IN-SITU MONITORING DURING PLD OF COMPLEX OXIDES USING RHEED AT HIGH OXYGEN PRESSURE

GUUS J.H.M. RIJNDERS, GERTJAN KOSTER, DAVE H.A. BLANK, AND HORST ROGALLA
Low Temperature Division, Department of Applied Physics, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.

ABSTRACT

Several groups have monitored the growth of complex oxides *in-situ* using Reflection High Energy Electron Diffraction (RHEED). In order to utilize RHEED during growth, films are deposited at low background oxygen pressures. Because of the low oxidation power at low pressures, low substrate temperatures have to be used. This hampers, in general, the film crystallinity. Furthermore, the background pressure in Pulsed Laser Deposition (PLD) is an important parameter, because it influences the shape and size of the plasma and, therefore, the deposition rate and homogeneity of the film.

We have developed a high-pressure RHEED system, which can be used for growth monitoring during the deposition of complex oxides at standard PLD conditions. Clear diffraction patterns are observable up to 50 Pa, due to the minimized scattering losses.

$SrTiO_3$ substrate treatments as well as growth studies of $YBa_2Cu_3O_{7-\delta}$, using atomic layers of SrO or BaO as a buffer-layer, will be discussed in this contribution. It will be shown that monitoring and control of thin film growth by PLD on an atomic level is feasible, even in quite high background pressures.

INTRODUCTION

Reflection High Energy Electron Diffraction (RHEED) is widely established as a versatile *in-situ* diagnostics tool for thin oxidic film growth [1], especially in ultra-high vacuum (UHV) systems like molecular beam epitaxy (MBE) systems. It provides information on surface perfection by analysis of the diffraction pattern, while variations of the intensity of the diffraction spots is used to monitor the film growth. Layer-by-layer growth is indicated by RHEED as oscillations of the diffracted intensity. Sharp spots in the diffraction pattern indicate a flat and crystallographically perfect surface.

The epitaxial deposition of oxides by Pulsed Laser Deposition (PLD) takes place in a well-controlled oxygen atmosphere, allowing oxygen incorporation in the as-grown film. Moreover, the oxidation power at high oxygen pressures allows for higher deposition temperatures and, therefore, improved crystallinity is expected. Using low pressures during PLD can lead to the bombardment of the film by high energetic particles originating from the plasma. In general, due to scattering losses, the relatively high oxygen pressure in PLD hampers the diagnostics of the growing film surfaces by *in-situ* RHEED.

The growth of $YBa_2Cu_3O_{7-\delta}$ (YBCO) on $SrTiO_3$ has been subjected to many studies. It is believed that, because of charge neutrality, YBCO growths in unitcells consisting of 6 atomic layers with BaO as the terminating layer [2,3,4]. Deposition of YBCO, using stoichiometric targets, on TiO_2 terminated $SrTiO_3$ can lead to the formation of Cu_xO crystals, since for the first completed monolayer of YBCO, one CuO monolayer, the "chain" layer, is not incorporated. These crystals act as a getter for the rest of the deposited copper, leading to large Cu-rich precipitates.

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The influence of the substrate termination of $SrTiO_3$ substrates on the growth of YBCO is studied in this contribution. Surface treatments of $SrTiO_3$ substrates, as well as deposition of one monolayer of SrO or BaO prior to the deposition of YBCO, will be discussed.

EXPERIMENTAL

In this contribution we have studied the growth *in-situ* using a PLD-RHEED system, which is described by Rijnders *et al.* [5], at high oxygen pressure. In this system, a low-pressure stage ($P < 10^{-1}$ Pa), which encloses the electron beam, is placed on a differentially pumped electron gun. The pressure in the gun is maintained below 10^{-4} Pa to ensure long lifetime for the tungsten filaments. The electrons enter the high-pressure region close to the substrate. Furthermore, the fluorescent phosphor screen is placed near the substrate. Hence, scattering losses are minimized by keeping the traveling path (~100 mm) of electrons in the high-pressure region as short as possible. Using this setup clear diffraction patterns have been observed up to 50 Pa of oxygen. Real-time analysis of the RHEED patterns, captured by a CCD camera, is done with a computer. In this study, the angle of incidence of the electron beam with an energy of 20 keV is set to ~1°.

A KrF excimer laser beam (248 nm wavelength) is focused on a target with an energy density of 1.3 J/cm^2. Sintered pellets are used as target in the case of YBCO and single crystals in the case of SrO and BaO. The spotsize is 5.7 mm^2 in the case of YBCO and 2.6 mm^2 in the case of SrO and BaO. The substrate temperature during deposition is 760 °C, while an oxygen pressure of 15 Pa is used.

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 springconstant k = 20-100 N/m are utilized in an attractive mode.

RESULTS AND DISCUSSION

Substrate treatment

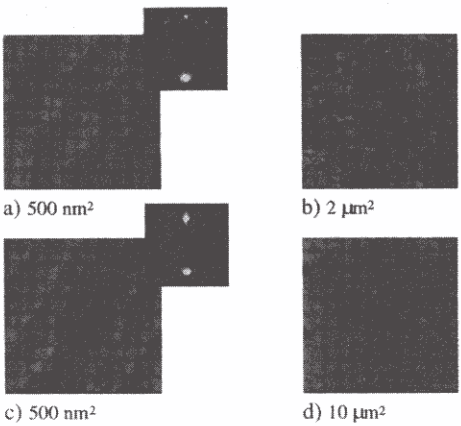


Figure 1: AFM micrographs of $SrTiO_3$ substrates after 4 hours in a flow of oxygen at 950 °C with a miscut angle of approximately 0.15 degrees (a) and a miscut angle smaller than 0.05 degrees (b) and an etched $SrTiO_3$ substrate (c and d). The insets show the diffraction pattern.

Figure 1a shows an AFM-micrograph of a $SrTiO_3$ (001) substrate, which have been annealed at 950 °C in a flow of oxygen for 4 hours. Using this treatment, a well-crystallized and atomically smooth surface is obtained by rearrangement of surface ions. However, depending on the 'miscut' angle, which is defined as the angle between the (001)-plane and the actual surface plane, a variety of surface morphologies are observed. As indicated in figure 1a, substrates with a miscut angle of approximately 0.15 degrees show a terraced surface with straight ledges, whereas, irregular ledges are observed on a substrate with a miscut angle smaller than 0.05 degrees (see figure 1b). Step-heights of approximately one unitcell are measured. Occasionally, besides unitcell steps also steps with height differences smaller then one unitcell are measured. Either SrO or TiO_2 can terminate the surface, due to the layered structure of $SrTiO_3$ (001). The diffraction pattern of these substrates shows sharp diffraction spots, as shown in the inset in figure 1a.

Besides annealing in oxygen also a chemical treatment (etching in a pH-controlled HF-NH_4F solution) is used to obtain atomically smooth surfaces with TiO_2 termination, as indicated by Kawasaki *et al.* [6]. As depicted from figure 1c, ultrasonic stirring of a substrate in a solution with a pH-value of 4.9 provides a stepped surface with flat terraces. The measured step heights are approximately one unitcell. However, on a larger scale (see figure 1d) also etch pits are formed. In this case, approximately 25, deep and square, etch pits are observed, on a surface of 10 μm^2, with a maximum depth of approximately 4 nm. Although clear diffraction spots are visible in the diffraction pattern (see inset in figure 1c), the intensity is lower compared to an annealed surface. Surface termination and roughness could be responsible for this difference.

Deposition of SrO and BaO monolayers

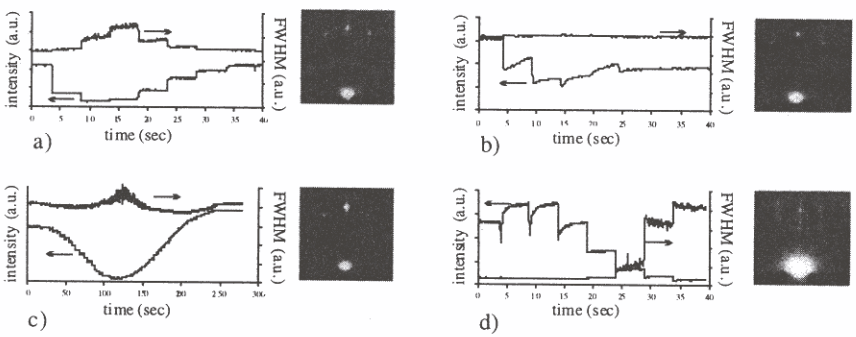


Figure 2: RHEED intensity and FWHM of a diffraction spot during deposition and diffraction patterns after deposition of one monolayer of BaO on an annealed $SrTiO_3$ substrate (a) and an etched $SrTiO_3$ substrate (b) and, next, one monolayer of SrO on an etched $SrTiO_3$ substrate (c) followed by deposition of BaO (d).

Using a laser repetition rate of 0.2 Hz, one monolayer of BaO (see figure 2a) is grown on an annealed $SrTiO_3$ substrate and, subsequently, on an etched $SrTiO_3$ substrate (see figure 2b). Recovery of the RHEED intensity and FWHM of a diffraction spot is obtained after 8 pulses in the case of deposition on an annealed $SrTiO_3$ substrate and 5 pulses on an etched $SrTiO_3$

substrate. Fluctuations of the deposition rate is not expected, and therefore, not responsible for this difference. A difference in wetting properties, due to a difference in surface termination, can lead to the formation of islands which might be responsible for the difference in the number of pulses, needed for the completion of one monolayer.

The intensity is clearly modulated by the laser pulse. A sharp decrease of the intensity, due to the increased disorder on the surface caused by the deposition after one pulse, is followed by an exponential rise, caused by rearrangement of the deposited material. Relaxation of the intensity, during deposition on an etched substrate, is slower compared to deposition on an annealed substrate. This can be explained by a difference in initial roughness or surface termination, which can lead to different wetting properties. Streaking of the spots in the diffraction pattern also indicate roughening of the surface.

Figure 2c shows the intensity and the FWHM of a diffraction spot during the growth of one monolayer of SrO on an etched substrate. After approximately 40 pulses, both intensity and FWHM are recovered. In this case, due to the difference in deposition rate compared to BaO, the amplitude of the relaxations is small. After completion of the SrO monolayer, 7 pulses of BaO are deposited *in-situ* (see figure 2d). No recovery of the intensity and FWHM is obtained. The spots in the diffraction pattern are clearly blurred into streaks. Deposition of additional BaO did not change the intensity. A three-dimensional growth mode, due to poor wetting properties, is expected.

Deposition of YBCO

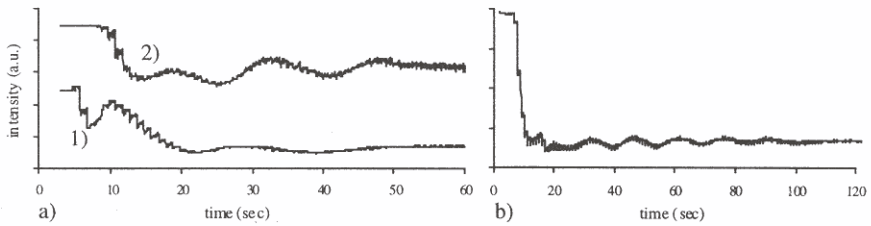
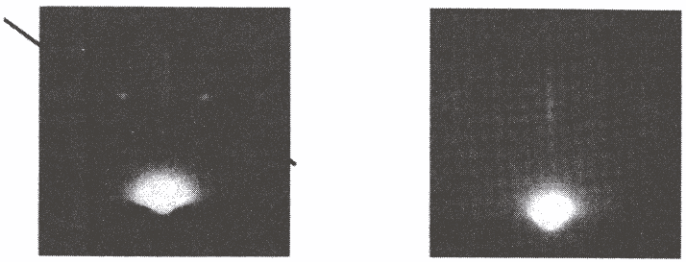


Figure 3: Intensity oscillations during deposition of 3 monolayers of YBCO on an annealed $SrTiO_3$ substrate (a1) and on an etched $SrTiO_3$ substrate (a2) and, next, 7 monolayers of YBCO on an etched $SrTiO_3$ substrate with a SrO bufferlayer (b).

The diffracted intensity during the growth of YBCO on an annealed and etched $SrTiO_3$ substrate is shown in figure 3a. A rapid decrease of the intensity followed by 3 distinct oscillations is observed. The first maximum of intensity is reached after approximately 10 pulses of YBCO in the case of deposition on an etched substrate and 6 pulses in the case of deposition on an annealed substrate. Both, surface chemistry and initial surface roughness could be responsible for this different behavior. Using an intermediate SrO monolayer enhances the layer by layer growth, as indicated by the intensity oscillations in figure 3b. Here, 7 oscillations are observed.

The diffraction pattern, taken at deposition conditions (figure 4a) after deposition of approximately 30 unit cells on an etched $SrTiO_3$ substrate, shows streaks, indicating a roughened surface. The arrows in figure 4a indicate additional weak spots. The horizontal distance between these spots corresponds with a real space distance of 4.27 Å, which can be associated with Cu_2O crystallites. When an intermediate monolayer of BaO is used between YBCO film and etched

substrate, only streaks are observed (see figure 4b). In this case, the formation of Cu_2O crystallites is prevented, as indicated by RHEED.



a) b)

Figure 4: Diffraction patterns after deposition of approximately 25 monolayers of YBCO on an etched $SrTiO_3$ substrate (a) and, subsequently, on an etched $SrTiO_3$ substrate with an intermediate BaO monolayer (b). The arrows in figure 4a indicate additional weak spots. The horizontal distance corresponds to a real space distance of 4.27 Å.

CONCLUSIONS

Both $SrTiO_3$ surface treatments, annealing at 950 °C in a flow of oxygen and etching with a buffered HF solution with a pH value of 4.9, provide well defined stepped surfaces with smooth terraces. The terminating layer, in case of the annealed surface, is not clear and can be either SrO or TiO_2. The growth of SrO and BaO monolayers depends on the surface chemistry, e.g., surface termination and initial roughness. Using intermediate BaO monolayers, prior to the growth of YBCO on TiO_2 terminated $SrTiO_3$, formation of Cu_xO precipitates can be prevented, as indicated by the diffraction patterns. These results indicate the possibility of using the PLD-RHEED system for control of thin film growth on an atomic level even in quite high background pressures.

REFERENCES

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

2. J.-P. Locquet, Y. Jaccard, C. Gerber, and E. Mächler, *Appl. Phys. Lett.* **63** (1993) pp. 1426

3. J.-P. Locquet, and E. Mächler, *MRS Bulletin* **19**, (1994) pp. 39

4. R. Tsuchiaya, M. Kawasaki, H. Kubota, J. Nishino, H. Sato, H. Akoh, H. Koinuma, *Appl. Phys. Lett.* **71** (1997) pp. 1570

5. Guus J.H.M. Rijnders, Gertjan Koster, Dave H.A. Blank, and Horst Rogalla, *Appl. Phys. Lett* **70** (14), (1997) pp. 1888

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