High T_c Superconductor Thin Films
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DROPLETS AND OUTGROWTHS ON HIGH-Tc LASER ABLATED THIN FILMS

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Abstract

$YBa_2Cu_3O_x$ thin films have been grown on silicon, $SrTiO_3$ and ZrO_2 substrates using the pulsed laser deposition technique. Special attention has been paid to droplets and outgrowths which appear on the thin films during the growth process. The droplet density was studied as a function of the laser spot size, the laser energy and the target density. The number of droplets could be reduced to 1 per 100 μm^2 for a 100 nm thick film, by taking a large laser spot size and low energy density. The droplet density does not depend on the target density in the range from 80 to 94 %. The number of outgrowths could be reduced to 1 per 100 μm^2 for a 100 nm thick film by reducing the deposition temperature or increasing the laser frequency. However, the critical temperature of these layers was reduced by 5 to 10 K. Using SAM no differences in composition between an outgrowth and the rest of the film could be detected.

1. INTRODUCTION

We report on a parameter study concerning the number of droplets (ball shaped particles coming from the target with a typical diameter of 1-2 μm) and outgrowths (0.3 μm centres peaking out of the film) per unit area. Droplet formation is a typical feature of the laser deposition technique. The outgrowths are a more common problem in the different deposition methods for c-axis oriented $YBa_2Cu_3O_{7-d}$ layers. In order to produce well defined multilayers these particles have to be eliminated.

In literature some attention has been paid to the reduction of the number of droplets by using a second laser beam parallel to the substrate [1], a high density target [2] or a large laser spot size [3]. However, no systematic study about the occurrence of droplets and outgrowths in relation to deposition parameters has been performed to our knowledge. Wu et al. [4] report that the outgrowths are crystalline centres with the c-axis parallel to the substrate. The outgrowths nucleate on second phases, like $YBa_3Cu_2O_7$ [5].

We report on the influence of the laser spot size, the laser pulse energy and the target density on the number of droplets coming from the target. The number of outgrowths is studied varying the substrate temperature, the laser repetition frequency and the number of pulses.

The composition of an outgrowth is compared with that of the rest of the $YBa_2Cu_3O_7$ thin film using Auger Measurements.

2. EXPERIMENTAL

Thin $YBa_2Cu_3O_x$ layers were deposited using the pulsed laser deposition technique. In the experiments an excimer laser (λ=308 nm, τ=20 ns) is focused via a quartz lens onto a rotating $YBa_2Cu_3O_x$ target which is placed inside a vacuum chamber [6]. The spot size of the laser beam can be adjusted by moving the lens on an optical rail and is varied in these experiments between 0.8 and 7.3 mm^2. We used laser pulse energies between 58 and 98 mJ. The $YBa_2Cu_3O_x$ targets were prepared by the citrate pyrolysis method [7]. The density of the targets varied between 80 and 94 % of the theoretical density and was measured by immersing the target in a mercurial bath, placed on a balance. Different target densities were obtained by changing the pressure at which the targets are pressed from the calcinated powder and by changing the sinter temperature.

The droplet density was studied using 2 inch silicon wafers at ambient temperature as a substrate. Because of the low deposition temperature no crystalline growth centres will appear in the film and all irregularities in the amorphous $YBa_2Cu_3O_x$ layer will be caused by clusters of material (droplets) coming from the target or possibly clusters of material created by collisions of the evaporated material in the plasma. The number of droplets is counted using optical microscope pictures. The deposition conditions were comparable with the ones used for the preparation of c-axis oriented thin $YBa_2Cu_3O_7$ layers. We used an oxygen pressure of 25 Pa, a laser frequency of 2 Hz and a target substrate distance of 35 mm.

Because the number of droplets is linear dependent on the amount of ablated material, the thickness of the deposited layer (not necessarily uniform) also has to be known. To determine the thickness profiles, an 18 x 18 grid consisting of 0.5 x 0.5 mm^2 holes, 2 mm apart, is etched in the amorphous layer using standard photoresist and diluted H_3PO_4 as etchant. The thickness is measured by an Alpha Stepper.

To study the outgrowths we used (100) oriented $SrTiO_3$ and ZrO_2 at elevated temperatures as substrates. The droplet density was minimized by using the optimized deposition conditions found in the experiments with the silicon substrates. The outgrowth density and critical temperature of the thin $YBa_2Cu_3O_{7-d}$ layers were determined as a function of deposition temperature and laser frequency. The deposition temperature varied between 700 and 770 °C, the laser frequency between 0.2 and 100 Hz. The number of pulses was varied between 120 and 3000, each pulse depositing 1 Å $YBa_2Cu_3O_{7-d}$. The number of outgrowths was counted using an optical microscope, equiped with a differential interference contrast filter. The critical temperature was measured using a standard 4 point DC measurement.

The composition of an outgrowth was compared with a smooth part of the $YBa_2Cu_3O_7$ thin film using Auger Measurements, on a PHI 600 multiprobe.

3. RESULTS

3.1 Droplets

Two series of layers were made at two different spot sizes: 1.45 x 0.55 mm^2 (I) and 2.8 x 0.9 mm^2 (II) at different laser energies. A third series of experiments was made at a constant laser energy of 90 mJ, but variable spot size (III).

In order to account for the linear proportionality between the number of droplets per unit area and the amount of deposited material the number of droplets should be corrected for the local film thickness. In table 1 the laser energy E, the laser spot size S, the maximum thickness d_{max}, and the normalized number of droplets $\tilde{N}$ of series I, II, and III are given. $\tilde{N}$ is obtained by dividing the number of droplets counted in an area of 100 μm^2 by the thickness, at the position of the maximum thickness of the layer.

It is found from table 1 that $\tilde{N}$ is in good approximation linear proportional to the laser energy E for the series I and II. Series III shows that $\tilde{N}$ varies with 1/S at constant E, so that in fact $\tilde{N} \propto E/S$ or $\tilde{N}$ is linear dependent on the energy density. In figure 1 we present $\tilde{N}$ as a function of the energy density. A threshold value of approximately 1 J/cm^2 for the appearance of droplets is found.

Table 1
Droplet density for series I, II and III

series	E (mJ)	S (mm^2)	d_{max} (nm)	$\tilde{N}$ (per 10 μm^3)
I	98	0.8	120	29.0
I	88	0.8	112	23.0
I	78	0.8	99	21.5
I	68	0.8	84	16.4
I	58	0.8	73	19.0
II	98	2.5	437	3.5
II	88	2.5	396	1.9
II	78	2.5	361	2.1
II	68	2.5	301	2.3
II	58	2.5	211	3.0
III	90	1.4	188	12.0
III	90	2.4	300	4.8
III	90	4.2	480	2.7
III	90	5.3	550	1.1
III	90	7.3	750	0.4

Table 2 shows the normalized number of droplets for different target densities. By increasing the target density no reduction in the normalized number of droplets is observed.

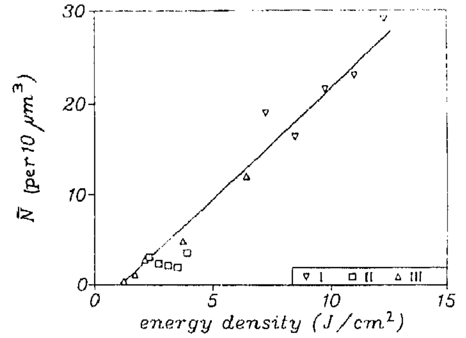
Table 2
Droplet density for different target densities

Target density (%)	$\tilde{N}$ (per 10 μm^3)
80	3.5
86	2.4
94	3.2

In figure 2 the distribution of the ablated material as well as the distribution of the droplets is given. No differences in distribution between the deposited material and the droplets can be seen.

3.2 Outgrowths

To study the outgrowths 100 nm thick $YBa_2Cu_3O_{7-d}$ layers have been deposited on (100) oriented $SrTiO_3$ and (100) oriented Yttria Stabilized ZrO_2 (YSZ) substrates. A series of layers were grown at different substrate temperatures ranging from 700 to 770 °C. The laser frequency was 2 Hz, the laser fluence 1.2 J/cm^2, the target substrate distance 45 mm, the spot size 7.3 mm^2 and the oxygen pressure during ablation 25 Pa. In figure 3 the number of outgrowths and the critical temperature of the layers on $SrTiO_3$ are given as a function of the deposition temperature. By lowering the deposition temperature both the number of outgrowths and the critical temperature reduce. The results for layers on YSZ show similar results, although the reduction of the critical temperature at low deposition temperature is higher.



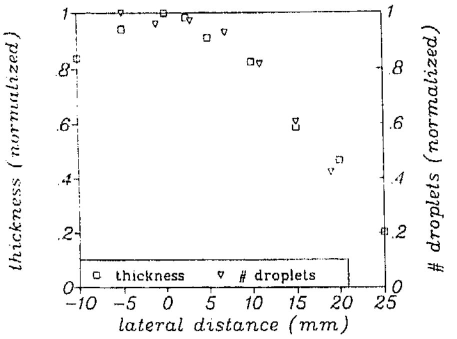
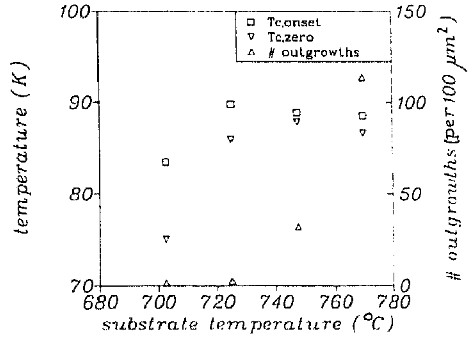


Figure 1. Normalized number of droplets as a function of the laser intensity.

Figure 2. Distribution of the atomic material and droplets.

A second series of layers is made by changing the pulse frequency between 0.2 and 100 Hz using a deposition temperature of 770 °C, a laser fluence of 1.2 J/cm², a target substrate distance of 45 mm and an oxygen pressure of 25 Pa. The number of pulses during each deposition was 960 what results in layers of about 100 nm thickness. In figure 4 the density of outgrowths and the critical temperature of the $YBa_2Cu_3O_{7-d}$ layers are given as a function of the laser frequency. By increasing the frequency, the number of outgrowths reduces to 0.4 per 100 µm² for 100 Hz. The critical temperature has a value of 90 K for a laser frequency of 2 Hz and decreases to about 85 K for 100 Hz. The layer prepared at 0.2 Hz was semiconducting.

Many small particles are found for very thin layers. By increasing the number of pulses a substantial part of these particles disappear and outgrowths of sizes of 0.3 µm are formed. The number of outgrowths per unit area remains more or less constant when film thicknesses of 100 nm are reached.



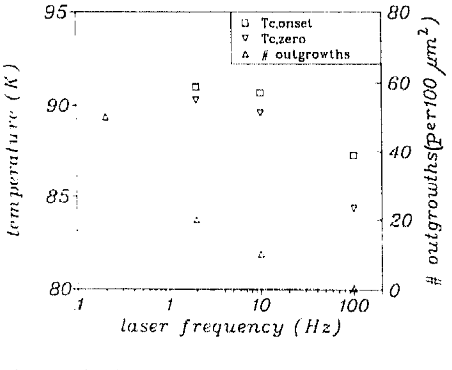


Figure 3. Outgrowth density and critical temperature as a function of deposition temperature.

Figure 4. Outgrowth density and critical temperature as a function of laser repetition frequency.

The composition of an outgrowth of 300 nm is compared with that of the rest of the film using Auger measurements. The electron beam is focused to 100 nm. The results are given in table 3 for a film with a critical temperature of 89 K. The numbers in table 3 are not corrected for the sensitivity factors for the different elements. No relevant composition differences between an outgrowth and the rest of the film have been found.

Table 3
composition of an outgrowth

element	composition	
	outgrowth	rest of the film
Y	5	7
Ba	31	30
Cu	35	45
O	100	100

4. DISCUSSION AND CONCLUSIONS

As is demonstrated in figure 1 there is a linear relationship between the normalized droplet density and the laser fluence. The laser beam with an energy density above the threshold value of 1 J/cm^2 creates a very hot and dense gas just in front of the target that expands in all directions splashing out droplets from the molten surface layer of the target [8]. Apparently, mainly droplets are formed at these high energies and to a much lesser extent atomic material for layer growth. The appearance of the threshold value, reachable by decreasing the laser energy and/or the spot size, is a clear key to the elimination of the droplet problem. The number of droplets seems to be independent of the target density for densities ranging from 80 to 94 %. This is to be expected because the density at the surface of the target will be increased due to the solidification of the molten $YBa_2Cu_3O_x$ at the surface of the target. In this way a high density layer will be present at the outside of each target, independent of the target density. The fact that the normalized droplet density exhibits the same lateral behaviour on the substrate as the film thickness indicates that the spatial distribution of atomic material and droplets in the plasma is equivalent.

The number of outgrowths is reduced by lowering the deposition temperature at a constant oxygen pressure. This can be explained by the different growth rates of $YBa_2Cu_3O_{7-d}$ in the ab-plane and perpendicular to this plane at different temperatures. At high temperatures the growth rate in the ab-plane is higher than the growth rate perpendicular to this plane, resulting in a c-axis oriented film with a-axis oriented outgrowths. By lowering the deposition temperature the growth rate in the ab-plane decreases compared to the growth rate along the c-axis and a-axis nuclei will be covered with c-axis material.

By increasing the frequency both the number of outgrowths and the critical temperature decrease. The decrease of the critical temperature for high frequencies may be explained by a not sufficiently large oxygen take up from the plasma. Improvements can be obtained by increasing the oxygen pressure. The reduction of the outgrowth density at higher frequencies indicates that the a-axis growth in plane is favourable with respect to a-axis growth perpendicular to the plane of the substrate. Obviously the formation of large outgrowths needs more time.

In conclusion, by incresing the laser spot size and reducing the energy density to about 1.2 J/cm^2, the number of droplets coming of the target can be reduced to about 0.1 per μm^3. No differences can be found between the lateral distribution of the ablated material and the droplets. The number of outgrowths can be reduced by lowering the deposition temperature or by increasing the laser repetition frequency. This will also reduce the critical temperature of the thin films. No compositional differences between an outgrowth and the rest of the film were found.

5. ACKNOWLEDGEMENTS

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