Interval deposition: Growth manipulation for use in fabrication of planar REBa$_2$Cu$_3$O$_{7-\delta}$ junctions

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ABSTRACT: Planar REBa$_2$Cu$_3$O$_{7-\delta}$ junctions are, due to the geometry, very suitable for use in integrated superconducting electronics and devices. A prerequisite is smooth barrier interfaces to avoid mixing of the anisotropic properties of the high-$T_c$ superconductors. We present a growth method, based on a periodic sequence: fast deposition of the amount of material needed to complete one monolayer followed by an interval in which no deposition takes place and the layer can reorganize. Starting with an atomically smooth substrate, we studied the growth, using the interval deposition technique, of SrO, La$_{2-x}$Sr$_x$CuO$_4$ and DyBa$_2$Cu$_3$O$_{14+\delta}$, with reflection high-energy electron diffraction and scanning probe microscopy.

I. INTRODUCTION

One of the key-goals in High Temperature Superconducting (HTS) electronics is the development of (tunnel) junctions. Due to the anisotropy of the coherence length in cuprates, i.e., 10-20 Å in the ab-direction and ~1-2 Å in the c-axis direction many groups have directed their research towards the development of junctions in the ab-direction. Different kinds of junctions, including grain boundary, ramp-type, step edge and a-axis sandwich-type have been realized by several groups.

In complex HTS electronic circuits and devices which include a large number of Josephson junctions a planar technology is desirable. Despite research efforts on a-axis junctions and planar microbridges, they have not (yet) been proven to be viable for complex circuits. Planar c-axis junctions with an artificial barrier are expected to yield better results, provided that the junction interfaces can be controlled on an atomic level. The planar geometry of the c-axis junctions combines the in situ deposition of both electrodes and barrier with the relative easy integration in electronics.

As already mentioned above, it is necessary to grow smooth layers to avoid the mixing of properties. The roughness of the surfaces and interfaces must be small compared to the barrier thickness. Moreover, the superconducting properties are easily degraded at the interfaces due to the short coherence length in the c-axis direction.

Occasionally, the deposition conditions such as the substrate temperature and ambient gas pressure (oxygen in the case of oxide materials) can be optimized for true two-dimensional (2D) growth, e.g., homo-epitaxy on SrTiO$_3$ (001). True 2D reflection high-energy electron diffraction (RHEED) specular intensity oscillations are observed depositing SrTiO$_3$ with pulsed laser deposition (PLD) at a temperature of 850 °C and an oxygen pressure of 0.04 mbar (Koster 1998). The relatively high temperature in combination with a low oxygen pressure enhances the mobility of the ad-atoms on the surface and, therefore, the probability of nucleation on top of a 2D island is minimized. The as-deposited ad-atoms can migrate to the step edges of 2D islands and nucleation only takes place on fully completed layers.
In general, during deposition of different kinds of materials, i.e., metals, semiconductors and insulators, by different deposition techniques, a roughening of the surface is observed. In case of 2D nucleation, determined by the supersaturation, limited interlayer mass transport results in nucleation on top of 2D islands before completion of a unit cell layer. Still, one can speak of a 2D growth mode. However, nucleation and incorporation of ad-atoms at step edges is proceeding on an increasing number of unit cell levels, which is exhibited by damping of the RHEED intensity oscillations.

Several groups have investigated the possibility to apply a form of growth manipulation to promote interlayer mass transport (Rosenfeld 1993). They suggest applying two different temperatures, two different growth rates or periodical ion bombardment to increase the number of nucleation sites and thus decrease the average island size. This will enhance the transport of material on an island to a lower lying level. Usually, for epitaxy of complex oxide materials, the regime of temperatures and pressures is limited by the stability of the desired phases, e.g., YBa$_2$Cu$_3$O$_{6.6}$ can only be grown in a specific temperature and pressure regime (Hammond 1989). At low temperatures, a-axis oriented films are formed whereas at high temperatures the material decomposes. Periodic ion bombardment is very difficult to realize in view of the stoichiometry of oxide materials. Growth rate manipulation to impose layer-by-layer growth could be a possibility to overcome this problem. In case of PLD, a typical value for the deposition rate within one pulse is of the order of 10 nm/s (Geoghegan 1995). Therefore, a high supersaturation is expected when the plume is on and thus the number of very small 2D nuclei can be very high. Subsequently, when the plume is off, larger islands are formed through recrystallization, exhibited by the typical relaxation of the RHEED intensity of the specular spot during PLD (Karl 1992). Since small islands promote interlayer mass transport, one can utilize the high supersaturation achieved by PLD by maintaining it for a longer time interval and suppress subsequent coarsening.

Accordingly, to circumvent premature nucleation due to the limited mobility of the ad-atoms at a given pressure and temperature, causing a multi-level 2D growth mode, we introduce the possibility of interval deposition. Exactly one unit cell layer is deposited in a very short time interval, i.e., of the order of the characteristic relaxation times, typically 0.5 s (Koster 1990), followed by a much longer interval during which the deposited material can rearrange. During the short deposition intervals, only small islands will be formed due to the high supersaturation typical for PLD. The probability of nucleation on the islands increases with their average radius (Rosenfeld 1993) and is, therefore, small in case of fast deposition. The total amount of pulses needed to complete one unit-cell layer has to be as high as possible, to minimize the error introduced by the fact that only an integer number of pulses can be given. Both, a high deposition rate and sufficiently accurate deposition of one unit-cell layer can be obtained by PLD using a high laser-pulse frequency.

![Fig. 1: Intensity of the specular spot during growth of LnBa$_2$Sr$_2$Cu$_3$O$_{7-x}$ at 2 Hz (a) and with interval deposition, 20 pulses at 10 Hz for every monolayer (b).](image-url)

2. EXPERIMENTAL

For this study, thin films are deposited using PLD in combination with high pressure RHEED (Rijnders 1997). For deposition of SrO a single crystalline target was used, whereas sintered pellets were used for deposition of B$_2$Ba$_2$Cu$_3$O$_{7-x}$ and La$_{1.8}$Sr$_2$CuO$_5$. The incident angle of the 20 keV electrons was set at 1°, while the intensity of the specular reflection was recorded with a CCD camera.
SrTiO$_3$ substrates were specially prepared to obtain a single terminated surface with only unit cell steps (Fig. 2a). The substrates were pretreated in H$_2$O before etching in an NH$_3$-HF solution followed by an anneal step at 950 °C in 1 bar of oxygen. Using this procedure (Koster 1998) atomically smooth substrates, with TiO$_2$ as the terminating surface layer, are obtained. The miscut angle of the substrates used in this study is below 0.2°.

3. RESULTS AND DISCUSSION

A possible candidate for barrier material in a superconductor-normal metal-superconductor (SNS) junction is La$_2$Sr$_x$CoO$_{4-y}$ due to the small lattice mismatch with REBa$_2$CuO$_{4}$. In Fig. 1a the RHEED intensity is given during the growth of La$_2$Sr$_x$CoO$_{4}$ at 20 Pa of oxygen and a substrate temperature of 650 °C with a continuous pulse frequency of 2 Hz. The surface is transitioning from a single level system to a multi level system, as indicated by the damping of RHEED intensity oscillations.

Fig. 1b shows the RHEED intensity during 10 cycles of deposition (at 10 Hz) followed by a time interval of no deposition, using the same oxygen pressure and substrate temperature, according to the new approach. In this case the number of pulses needed per unit cell layer was estimated to be about 20. The decay of the intensity after each unit cell layer is significantly lower compared to the situation in Fig. 1a. The recovery of the intensity after each deposition interval is fast when exactly one unit cell layer is deposited. Note that, besides nucleation on the next level, the decrease in intensity also can be ascribed to the fact that only an integer number of pulses can be given to complete a unit cell layer. A slightly lower or higher coverage causes a longer recovery time. This situation will deteriorate with every subsequent unit cell layer, also indicated by increasing relaxation times.

Deposition of SrO using PLD with a pulse repetition rate of 1 Hz leads to a multi level surface, as can be seen in Fig. 2b. Before completion of a monolayer, nucleation takes place on a 2D island. To overcome this problem interval deposition is applied. Fig. 2c and 2d shows the atomic force micrograph of a SrO monolayer applying 40 and 50 pulses, respectively, at 10 Hz. In these cases the deposition temperature is set to 500 °C. Subsequently, a one-hour in situ anneal step at 850 °C is applied. Fig. 2c shows a non-continuous monolayer, whereas in Fig. 2d small islands are visible.

The diffraction pattern (Fig. 3a) after deposition ($p$O$_2$ 15 Pa, substrate temperature 780 °C and a laser fluence on the target of 1.3 J/cm$^2$), using standard PLD at 1 Hz, of approximately 4 unit cells on a treated SrTiO$_3$ substrate, shows streaks, indicating a roughened surface. Also clear three-dimensional (3D) spots are visible. These streaks and spots can be assigned to a pseudocubic structure of the SrO monolayer.
spots correspond with a real space distance of 4.27 Å, which can be associated with Cu₂O crystallites.
The terminating layer of REBa₂Cu₄O₈₋ₓ is expected to be a BaO layer (Streiffer 1991). The starting
layer on a TiO₂ terminated SrTiO₃ substrate is also a BaO layer. As a consequence, during deposition
of the first unit-cell layer, one CuO₂ layer is not incorporated when stoichiometric deposition takes
place. When a SrO terminated SrTiO₃ substrate is used, only streaks are observed (see Fig. 3b). Now,
the interface layer will be a CuO₂ layer. The perovskite stacking sequence is preserved. In this case,
the formation of Cu₂O crystallites is prevented, as indicated by RHEED.

Nevertheless, streaks in the RHEED pattern indicate a slightly roughened surface. The use of
interval deposition is hampered by the number of pulses needed for completion of one unit-cell layer.
In the case of DyBa₂Cu₄O₈₋ₓ, using the deposition conditions mentioned above, approximately 12
pulses are needed. To minimize the error in the number of pulses, alternative settings (pO₂ 50 Pa,
substrate temperature 850 °C and a laser fluence of 8 J/cm²) are used. Using these settings the number
for completion of one unit-cell layer is approximately 40. Clear transmission spots are visible in the
RHEED pattern (Fig. 4a) taken after deposition of 50 nm using a laser repetition rate of 1 Hz. The
position of these spots corresponds with the lattice parameter of DyBa₂Cu₄O₈₋ₓ. Clearly, the surface
has become rough. Using the interval deposition technique, only streaks are visible, i.e., no
transmission spots, indicating a smoother surface.

4. CONCLUSIONS

Pulsed Laser interval Deposition is a suitable technique to enhance layer-by-layer growth as
shown by the heteroepitaxial growth of La₂Sr₂CaCu₂O₈ and SrO on TiO₂-terminated SrTiO₃. It
enhances the layer-by-layer growth of DyBa₂Cu₄O₈₋ₓ resulting in smooth surfaces as shown by
RHEED. Here, on SrO-terminated SrTiO₃, the formation of Cu₂O precipitates is prevented, as
indicated by RHEED. Especially Pulsed Laser Deposition is appropriate for use of interval deposition
because of the high deposition rate during every pulse. In combination with high pulse repetition rates
a unit-cell layer can be deposited in a very short interval.

REFERENCES
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Fig 4: RHEED pattern after deposition of a 50 nm thick film of DyBa₂Cu₄O₈₋ₓ using standard PLD with
a repetition rate of 1 Hz (a), and using interval deposition, 40 pulses at 10 Hz for every unit-cell layer (b).