the RHEED intensity will recover. Because of the discontinuity during deposition we call this approach interval deposition.

To show the ability of interval deposition, we deposit $SrTiO_3$ in a 2D mode at higher pressures (0.15 mbar). Figure 8 shows the RHEED intensity, applying this method of interval deposition with a pulse frequency of 10 Hz. After depositing exact the amount material to form one unit cell of $SrTiO_3$ (i.e., 27 pulses) 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 imposed layer by layer growth. Note that in the case of the continuos deposition, the intensity has been dropped almost completely after 10 unit cell layers, see Fig. 5. This interval procedure has also been applied, using a laser pulse frequency of 100 Hz and the AFM image in Fig. 9 shows the result. Clearly visible are the terraces, initiated by the miscut angle of the $SrTiO_3$ substrate. Only heights steps of one unit cell of $SrTiO_3$ could be find.

This way of interval deposition is not restricted to $SrTiO_3$-like materials, but can also be applied to, e.g., superlattices [8]. In this case each block of, e.g., $BaCuO_2$ and $SrCuO_2$ is deposited by interval. Figure 10 shows two examples of X-ray diffraction intensity profiles of superlattices fabricated with pulsed laser interval deposition. First, a supperlattice of $2xBaCuO_2/2xSrCuO_2$ with a *c*-axis length of ~ 1.58 nm (a) and, second, a superlattice with $2xBaCuO_2/3xSrCuO_2$ and a *c*-axis length of ~ 1.91 nm (b). The arrows indicate the (0 0 1) reflections originated from the supperlattice, the stars are the $SrTiO_3$ substrate reflections.

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) [9]. An example of real time monitoring with RHEED during the growth of layered material.

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, i.e., surface roughness.

In-situ anneal steps between deposition runs improve the smoothness of the $SrTiO_3$ surface, as indicated by the RHEED patterns. Depositing every unit cell layer at a very high deposition rate followed by a relaxation interval, we extend the typical high super saturation for PLD keeping the average islands size as small as possible. Therefore, the interlayer mass transport is strongly enhanced and the formation of a multi level growth front can not occur. This technique can only be applied using PLD, since no other technique has the possibility to manipulate the deposition rate over a wide range, from very fast to an immediate stop of deposition. We have shown that thin films grown with this pulsed laser interval deposition can be controlled and engineered at an atomically level.

Acknowledgments

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