In situ monitoring during pulsed laser deposition of complex oxides using reflection high energy electron diffraction under high oxygen pressure

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A suitable *in situ* monitoring technique for growth of thin films is reflection high energy electron diffraction (RHEED). Deposition techniques, like pulsed laser deposition (PLD) and sputter deposition, used for fabrication of complex oxide thin films use relatively high oxygen pressures (up to 100 Pa) and are, therefore, not compatible with ultrahigh vacuum RHEED equipment. We have developed a RHEED system which can be used for growth monitoring during the deposition of complex oxides at standard PLD conditions. We are able to increase the deposition pressure up to 50 Pa using a two-stage differential pumping system. Clear RHEED patterns are observable at these high pressures. The applicability of this system is demonstrated with the study of homoepitaxial growth of $SrTiO_3$ as well as the heteroepitaxial growth of $YBa_2Cu_3O_{7-\delta}$ on $SrTiO_3$. Intensity oscillations of the RHEED reflections, indicating two-dimensional growth, are observed up to several tens of nanometers film thickness in both cases. © *1997 American Institute of Physics.* [S0003-6951(97)02114-1]

Pulsed laser deposition (PLD) is very suitable for the deposition of thin films made of complex oxides like high-Tc superconductors, e.g., $REBa_2Cu_3O_{7-\delta}$ and dielectrics, e.g., MgO and $SrTiO_3$. This technique uses mostly a focused beam of an excimer laser to evaporate material from a stoichiometric target. Especially in PLD, the deposition pressure is an important parameter because it influences the size and shape of the plasma and, therefore, the deposition rate and the homogeneity of the thin film. The deposition of oxides takes place in a well controlled oxygen atmosphere, allowing oxygen incorporation in the as-grown film. The substrate temperature is elevated (typically up to 800 °C) in order to obtain epitaxial growth.

Reflection high energy electron diffraction (RHEED) is often used for the analysis and monitoring of thin film growth in ultrahigh vacuum (UHV) deposition systems.[1] 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 diagnostics of the growing film surfaces by *in situ* RHEED are hampered by the relatively high oxygen pressure. 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,[2,3] NO_2,[4,5] or O_3,[6] and alternatively pulsed oxygen sources.[7] 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. 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.

In this letter we present a RHEED system designed for growth monitoring under high deposition pressures (up to 50 Pa). The main problem to be solved is the increased scattering loss. In order to minimize the losses, the traveling path of the electrons in the high pressure region has to be kept as short as possible. Most of the commercial available electron sources use heated tungsten filaments to emit electrons. The pressure in the source should be very low ($<5\times10^{-4}$ Pa) to avoid short lifetimes of the filaments. Our system satisfies these requirements, i.e., a low pressure in the electron gun and a high pressure in the deposition chamber.

A schematic view of the deposition chamber, including the electron source assembly, is given in Fig. 1. Both heater and multi-target holder are mounted on a computer-controlled *XYZ*-rotation stage and can be inserted via a load-lock system without breaking the vacuum.

With the electron source (EK-2035-R, STAIB Instrumente) a minimum beam size of 100 μm can be obtained even at large working distances. A differential pumping unit is used to maintain a vacuum of better than 5×10^{-4} Pa in the electron source. The source is mounted on a flange con-

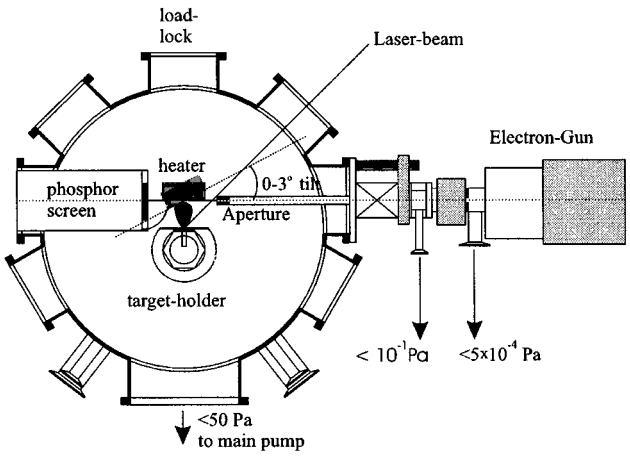

FIG. 1. A schematic view of the deposition chamber, including the electron source assembly.

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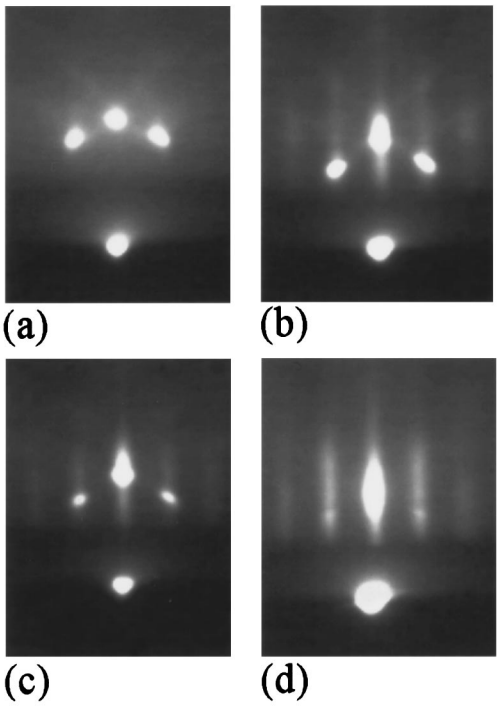

FIG. 2. RHEED patterns of the $SrTiO_3$ substrate surface in 15 Pa oxygen prior to the growth, (a) at room temperature and (b) at 760 °C and subsequently after deposition of (c) 10 nm of $SrTiO_3$ and (d) 6 nm of YBCO, both after an *in situ* anneal step at 850 °C.

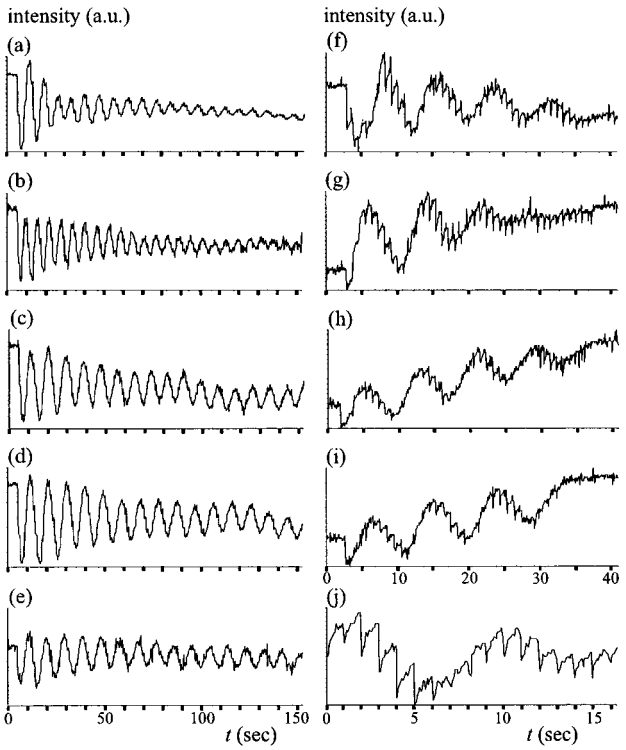

FIG. 3. Intensity oscillations of a diffraction spot during the growth: (a) homoepitaxial growth of $SrTiO_3$; (b)–(e) homoepitaxial growth of $SrTiO_3$ after intermediate *in situ* anneal steps; (f) heteroepitaxial growth of YBCO on $SrTiO_3$; (g)–(i) heteroepitaxial growth of YBCO on $SrTiO_3$ after intermediate *in situ* anneal steps. (j) shows the modulation of the intensity oscillations, due to the laser pulses.

nected 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, which depends on the pump speed and the size of the aperture, is kept below 10^{-1} Pa. Using this two-stage pumping system, the pressure in the deposition chamber can be increased up to 50 Pa, maintaining the vacuum in the electron source. The electron beam, which passes through the apertures inside the differential pumping unit and the tube, enters the deposition chamber near the substrate. The *XY* deflection facility of the electron source is used to direct the electron beam through the aperture at the end of the tube.

Small magnetic fields, like the earth magnetic field, can influence the electron beam. Therefore, special care has been taken to shield the electron beam from magnetic fields.

The fluorescent phosphor screen (diameter 50 mm) is mounted on a flange located near the substrate. The distance between the screen and substrate is 50 mm. The screen is shielded from the plasma in order to minimize contamination. The electron source, including the extension tube, is mounted on an *XYZ* stage allowing to adjust the distance between substrate and end of the tube. 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. The diffraction pattern is monitored by a charge coupled device (CCD) camera.

To demonstrate the applicability of this RHEED system we studied the homoepitaxial growth of $SrTiO_3$ and the heteroepitaxial growth of $YBa_2Cu_3O_{7-\delta}$(YBCO) on $SrTiO_3$.The $SrTiO_3$ (100) substrates were pretreated with a NH_4F-HF buffer solution[9] which is optimized adjusting the *p*H value. This results in a well-defined surface which is terminated by TiO_2 planes without etch pitches.

The substrates are mounted onto the heater using silver paint allowing for good thermal contact. The temperature of the heater during growth, measured by a thermocouple in the heater block, is 760 °C. The distance between target and substrate is set to 55 mm. The spot size of the KrF laser beam is 8.6 mm^2, with an energy density of 1.2 J/cm^2. The repetition rate is 1 Hz. Both $SrTiO_3$ and YBCO films are grown using PLD from stoichiometric targets at an oxygen pressure of 15 Pa. The angle of incidence of the 35 KeV electron beam is set to 1.5°.

The RHEED pattern at room temperature prior to the growth [see Fig. 2(a)] consists of spots on the 0th-order Laue circle, corresponding to the intersection of the Ewald sphere and the reciprocal lattice, and indicates a smooth surface. The reciprocal lattice is represented by narrow rods assuming a substrate with an almost two-dimensional surface. The pattern at the deposition temperature of 760 °C is depicted in Fig. 2(b). The shape of the spots is blurred into streaks. During the growth of $SrTiO_3$ the diffracted intensity is monitored. Clear oscillations, as shown in Fig. 3(a), are observed, indicating a two-dimensional layer-by-layer growth. The amplitude of the oscillations decreases with increased layer thickness due to an increasing degree of disorder. Figure 2(c) shows the RHEED pattern as observed after the deposition of 10 nm of $SrTiO_3$ followed by an *in situ* anneal step at 850 °C. This pattern does not differ from the pattern as ob-

tained prior to the growth. The diffracted intensity, as measured during *in situ* growth, is regained [Fig. 3(b)]. Increased mobility at the surface during the anneal step is expected to improve the surface smoothness and therefore an enhanced two-dimensional layer-by-layer growth is observed. This sequence, i.e., 10 nm deposition of $SrTiO_3$ followed by an anneal step at 850 °C, can be repeated several times (*in situ*) maintaining the oscillations, as can be seen in Figs. 3(c)–3(e). As an example, Fig. 3(e) shows the intensity oscillations corresponding to the growth of the 150th until the 165th unit cell of $SrTiO_3$.

Atomic force microscopy (AFM) pictures show smooth surfaces with a step-terrace structure, prior to the growth and after the deposition of $SrTiO_3$. Only step heights of 0.2 and 0.4 nm are observed, corresponding to, respectively, half and unit cell steps. In a pending paper a detailed study will be presented.

In addition, the heteroepitaxial growth of YBCO on $SrTiO_3$ is monitored using this high pressure RHEED setup. In this case a 6-nm-thick film of $SrTiO_3$ is deposited prior to the growth of YBCO. The intensity, measured during the growth of YBCO, shows clear oscillations, as can be seen in Fig. 3(f), indicating a layer-by-layer growth of the first few monolayers. Continuing the growth, no clear oscillations could be observed. However, after an *in situ* anneal step at 850 °C, the oscillations are regained. Figures 3(g)–3(i) show intensity oscillations if this sequence, i.e., 6 nm deposition of YBCO followed by an *in situ* anneal step, is repeated. The RHEED pattern after deposition of 5 ML followed by an *in situ* anneal step at 850 °C is shown in Fig. 2(d). This pattern shows streaked spots on the 0th-order Laue circle, indicating a smooth surface.

Figure 3(j) shows the intensity of a diffraction spot at a magnified time scale. As can be seen from this figure, the oscillations are modulated by the laser pulse. The intensity decreases significantly directly after the laser pulse followed by an exponential rise caused by recrystallization of initially disordered material as reported by Karl *et al.*[2] and Achutharaman *et al.*[10]

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 $SrTiO_3$ and YBCO using PLD at 15 Pa of oxygen. In both cases clear oscillations of the diffracted intensity are an evidence for two-dimensional growth, as expected from the crystal structure.

In situ anneal steps between deposition steps improve the smoothness of the surface as indicated by the RHEED patterns. The layer-by-layer growth is enhanced by the intermediate anneal steps. These results indicate the possibility of using the system for control of thin film growth on an atomic level even in quite high background pressures.

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