IN SITU INITIAL GROWTH STUDIES OF $(Sr,Ca)CuO_2$ ON $SrTiO_3$ BY HIGH PRESSURE RHEED

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ABSTRACT

The initial growth of pulsed laser deposited $SrCuO_2$ (SCO) and $CaCuO_2$ (CCO) on $SrTiO_3$ has been studied using high pressure Reflection High Energy Electron Diffraction (RHEED) and Atomic Force Microscopy (AFM). For this, we developed a Pulsed Laser Deposition (PLD)-RHEED system, with the possibility to study the growth and to monitor the growth rates, *in situ*, at typical PLD pressures (10-50 Pa). In case of depositing oxide materials, high oxygen pressures are desired. Moreover, crystallinity can be improved using higher oxygen pressures and therefore higher temperatures. With this technique we are able to obtain atomically flat films, a first step towards multi-layer structures.

In this paper we present the initial growth studies of SCO and first results incorporating CCO layers in a SCO matrix.

INTRODUCTION

New developments in thin film techniques offer the possibility for atomic engineering of oxide materials. Especially in the case of perovskite-like oxidic materials one has the ability to form new, artificial layered crystal structures. Several groups have successfully made metastable structures in, for example, the 'infinite layer' cuprates [1], the $(Ba,Sr,Ca)TiO_3$ system [2] and the BiSrCaCuO system [3,4]. Sputter Deposition, Pulsed Laser Deposition or Molecular Beam Epitaxy has been used as deposition technique, usually in combination with a thickness monitoring system.

In this paper we present RHEED in combination with PLD [5] as a suitable Atomic Layer-by-Layer or Molecular Block-by-Block (ALL) technique, here used for the fabrication of thin films of the 'infinite layer' system ($ACuO_2$, A=Sr or Ca). The RHEED monitoring system, usually used at a low pressure, has been modified to operate at relatively high oxygen pressures, needed for the synthesis of oxide materials by PLD.

Norton et al. have shown the possibility to grow artificial layered structures of $ACuO_2$ by PLD. After calibration of the growth rates, they verified the artificial periodicity of the as-grown films with XRD [1]. However, creating these layered structures, real-time monitoring of the growth rate per layer is essential, since it may vary with the changing sticking coefficient, going from one layer to the other.

In order to use RHEED as growth rate monitor, it is necessary that the growth proceeds in a Layer-by-Layer (2D) mode. In this mode, the intensity oscillates during growth with a period equal to the deposition of one monolayer (ML).

By analyzing the RHEED pattern before and after growth as well as looking at the intensity variations during growth, we were able to optimize for layer-by-layer growth and atomically flat thin films. Apart from the oscillations due to 2D growth, the modulation of the intensity due to one laser pulse gives additional information about the smoothness of the surface during growth. The relaxation of the RHEED intensity after each pulse can be ascribed to crystallization of

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deposited material [4]. The intensity is most sensitive to this effect if the surface is atomically flat [5].

In this paper we will use this additional modulation during the deposition of SCO to find the optimum deposition parameters [7]. From the shape, intensity drop as well as relaxation time, we determined an optimum deposition temperature of 600°C. This is significantly higher than temperatures as reported elsewhere where NO_2 as ambient gas at low pressures (10^{-3} Pa) is used [9,10]. This supports the idea that good quality SCO films can be deposited at higher temperatures, using higher pressures.

Furthermore first artificial layered crystal structures of SCO and CCO grown with this ALL-PLD system are presented.

EXPERIMENTAL

The thin films were grown in the ALL-PLD system described by Rijnders et al. [5]. The targets used were sintered pellets in the case of SCO and CCO and a single crystal was used for SrO. Using a KrF laser, the energy density on the targets was 1.3-1.4 J/cm^2, with a repetition rate of 1 Hz. The target-substrate distance was set at 55 mm. For the experiments described here, the oxygen pressure was kept at 15 Pa. The amount of deposited material per pulse has been varied by changing the spot size S on the target, keeping the energy density constant.

For the RHEED analysis, 20 keV electrons were used with an incident angle of 1°. The diffraction pattern on the phosphor screen was monitored during growth by a CCD camera.

Mechanically polished $SrTiO_3$ substrates were treated according to an optimized anneal process proposed by Rijnders et al. [8]. A (001) vicinal surface was obtained with only unit cell steps depicted in the Atomic Force Micrograph (AFM Micrograph) of Fig.1a . The RHEED pattern shows sharp Bragg reflection indicating a smooth well ordered surface.

The AFM measurements were done on a Nanoscope III and the XRD measurements were performed on a Philips X'pert system.

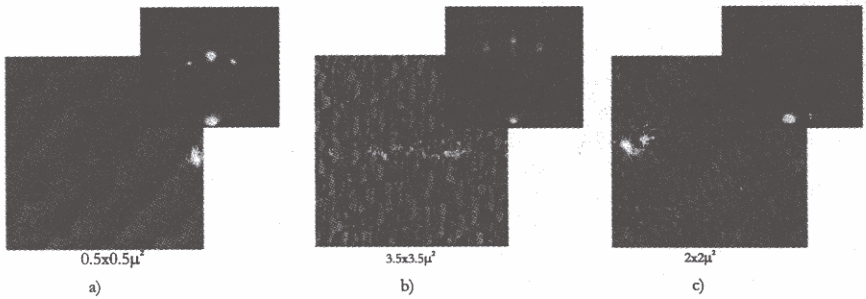


Fig 1: AFM Micrographs and RHEED diffraction patterns of a) an annealed $SrTiO_3$ substrate surface, b) after deposition of 15 ML of SCO at 650°C and c) after deposition of 14$(SCO)_3/(CCO)_3$ at 600 °C. Height differences are all in the order of unit cell.*

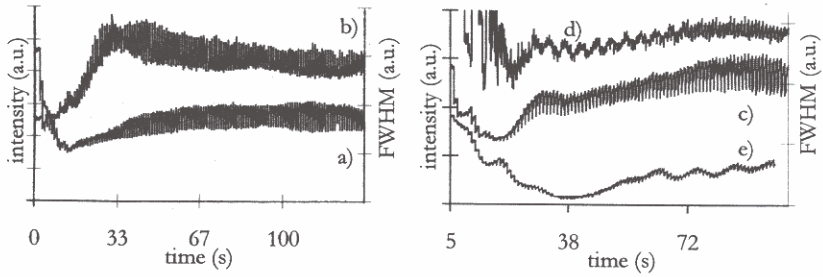


Figure 2: Intensity changes a) and FWHM changes b) of the specular spot during growth of SCO at 650 °C and idem c) d) at 600 °C. The intensity changes during growth of SCO at 600 °C with half laser spot size S on the target e).

RESULTS

$SrCuO_2$

From literature it is known that 2D growth of SCO becomes favorable, if depostion starts on a SrO terminated surface [9,11]. Therefore, one ML of SrO was deposited before deposition of SCO,.

In Figure 2 the intensity of the specular spot reflection and its full width half maximum (FWHM) during the deposition of SCO are presented for two different temperatures (respectively, 650 and 600 °C). After an initial drop, due to the transition from a SrO to a SCO surface, the intensity (Fig 2a,c) does not change, apart from the relatively large relaxation pulses. In the case of a deposition temperature of 650°C, the intensity (Fig 2a) and the FWHM (Fig 2b), both, don't change in time and thus indicate step-flow growth. This is also supported by the AFM micrograph on which the underlying substrate terrace morphology is still visible (Fig 1b). In the case of 600°C, the FWHM of the specular spot during growth (Fig.2d) shows an oscillatory behavior with a period of 4 laser pulses. This is not seen in the specular intensity (Fig 2c), because the relaxation pulses conceal the 2D intensity oscillations. By decreasing the amount of material deposited per pulse, the number of pulses needed to complete a ML was increased from 4 to 10. In this case clear 2D intensity oscillations can be seen (Fig. 2e).

Throughout depositing a 23-nm thick film at 600°C, RHEED intensity oscillations as well as relaxation pulses could be observed, see Fig 3a. The latter indicates a very smooth film surface during growth. From the Figure it can be seen that the intensity changes reveal an extra periodicity, corresponding with the deposition of 7 ML. Since the number pulses per ML is not exactly an integer, this extra periodicity could be explained by an aliasing effect. The deposition rate can be determined very accurately from this extra periodicity, in this case 8.85 laser pulse per ML.

The θ-2θ XRD-data, see Fig 4a, show (001) and (002) reflections that correspond to a c-axis of 0.344 nm, close to the value reported in literature [10].

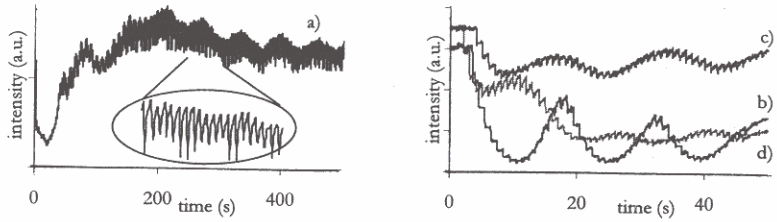


Figure 3:Intensity changes during deposition of a) 23 nm of SCO and for calibration of the deposition rate, deposition of b) 3 ML of SCO, c) subsequent deposition of 3 ML of CCO and d) 3 ML of SCO.

Artificially layered structures

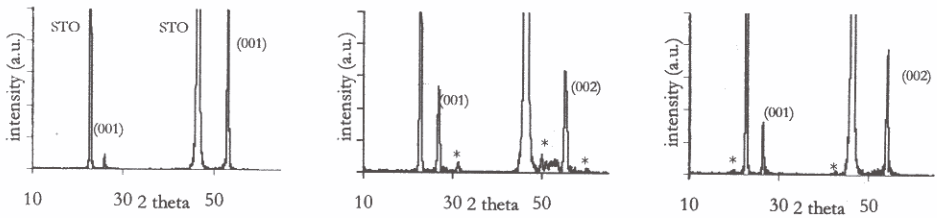
CCO layers were periodically inserted in the SCO matrix. From the intensity oscillations during deposition of a thin layer (typical 3-4 ML) of CCO and SCO, the deposition rate was determined, see Fig 3 b,c,d.

In Fig 3b, the intensity changes are depicted during the deposition of SCO on SrO. Subsequently, the growth of CCO has been recorded (Fig 3c). Finally, we deposited again SCO (Fig 3d). It can clearly be seen that the deposition rate of SCO has considerably changed. This result immediately stresses the importance of *in situ* monitoring. The values obtained from Figure 3 were used to deposited different (CCO)n/(SCO)m structures, with n=1,3 and m=3.

Fig 4b,c shows the XRD data for $(SCO)_3/(CCO)_3$ and $(SCO)_3/(CCO)_1$, respectively. Both c-axis values, derived from the position of the (001) and (002) peaks, correspond to an average value based on the c-axis of pure SCO (0.345 nm) and CCO (0.319 nm) [1]. The values found are 0.333 nm and 0.338 nm, respectively.

In addition, satellite peaks could be indexed with the c-axis corresponding to the superstructures (1.992 nm and 1.354 nm, respectively). The c-axis value derived from Fig. 4c (1.27 nm) does not correspond exactly with the calculated one, although, according to the average c-axis value, the ratio of material deposited per layer was correct.

The AFM micrograph taken after deposition reveals a flat surface (Fig 1c). The features are of unit cell height. The RHEED pattern also indicates a crystalline surface.



a) b) c)

*Figure 4: XRD θ-2θ scans for a) SCO, b) $(SCO)_3/(CCO)_3$ and c) $(SCO)_3/(CCO)_1$. The * marked peaks correspond with the superstructure*

CONCLUSIONS

To summarize, atomically flat SCO thin films have been deposited at standard PLD oxygen pressures and the growth rate could be monitored with RHEED. Working with higher oxygen pressures, considerable higher temperatures could be used, compared with deposition in a low pressure ambient, leading to films with high crystallinity. These results have been used to fabricate artificially layered structures, here demonstrated for SCO/CCO.

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