***In-Situ* Monitoring during PLD of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ using RHEED at High Oxygen Pressure**

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Abstract—The surface morphology and initial growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, using Pulsed Laser Deposition (PLD), have been subject to in many studies. Both, Scanning Probe Microscopy (SPM) as well as Reflection High Energy Electron Diffraction (RHEED) have been applied. The latter is mostly operated using modified deposition parameters, like a reduced oxygen pressure. Here, we have studied the initial growth using a PLD-RHEED system at standard PLD pressures. In this system, *in-situ* RHEED can be applied in a background pressure of oxygen up to 50 Pa. The initial growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on SrTiO_3 substrates is studied. The influence of the substrate termination, i.e., SrO or TiO_2 , on the growth will be discussed.

I. INTRODUCTION

The need for atomically smooth films as well as thickness control on an atomic level has made Reflection High Energy Electron Diffraction (RHEED) a versatile *in-situ* diagnostics tool for thin film growth [1]. It provides information on surface perfection by analysis of the diffraction pattern, while variations of the diffracted intensity is used to monitor the film growth-rate. 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. In PLD the diagnostics of the growing film surfaces by *in-situ* RHEED is hampered by the relatively high oxygen pressure.

By depositing at low pressures compatible with their RHEED setup, several groups have studied and monitored the growth of complex oxides with RHEED. 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] were used to incorporate oxygen in the as-grown films. 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.

We have used a specially equipped PLD-RHEED system to study the initial growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ on SrTiO_3 . This

PLD-RHEED system allows us to study growth at high oxygen pressures.

SrTiO_3 is often used as a substrate for epitaxial growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ thin films because of the small lattice mismatch and the good in-plane alignment. SrTiO_3 has an ABO_3 perovskite structure with alternating layers of SrO (A-site plane) and TiO_2 (B-site plane). The dependence of the termination layer of the SrTiO_3 substrate on the growth will be discussed.

II. EXPERIMENTAL

In this paper we present a RHEED system designed for growth monitoring under high deposition pressures (up to 50 Pa). A detailed description of the system is published elsewhere [9]. Here, we briefly mention the most important aspects. The main problem that has been solved is the scattering loss due to the high pressures. The system satisfies the two requirements, a low pressure in the electron gun and a high pressure in the deposition chamber, using a differential-pumping unit. The source is mounted on a flange connected to a stainless steel extension tube with an inner diameter of 8 mm. An aperture (diameter 250 μm) separates the tube from the deposition chamber. The pressure in the tube is kept below 10^{-1} Pa, whereas the pressure in the deposition chamber can be increased up to 50 Pa.

With the electron source (EK-2035-R, STAIB Instrumente) a minimum beam size of 100 μm can be obtained even at large working distances. The XY deflection facility of the electron source is used to direct the electron beam through the aperture at the end of the tube. Special care has been taken to shield the electron beam from magnetic fields.

The fluorescent phosphor screen (diameter 50 mm) is located near the substrate. The screen is shielded from the plasma in order to minimize contamination. The heater can be rotated in order to adjust the angle of incidence of the electron beam on the substrate. The azimuthal angle can be changed by additional rotation of the heater. A CCD camera monitors the diffraction pattern.

Deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ took place in 20 Pa pressure of oxygen, whereas for deposition of SrO an oxygen pressure of 4 Pa was used. The substrate temperature for, both, SrO and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was set to 780 °C. A KrF excimer laser was used at a repetition rate of 1 Hz. The energy density on the targets was estimated to be 1.3 J/cm² for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and 2 J/cm² for SrO . A single crystal was used as target for the deposition of SrO and a sintered pellet for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The surface morphology of the substrates and thin films are characterized

Fig. 1. Surface morphology of a TiO_2 terminated SrTiO_3 substrate (scan size is $1\ \mu\text{m}$ by $1\ \mu\text{m}$). The inset shows the RHEED pattern.

in contact mode using a Nanoscope IIIa atomic force microscope in air. Tapping mode tips with spring constant $k = 20\text{--}100\ \text{N/m}$ are utilized in an attractive mode.

III RESULTS AND DISCUSSION

A. SrTiO_3 substrate treatment

The SrTiO_3 substrates were pretreated before etching in an $\text{NH}_4\text{--HF}$ solution followed by an anneal step at $950\ ^\circ\text{C}$ in 1 bar of oxygen. Using this procedure [10] atomically smooth substrates, with TiO_2 as the terminating surface layer, are obtained. Figure 1 shows an AFM micrograph of the surface. Seven terraces with only single unit cell steps of $3.905\ \text{\AA}$ are visible. For a miscut angle, which is defined as the angle between the substrate surface and the (001) plane of the SrTiO_3 substrate, between 0.05° and 0.15° , the terrace width is approximately $400\ \text{nm}$ to $150\ \text{nm}$. The inset shows the RHEED pattern for this surface with an angle of incidence of the electron beam of approximately 1° . This pattern shows a very intense specular spot and sharp Bragg reflections, indicating a smooth, crystalline surface.

Fig. 2. RHEED pattern after deposition of approximately 1 monolayer (a) and 4 monolayers (b) of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ on a TiO_2 terminated SrTiO_3 substrate.

B. $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ deposition on SrTiO_3

The RHEED pattern, recorded after deposition of approximately 1 monolayer (ML) of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$, on a TiO_2 terminated SrTiO_3 , is shown in figure 2a. Clear 3D spots, corresponding with a cell constant of $4.27\ \text{\AA}$, are visible. These spots can therefore be associated with Cu_2O crystallites. Furthermore, the intensity of the specular spot is decreased significantly, which indicates an increased roughness.

Because of charge neutrality, $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ is believed to grow in unitcells consisting of 6 atomic layers with BaO as the terminating layer [11,12]. The wettability of CuO (B-site material) is poor on TiO_2 (also B-site material) terminated SrTiO_3 and, thus, BaO is the interface layer between $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ and SrTiO_3 [13]. Deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ using stoichiometric targets can, consequently, lead to the formation of Cu_xO crystallites, since for the first completed monolayer of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ one CuO monolayer, the 'chain layer', is not incorporated. After deposition of approximately 4 ML also streaks, corresponding to the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ lattice parameter, are visible, as shown in figure 2b.

C. $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ deposition on SrTiO_3 with SrO bufferlayer

To prevent the formation of Cu_xO crystallites, we have deposited 1 ML of SrO before the deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$.

Fig. 3. The intensity and FWHM of the specular spot during deposition of SrO at a laser repetition rate of $1\ \text{Hz}$.

Fig. 4. RHEED pattern after the deposition of 1 ML of SrO .

Fig. 5. The intensity of the specular spot during deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ at a laser repetition rate of 1 Hz.

In this case, we have used 35 pulses at a repetition rate of 1 Hz. The intensity and the full width at half maximum (FWHM) of the specular spot during deposition of SrO is shown in figure 3. At the RHEED conditions used, it is seen that the intensity of the specular spot, after a sharp decrease, is only partially recovered. Besides the intensity also the FWHM of the specular spot is dependent on the coverage during layer-by-layer growth. The FWHM is maximal at a coverage of approximately half a ML and minimal at full coverage. The FWHM can, therefore, also be used to determine the completion of a monolayer. The RHEED pattern after the deposition of SrO is given in figure 4. The intensity of the Bragg reflections is increased. Sharp spots in the RHEED pattern indicate an atomically flat and crystallographic perfect SrO surface.

The intensity of the specular spot during deposition of 4 ML of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ is shown in figure 5. The intensity clearly oscillates, indicating a 2D-growth mode. Besides the oscillating behavior, the intensity is also modulated by the laser pulse. The intensity decreases directly after every laser pulse due to the increased disorder on the surface caused by the deposited material. The decrease of the intensity is followed by an exponential rise due to recrystallization of the initially disordered material.

Due to roughening of the surface, the intensity dropped significantly. The spots in the RHEED pattern (not shown)

after deposition are blurred into streaks.

In the experiment described above, we have placed the substrate just at the top of the visible plasma. The distance between target and substrate was 56 mm. The energy of the constituents of the plasma and, therefore, the kinetic energy of the impinging adatoms, are dependent on the ambient pressure and distance between target and substrate [12]. Figure 6a shows the RHEED pattern after deposition of approximately 8 ML of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ at a target-substrate distance of 66 mm instead of 56 mm. In this case the visible plasma did not reach the surface of the growing film. Clear 3D spots are visible on the 2D streaks. 3D islands are formed due to lower mobility of the adatoms caused by decreased kinetic energy of the adatoms on arrival. After a short anneal-step of 5 minutes at 850 °C, the intensity of these 3D spots is decreased significantly (see figure 6b). The higher mobility of the deposited material at the anneal temperature smoothens the surface.

IV CONCLUSIONS

We have shown that, using a two-stage differential pumping system, growth monitoring with RHEED is possible at standard oxygen pressures used in PLD. Specially treated SrTiO_3 substrates have an atomically smooth and crystallographically perfect surface as revealed by RHEED. Deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ on these TiO_2 terminated substrates can lead to the formation of Cu_xO crystallites. Deposition of an intermediate SrO ML can be used to minimize the formation of these crystallites.

Typical values for parameters, such as substrate temperature, oxygen pressure, target-substrate distance, laser fluence and spot size, used in PLD of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ on SrTiO_3 by many groups did not show a layer-by-layer growth mode in our experiments. Although intensity oscillations indicate 2D nucleation, the significant drop of the intensity and the streaky pattern after deposition is an indication of a roughened surface.

Further research is necessary to find optimal growth parameters to enhance layer-by-layer growth.

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Fig. 6. RHEED pattern after deposition of approximately 8 monolayers of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$. Fig. 6(a) shows 3D spots on the streaks due to small islands. Fig. 6(b) shows the RHEED pattern after an *in situ* anneal step at 850 °C.

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