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In Situ RHEED during Pulsed Laser Deposition of complex oxides at high deposition oxygen pressures

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Abstract. This paper describes the deposition of $SrTiO_3$, $YBa_2Cu_3O_{7-d}$ and $SrCuO_x$ on $SrTiO_3$ substrates using PLD. *In Situ* monitoring during deposition was performed at standard PLD deposition pressures with RHEED. The changes in the diffracted intensity and different morphologies after growth revealed by AFM show three different growth modes for the different materials at the conditions used.

With this study we show the applicability of RHEED used in combination with PLD at standard pressures (10-50 Pa).

1. Introduction

Thin film techniques offer the possibility for atomic engineering of new, artificial layered oxide materials. Several groups have successfully made metastable structures in, for example, the infinite layer system [1], the (Ba,Sr,Ca)TiO_3 system [2] and the BiSrCaCuO system [3]. Sputter deposition, Pulsed Laser Deposition (PLD) or Molecular Beam Epitaxy have been used as deposition technique, usually in combination with a thickness monitoring system.

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 [4]. 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 RHEED pattern.

In PLD, the relatively high oxygen pressure hampers the diagnostics of the growing film surfaces by *in-situ* RHEED. 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 [5, 6], NO_2 [7, 8], or O_3 [9], and alternatively pulsed oxygen sources [10].

A low deposition pressure during PLD, however, can lead to, usually compressive, stress in the film [11]. This is caused by the bombardment of the film during the deposition by high energetic particles, originating from the plasma. 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. Finally, oxidation at these oxygen pressures can be done at higher temperatures, due to the better oxidation power. This, in turn, is favorable for crystallinity of the deposited material.

We developed a RHEED system for growth monitoring under high deposition pressures (up to 50 Pa) [12]. With this system we studied initial growth of $SrTiO_3$, $YBa_2Cu_3O_{7-d}$ and $SrCuO_x$ on $SrTiO_3$ substrates. We observed three different growth modes for these systems at the conditions we used, Frank-VanderMerwe (2D), Stransky-Krastanov (2D and 3D) and step flow, respectively.

2. Experimental.

The $SrTiO_3$ substrates, used in this study were annealed at 950 °C for 4 hours in an oxygen flow. The resulting surface morphology is shown in the Atomic Force Microscope (AFM) Micrograph in fig. 2 a). The inset gives the RHEED pattern for this surface; sharp Bragg reflections and Kikuchi lines indicate a smooth, crystalline surface. For the deposition of $SrTiO_3$ and SrO, we used single crystals as target; for $YBa_2Cu_3O_{7-d}$ and $SrCuO_x$ sintered pellets were used.

Deposition took place in 0.15 mbar of oxygen. The substrate temperature for SrO, $SrTiO_3$ and $YBa_2Cu_3O_{7-d}$ was set at 760°C, and 650 °C for $SrCuO_x$. A KrF eximer laser was used at a repetition rate of 1 Hz. The energy density on the targets was estimated to be 1.3 J/cm^2.

The high-pressure RHEED system is described in detail by Rijnders et al. [12]. The electron gun produces electrons with energy of 20 keV which strike the surface at angles of 1-3°. A CCD camera monitored the diffracted intensity; here we compare the intensity of the specular reflection during growth of the different materials.

The resulting surfaces were analysed with a NanoscopeIII AFM.

3. Results and discussion

3.1. $SrTiO_3$: Frank-VanderMerwe

Homo epitaxial growth of $SrTiO_3$ is known to be a good example for layer-by-layer growth. We used $SrTiO_3$ as a reference for our PLD-RHEED system. Starting with a surface with only unit cell steps (=0.39 nm, fig 2 a)), the intensity oscillations in fig 1 a) indicate layer-by-layer mode; 6 unit cells were deposited, 5 laser pulses were needed to complete 1 monolayer. The modulation on top of this signal is due to initial disorder at the surface, due to the material deposited during one laser pulse. Subsequent diffusion and crystallisation of the material result in a relaxation of the intensity. This effect can only be seen when the roughness of the surface does not exceed the variation in disorder due to the pulsed deposition.

3.2. $YBa_2Cu_3O_{7-d}$:Stransky-Krastanov

The intensity measured during the growth of YBCO, shows clear oscillations, as can be seen in figure 3a), indicating a layer-by-layer growth of the first few monolayers. Initially, intensity oscillations are detected, however the amplitude of the oscillations and intensity of the diffraction pattern rapidly decreases in time. This indicates initial 2D growth and within a few unit cells a transition to 3D growth. The AFM Micrograph (fig. 2 b)) clearly shows small islands with height of 1 unit cell (=1.17 nm). The streaky RHEED pattern confirms a more disordered surface; sharp Bragg spots can not be seen anymore.

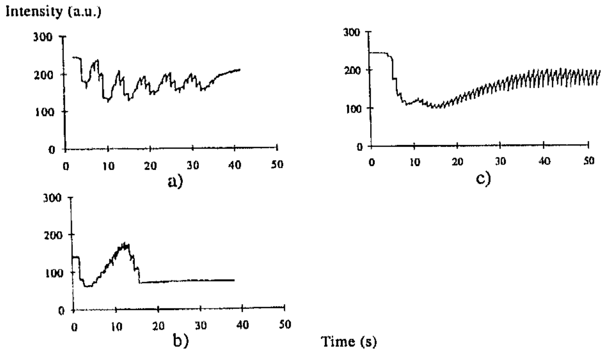

Figure 1: Intensities of the specular reflection during deposition of a) $SrTiO_3$ b) SrO and c) $SrCuO_x$

Continuing the growth, no clear oscillations could be observed. However, after an *in-situ* anneal step at 850 °C, the oscillations are regained. Figures 3b) through 3d) show intensity oscillations if this sequence, i.e., 6 nm deposition of YBCO followed by an *in-situ* anneal step, is repeated until a total thickness of 25 nm.

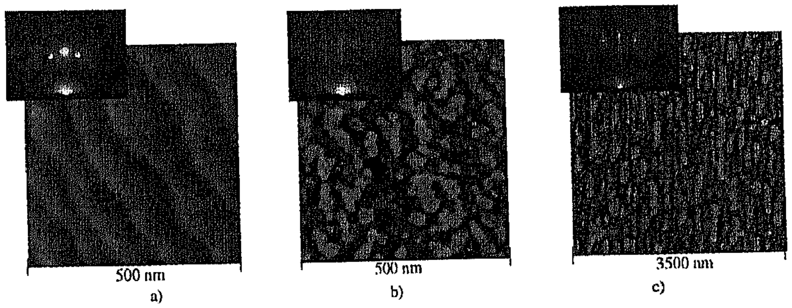

Figure 2: AFM Micrographs and corresponding RHEED patterns (inset) of a) annealed $SrTiO_3$ surface, with unit cell steps (= 0.39 nm), b) $YBa_2Cu_3O_{7-d}$ surface after deposition of 3-4 nm, islands of unit cell height (= 11.7 nm) and c) the $SrCuO_x$ surface after deposition of 5 nm, islands of unit cell height (= 0.34 nm).

3.3. $SrCuO_x$: Step flow

Prior to the deposition of $SrCuO_x$, one monolayer of SrO was deposited. Kawayama et al. show that this highly promotes smooth films because of the more stable SrO termination [13]. In Fig 1 b) the intensity during growth of SrO is shown. Initially the intensity oscillates, however if deposition is continued after the fist maximum, the intensity decreases very fast and the diffraction pattern shows 3D transmission spots. From this we conclude that we changed the substrate termination from TiO_2 to SrO after deposition of SrO is stopped at the first maximum.

Subsequent deposition of $SrCuO_x$ gives a change in intensity depicted in fig 1 c). After a dip, the intensity hardly changes. However, modulation due to the laser pulse still is present, indicating a flat surface. From this we conclude that growth proceeds in a step flow mode. The AFM Micrograph in fig. 2 c) shows the resulting surface. After deposition of about 15 unit cells (1 unit cell =0.34 nm) the underlying substrate morphology is still visible. The RHEED pattern still shows 0 th-order Bragg reflections.

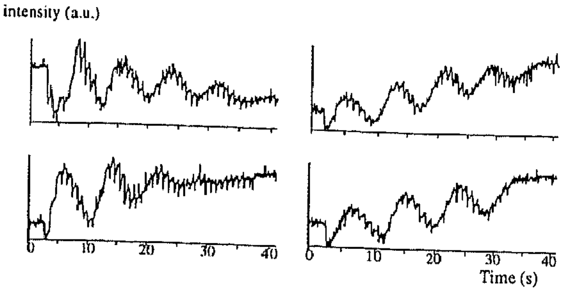

Figure 3: Intensity oscillations of a diffraction spot during the growth: (a) heteroepitaxial growth of YBCO on $SrTiO_3$. (b) through (d) heteroepitaxial growth of YBCO on $SrTiO_3$ after intermediate *in-situ* anneal steps

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. By two-stage pumping and enclosing the electron beam as long as possible in a vacuum tube, intensity losses due to scattering can be minimized.

With this system we have monitored the growth of $SrTiO_3$, YBCO and $SrCuO_x$ using PLD at 15 Pa of oxygen. *In Situ* RHEED monitoring was possible and the intensities of the specular reflections during growth revealed different growth modes.

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