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" The UV laser beam - YBCO target interaction for optimum preablation for the growth of YBCO thin films "

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ABSTRACT

The morphological and compositional changes which take place during the laser irradiation of YBCO targets are discussed. The understanding of the evolution of target composition, will lead to better control of film quality. In the case stated here, a XeCl excimer laser was used to irradiate rotated and also non-rotated $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ targets. The modified surface of these targets was systematically studied by scanning electron microscopy (SEM) and Energy Dispersive X-Ray microanalysis (EDX). It was observed that some crucial deposition parameters, such as the number of pulses and fluence has a strong effect on the roughening of the target. A comparative study was done on the derived High-Tc superconducting thin films. It was shown that the conditions during the preablation procedure which affect the target surface morphology correlate closely with the appearance of laser droplets on the film surface.

KEYWORDS : Pulsed-laser deposition, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, thin superconducting films, laser ablation, particulates, laser droplets, target modification.

1. INTRODUCTION

Laser ablation and deposition is a widely used technique for the fabrication of high quality epitaxial multilayer structures of high temperature superconducting (HTS) thin films in a fast and reproducible manner. However, the appearance of particles on their surface limits its applicability in microelectronics and multilayer technology¹. The most common particles are the "droplets" with typical sizes of 0.2 to 2 μm which are detrimental to the film surface smoothness. It is still under discussion whether the droplets originate from the target or they are related to the volume condensation of vapour². Several attempts have been made to reduce the density of droplets changing the deposition geometry³, using different laser wavelength beams⁴, using a freshly polished target^{5,6} or by preablating the target⁷. It has been also shown that for Si and FeSiGaRu alloy the droplet emission correlates closely with the surface roughness⁸. The target surface roughness depends on the laser fluence^{9,10}, the laser beam wavelength and also on the technique by which the laser beam moves relatively to the target during ablation¹¹. It has been also reported that the morphological and compositional changes undertaken on a laser ablated YBCO target are responsible for the change of the ablation and deposition rate and the shift of the plume axis¹².

In this work it will be shown that the droplets on the film correlate closely with the surface roughness of the target. The target roughening and the droplets can be reduced by using high laser fluences and certain number of pulses during the preablation procedure.

2. EXPERIMENTAL

The stoichiometric 1-2-3 YBCO targets, 15mm diameter and 3mm thickness, employed in the present experiments were prepared in-house, from commercial powder (Rhone Poulenc), using cold isostatic pressing and sintering to 93% of the theoretical density. The targets were mounted in a vacuum chamber and irradiated by a XeCl excimer laser ($\lambda=308\text{nm}$, $\tau_L=30\text{ns}$). The spot size on the target surface was $A_s=2\text{mm}^2$.

Non rotated targets were ablated with the number of pulses increased from 0 to 25, 300, 1000 with constant fluence $F=1.8\text{ J/cm}^2$, which is above the threshold fluence for stoichiometric ablation of YBCO ($F_{th}=1\text{ J/cm}^2$)¹⁰.

Rotated targets were irradiated with 25 shots/site and fluence increase from $F=1.8\text{ J/cm}^2$ (near the ablation threshold), to $F=3.5\text{ J/cm}^2$ (well above the ablation threshold). The influence of the energy fluence on the target surface, during this procedure was studied. During the film formation procedure, the above targets were irradiated with a constant number of pulses $N=4000$ (160 shots/site) for the above two values of laser fluence.

In order to see the effect of target conditioning on the YBCO films, rotated targets were preablating under the higher value of fluence, $F=3.5\text{ J/cm}^2$, with 25 shots/site or 185 shots/site and they were irradiated with an additional number of 4000 pulses (160 shots/site). The target- substrate distance was $d_{T-S}=35\text{ mm}$ in case of $F=1.8\text{ J/cm}^2$ and $d_{T-S}=45\text{ mm}$

for $F=3.5 \text{ J/cm}^2$ ($l_{\text{plume-substrate}} \approx 5 \text{ mm}$) and the laser pulse repetition rate was 10 Hz. The substrate temperature was 750°C and two types of substrates were used, LaAlO_3 and MgO . The surface morphology and chemical composition of the targets and films was investigated by SEM and EDX analysis. The structure and orientation of films was checked by X-ray diffraction analysis (XRD). The superconducting transition temperature and width were calculated from AC susceptibility measurements.

3. RESULTS AND DISCUSSION

3.1. The multiple pulses effect on a stationary YBCO target

SEM observations from a freshly polished stationary YBCO target after irradiation with a constant laser fluence of 1.8 J/cm^2 and an increased number of pulses from 0 to 1000 are shown in fig.1. Several morphology irregularities are observed in the central region of the irradiated area. At 25 pulses the initial rough surface shown in fig.1(a) has disappeared and a smooth, "melt-like" surface is observed, fig.1(b).

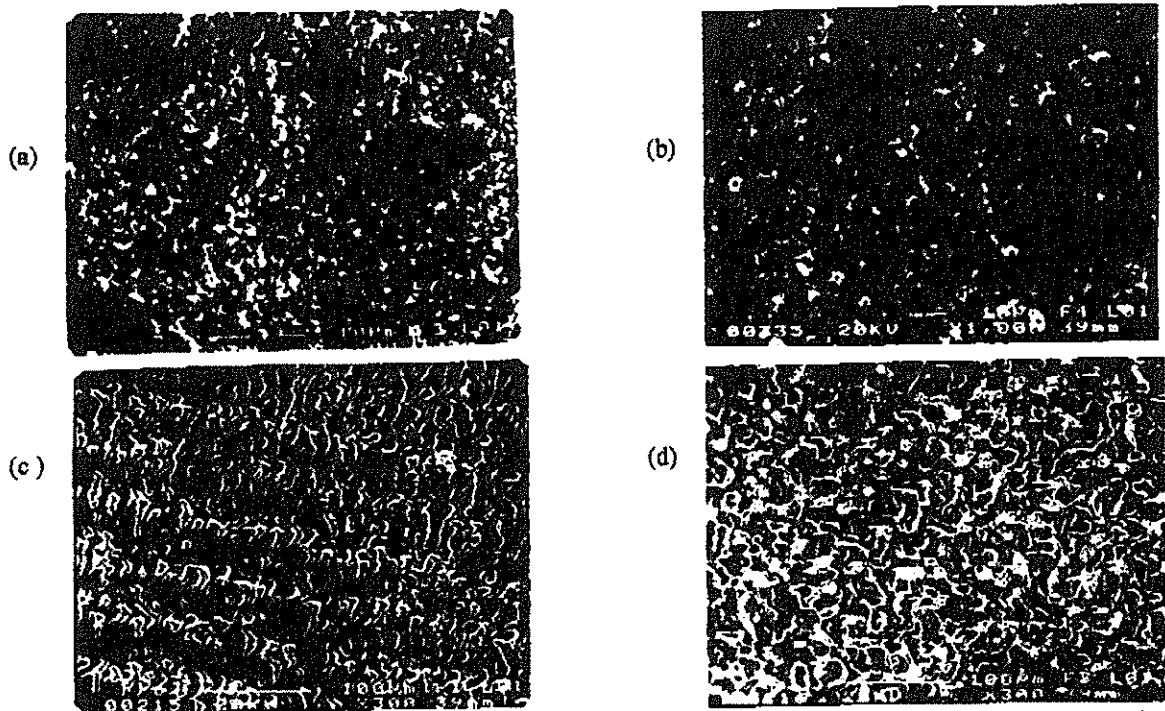


Fig.1. SEM micrograph of the central region of the irradiated crater: (a) before starting the irradiation, (b) at 25 pulses, (c) at 300 pulses and (d) at 1000 pulses.

As the number of pulses increases to 300 pulses small hillocks ($13\text{-}20\mu\text{m}$ height), start to form within the ledges, with some of their flat parts etched away, fig.1(c). After a prolonged ablation of 1000 pulses the target surface is transformed to closely packed and broad columnar structures ($30\text{-}35\mu\text{m}$ height), aligned in the direction of the laser beam, fig.1 (d).

The average stoichiometry for the presented areas is very close to 1-2-3 and does not change significantly with the increased number of laser pulses. However, for the presented morphological irregularities we found that: a) the hillocks to be Y rich and Cu deficient, b) the flat melted surface to have an almost stoichiometric composition and c) for the observed columns at 1000 pulses, the tip of the column has a smaller Y enrichment than the hillocks and their body side is Y-poor and Cu-rich. The SEM micrograph of the column main body, taken from some scraped columns reveals a polycrystalline interior with 1-2-3 stoichiometry.

The columns therefore exhibit phase segregation providing a mechanism for column formation. The Y-rich hillocks, formed on an initially smooth surface, they will act as a shield for the target, due to their greater resistance to laser vaporisation. As the surface become rougher, the effective irradiated area becomes larger and the incident laser energy begins to drop below the ablation threshold leading to preferential evaporation^{9,12}. In fig.2 we plot the stoichiometry

EDX analysis for the tip of the hillocks or columns (region A), for their body (region B) and for the flat areas between the columns (region C) of the target ablated with $F=1.8 \text{ J/cm}^2$ at various number of pulses.

It is then clear that the laser ablation above a few hundred pulses on the same area creates features of different shapes and stoichiometry.

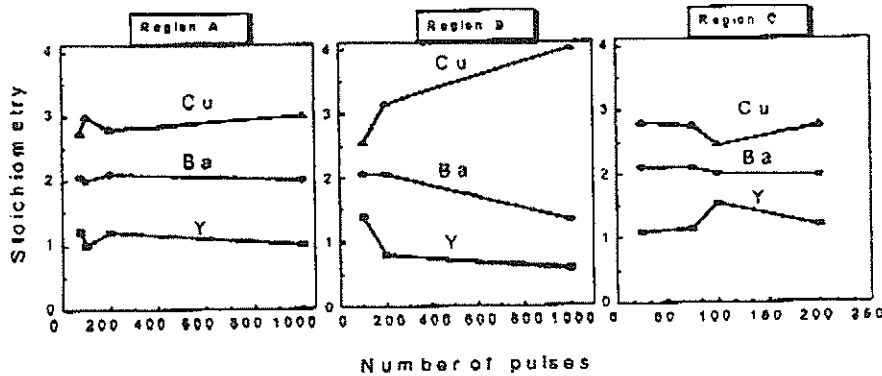


Figure 2. Stoichiometry of regions A, B and C of target irradiated with 0 to 1000 shots as measured by EDX analysis

3.2. The fluence and multiple pulses effect on a rotated YBCO target

From the above results, we can see that as the number of pulses increases the target surface roughness also increases leading to higher stoichiometry deviations. For this reason the target have to be rotated in order to have a limited number of shots per site. We used a freshly polished YBCO target, rotated with such a speed in order to have 25 shots/site and preablated (conditioned) it with two different laser fluences, one near the ablation threshold, $F=1.8 \text{ J/cm}^2$ and another well above the ablation threshold $F=3.5 \text{ J/cm}^2$. SEM observations (fig.3a) revealed in both cases a smooth, "melt-like" surface with no deviation from the 123 stoichiometry

The above rotated targets were irradiated with an additional 160 shots/site in order to deposit thin films. As observed from fig.3(b) the target irradiated under the lower fluence (1.8 J/cm^2) exhibits a surface populated with columns formed within the ledges, while the one irradiated with the higher fluence (3.5 J/cm^2) exhibited a smooth, "melt-like" surface with some morphological irregularities at the edges of the irradiated area fig.3(c).

This observation correlates the appearance of morphology irregularities with lower energy densities suggesting that in order to eliminate the target roughness, fluences well above the ablation threshold, have to be used.

In order to further investigate the multiple pulses effect on the rotated targets irradiated with the high value of $F=3.5 \text{ J/cm}^2$, we used the targets exhibited the morphology shown in figures 3 (a) and 3 (c) after the preablation procedure and ablated these with 160 shots/site. The target surface morphology after a total number of 185 shots/site and 345 shots/site are shown in fig. 3 (c) and 3 (d). It is shown that as this number increased to 345 shots/site the above described morphological irregularities at the edges of the irradiated area became wider and more intense.

3.3. The effect of target roughness on the appearance of laser droplets on the film surface morphology

In order to investigate the effect of laser induced surface modification on the film surface morphology, the films deposited from the above described targets were SEM analysed :

(a) The films deposited on LaAlO_3 , with 160 shots/site and with $F=1.8 \text{ J/cm}^2$ or $F=3.5 \text{ J/cm}^2$, are shown in fig. 4.(a) and 4.(b), respectively.

These films are produced from targets exhibited the smooth, "melt like" surface (fig. 3.a).

It is observed that films produced with the lower fluence exhibited a greater number of droplets, while the ones with the higher fluence had much smaller number of droplets.

The above observation demonstrates that the emission of droplets is strongly enhanced by the fluence.

(b) Films deposited on MgO with 160 shots/site and for $F=3.5 \text{ J/cm}^2$ after a preablation with 25 shots/site or 185 shots/site, are shown in fig. 5. (a) and 5 (b), respectively. It is apparent that the film which came from the target with the extended preablation, exhibited a higher number of droplets with larger average size.

The strong correlation between the droplet number and the target surface roughness associated with the preablation is shown.

films exhibited transition temperatures above 91K and small transition widths ($\Delta T_c = 0.6-2.5$ K) while from XRD analysis they revealed high crystallinity.

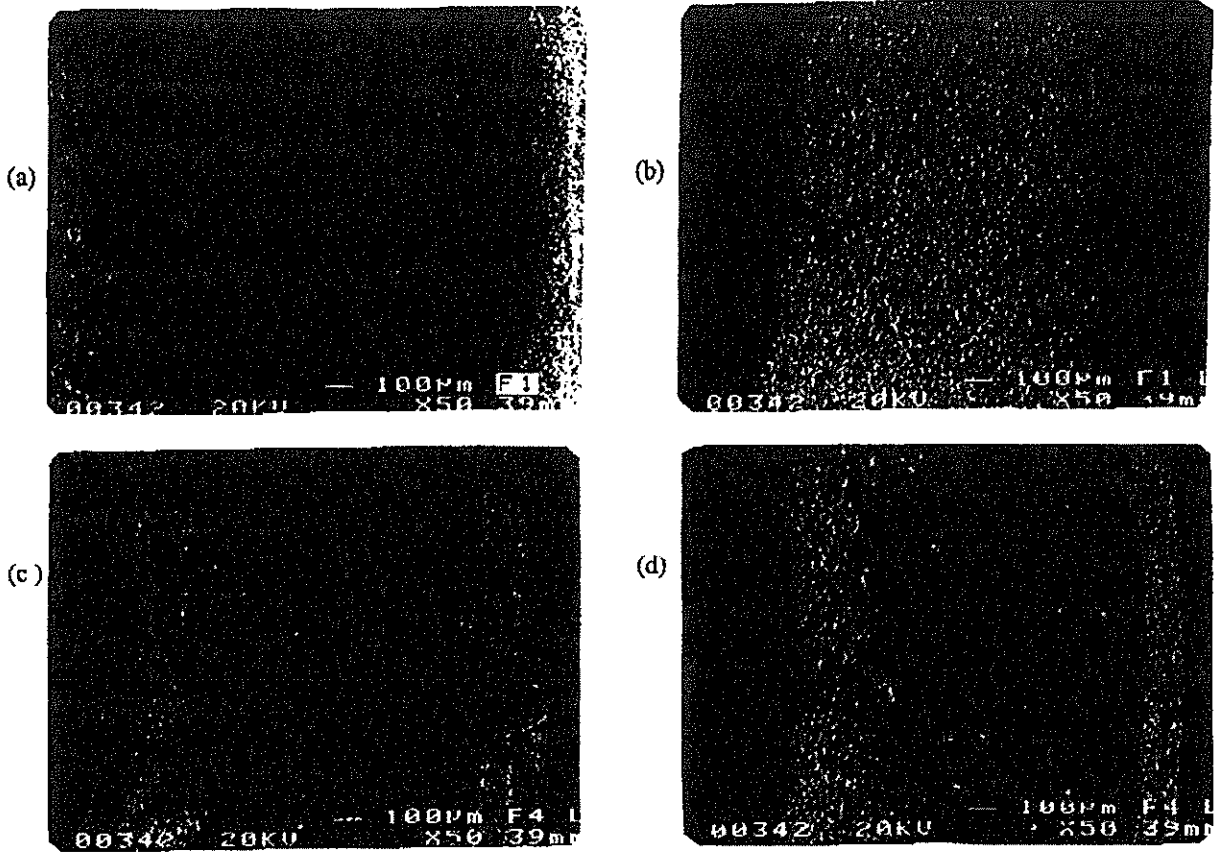


Fig. 3. SEM micrographs of target surface after a) 25 shots/site for $F=1.8$ J/cm² or $F=3.5$ J/cm², b) after 185 shots/site for $F=1.8$ J/cm², c) after 185 shots/site for $F=3.5$ J/cm² and d) after 345 shots/site for $F=3.5$ J/cm².

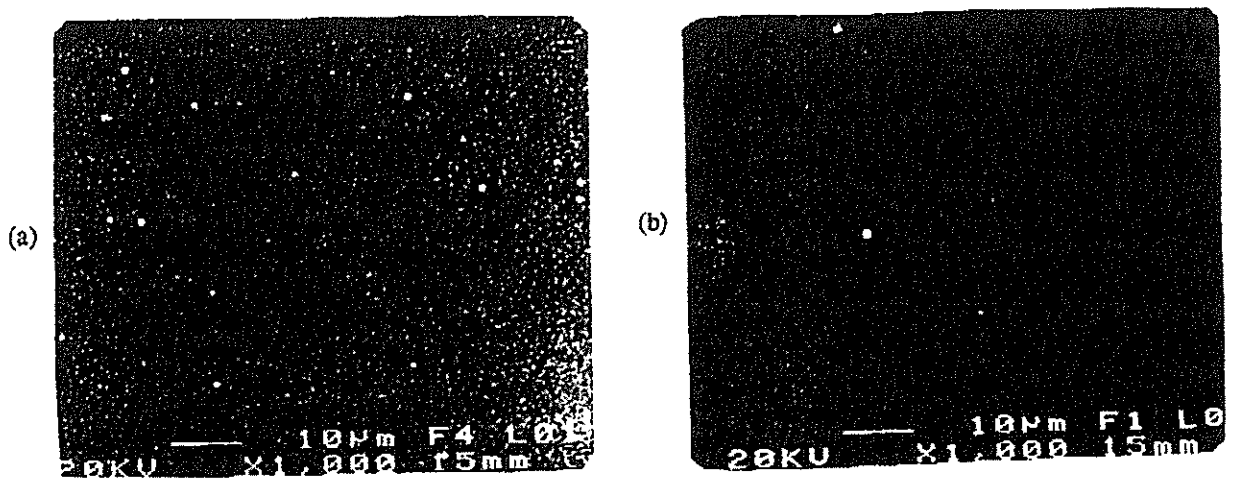


Fig. 4. SEM micrographs of film surface deposited from YBCO target after a preablation of 25 shots/site and with a) $F=1.8$ J/cm² and b) $F=3.5$ J/cm².

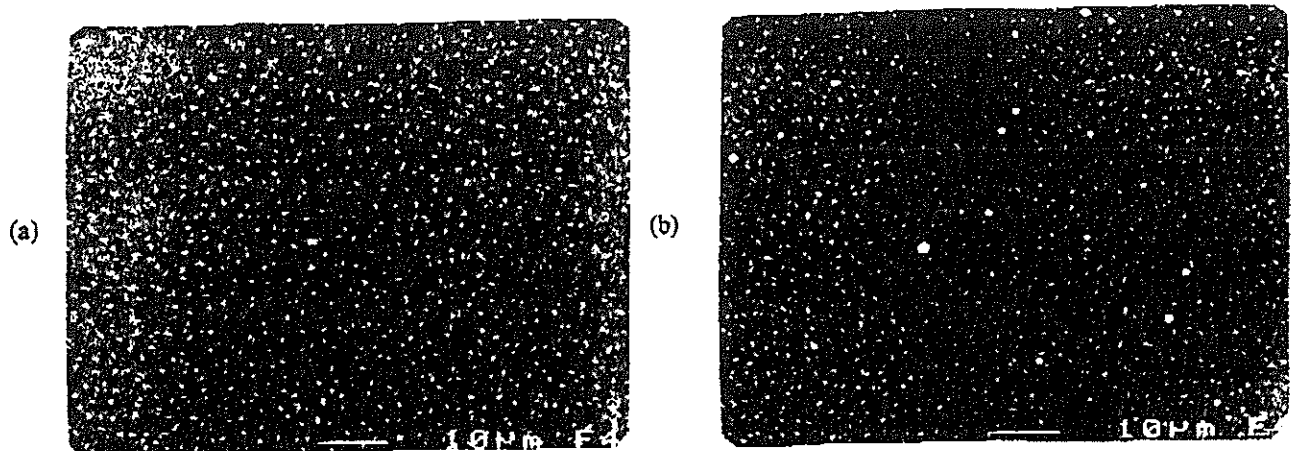


Fig. 5. SEM micrographs of film surface deposited with $F=3.5 \text{ J/cm}^2$ from YBCO target after a preablation of a) 25 shots/site and b) after 180 shots/site.

4. CONCLUSIONS

Sintered YBCO targets subjected to various number of pulses, without rotation, were studied by SEM and EDX measurements. We observed that as the number of pulses increases the target surface roughness also increases leading to higher stoichiometry deviations. For this reason the target have to be rotated but with such a speed in order to have a limited number of shots per site. For a rotated target, with limited laser pulses on the target, increasing roughening was observed for lower fluences, near the ablation threshold of YBCO while for fluences away from this threshold the target surface exhibited a smoother surface. These conditions have to be fulfilled during the preablation conditioning because as it was proved the number of droplets on the film correlates closely with the target surface roughness. The droplet size and number on the produced films are smaller when the films come from a smooth target ablated with fluence well above the ablation threshold.

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