Factors that determine the presence of particles in YBCO films grown by PLD

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Abstract. The method of growing thin films PLD, is widely used in applications and possesses great potential in thin YBa$_2$Cu$_3$O$_{7-\delta}$ films production with outstanding physical properties. However, it is limited in nano and micro technology due to the presence of particles on the surface of the films. This article describes some causes that create these particles. YBa$_2$Cu$_3$O$_{7-\delta}$ films have been grown on electrolytic copper used as a variable model the distance target-substrate. The effects are studied through Scanning Electronic Microscopy. It is observed particles with a large variety of shapes and distributions. The results show that ranging the target-substrate distance, the superficial morphology is modified. An evidence of it, is that the evaporation of d$_{B-S}=7$ cm, is more coherent that d$_{B-S}=3$ cm. Therefore, exist a relation between the morphology and the parameters of growing. Also affect, the structural change that exists among the substrate and the film formation, the substrate preparation and it must not be monocrystalline, these factors define a kinetic and a mechanism of growing that promotes a heterogeneous nucleation.

1. Introduction
Growing thin films with PLD (Pulse Laser Deposition) is the result of forming plasma making fall on laser radiation pulsed upon the surface of a solid target. It is used in a diversity of applications maintaining the capacity of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) thin films production with excellent properties [1,2] to be used in the manufacture of low temperatures high performance electronic devices [3,4].

However, its applicability is limited in nano and microelectronic mostly due to two factors: splashing, this is, expel of drops and fragments from the target during the ablation, for the creation of outgrowths upon the surface of the film. Both factors depend on the physical properties of the surface of the target and the substrate that include its temperature, density, optic absorption, chemical composition, steam pressure, texture and the net parameter adjustment and the film in formation; from thermodynamic conditions given for growing parameters, that, at the same time, define the mechanisms and the growing kinetic of films, examples of this are: the laser properties that include the fluency, wavelength, uniformity of the beam profile, repetition rate; gas pressure in the growing chamber; distance target-substrate, growth rate, dimensions and the beam print track size, among others. All these parameters are related, this is, exist a range of value for which reduce the splashing and outgrowths creation. This implies that the phenomenology associated to this interrelation is complex; part of this knowledge still is qualitative despite the effects being measured. These effects refer to physical properties of the grown material, for instance, electric transportation, thermo electronics, and
magnetics. Its phenomenology must be understood through the interrelation between the physical properties of the film and the thermodynamic limited for growing parameters, highlights that the approach to the explanation of the origin of the particles represents the capacity of diminish its density or even remove them, in the meantime, this represents be even closer of the optimum range of one or several interesting physical properties for the obtained film, which implies that the applications where are used these materials have competitive efficiencies with other technologies. This is one of the main reasons that justified the concern of the study of the particles origin upon the surface of YBCO films grown for PLD. The applications refer, since alternating current cables, generators, or engines operating at 77 K[5], until applications in nano and microelectronics[6,7], for example, in the last decades researches have been had great interest for superconducting nanostructures and semiconducting of low dimensionality [8,9], due to its low energy applications and energy harvesting devices[10,11]. Because of the surface effects, the performance of these devices depends of the morphology of the nanocrystals.

Outstanding efforts are being made to understand the origin of the particles and to find techniques to diminish its density upon the films surface. More likely, the best implement better classified, among the desirable and necessary to develop a technology that produces thin film crio electronic devices, based on super conductive materials of high $T_c$ (HTSC) as the YBCO, it is the one that gives the possibility of manipulate locally the superconductive properties as the critical current density, $J_c$, or the transitional temperature $T_c$, being possible in a nano metric scale.

An approach to achieve this is the one called “selected” or, more descriptively, “inhibited” growing [12]. The underlying idea is, to use optimized monocrystalline substrates[13,14], for example, YBCO films with a $c$ axis oriented perpendicular to the film plane, moreover, with a pre-structure located in the substrate areas where is desirable impede or inhibit entirely the epitaxial growing of the film HTSC[12]. Once more, through this alternative can be obtained high performance applications, it is necessary the lack of existence of particles upon the surface of the film, in other words, having nanometric control of the morphology of the surface of the film. Examples where the procedure has being applied to YBCO films grown are the deposition of Si[15,16], SiN, [17], Ti[18,19], Nb and W[19]. Another important progress regarding YBCO films with good morphology are the development of technologies for conductors covering that have achieved $J_c > 1$ mA/cm$^2$, which has stimulated greater interest in the comprehension and improvement of the deposition technique of YBCO films by PLD [20,21], being as its high $J_c$ and its intrinsic magnetic properties provide a widely range of solutions to engineering problems [22].

In this work is studied the origin of particles that are created during the deposit of YBCO, grown through the technique on steam phase PLD, considering the variation target-substrate and letting the rest of the growing parameters steady. The superficial morphology was analyzed and it was obtained the chemical composition in different regions of the thin film and a characteristic target using a scanning electron microscope (SEM). It is argued the correlation between the distances target-substrate, the particles density and their composition.

2. Experimental Description

YBCO films were deposited on electrolytic copper substrates with a Nd:YAG laser of $\lambda = 1064$ nm, a 650 mJ, with a pulse duration $\tau \approx 5$-7 ns and a frequency of 10 Hz. So as to, a steady target position, the beam image focused upon the target surface was adjusted experimentally with a round shape with 2 mm diameter and it was focused with a convex lens ($f = 50$ cm). For all the experiments the laser fluency, spot magnitude and the distance between the lens and the target were stable. The deposit time was $t = 5$ minutes, the distance between the target and substrate was modified in a range that went from $d_{TS} = 3$ cm to $d_{TS} = 7$ cm, the growing temperature was $T = 650^\circ C$ and the oxygen pressure into the chamber was $P_{O_2} = 200$ mTorr. The sole parameter that showed a variance was the distance between target-substrate. Once this distance was defined, all other parameters remain constant during the growing. The samples were exposed to an in situ annealing at the end of the growing to $T = 450^\circ C$ y $P_{O_2} = 270$ mTorr during two hours.
The microstructural superficial observation and the elemental chemic analysis were realized in a SEM, brand LEO 440 with a capacity of 40 KeV, adapted with a solid state detector of SiLi with 1024 channels and a range of 20 KeV, OXFORD brand. The micro photographs were obtained in an acceleration voltage of 20 KeV and a current density of 200 pA, through a secondary electron detector. The chemical analysis was obtained through X-ray diffraction with energy dispersion application (EDS) electrostatic dispersion, punctual analysis was realized with an acceleration voltage of 20 KeV and current density 1 nA, at the time of the acquisition of each specter was 60 seconds real time. All the elements that generate X-rays were detected from Beryllium. The calculus of semi quantifications was realized using the correction factor ZAF (atomic number effect, absorption, and fluorescence of the processed sample) al the results returned to normal.

3. Results and Discussion

Figure 1 reveals an expulsion direction of the preferential material, located in the internal part of the periphery of the crater caused by the “feeder” upon the target surface. It is observed, for the topographical characteristics of the surface, that experimented a re-solidification process of mould when it did not receive enough energy to sublimate.

Figure 1. Micrography that shows the preferential direction of the material. Amp: 500x; Esc: 1.7 cm = 500 μm.

Figure 2. Micrography that shows liquefaction effects and re–solidification of the periphery of the crater.

Figure 2 is a micrography of the external periphery of the crater, where is observed the liquefaction process that the material suffered, later on resolidify, without the influence of the impulsive force that produces the feeder.

Figure 3 shows solidified drops with an elliptic shape, in the periphery of the exterior edge of the crater, randomly distributed, produced for the splashing. The isotropic superficial tension of the liquid drives to the spherical shape equilibrium, it is possible that the spherical shape may not be entirely achieved before the solidification so that they possess that shape, even the biggest axis of all drops have the same direction, towards outside of the crater edge.

Figure 3. Random distribution of drops with elliptic shape, solidified with a preferential direction
Figure 4. Micrography of a YBCO surface film grown at $d_{T-S} = 3$ cm.

Figure 5. Micrography of a YBCO surface film grown at $d_{T-S} = 7$ cm.

In Figure 4, some drops between 0.4 y 1 μm of diameter are observed superficial, meanwhile other are subsequently covered by the deposit. As magnitudes, shapes and chemical composition are similar to observed drops upon the target surface. This implies that are drops of mould resolidified, which are expelled directly since the target. On the upper side of the micrography is observed a fractured outgrowth. Instead, in figure 5 shows that the density of particles has decreased and do not appear any outgrowth, this highlights the splashing and outgrowths reduction for $d_{T-S} = 7$ cm.

On the surface of the films, there exist areas with a different composition to phase 123. In other words, there are areas with a phase of CuO, with an abundant concentration of Ba and low concentration of Y. Figure 6 shows the EDS spectrum of a thin film, $d_{T-S} = 3$ cm, which is an example of a growth YBCO film.

Figure 6. EDS spectrum representative of the YBCO films grown by PLD.

In order to determine the effect of “splashing” in the composition, different areas were chosen to determine the EDS spectrum on the surface of a YBCO film at $d_{T-S} = 3$ cm. Before the growing, a screen of 2 mm width and 10 mm length was placed on the substrate surface, with the purpose of
avoiding that particles generated in the process of ablation are deposited under this area, but allowing that steam is deposited. After the growing, three areas were identified as: “step”, “outgrowth”, and “film”, as it is shown in Figure 7. The “step” is an area which denotes the height of the film after growing. The “outgrowth” is an area which comprises of a multiphase microstructure and the “film” represents the area of the growth film under the screen which is characterized by deposited steam without splashing. At the same time, four specific subareas were selected, in order to quantify their chemical composition, as it is shown in Figure 7.

Figure 8 shows the quantification of Cu for each subarea. A significant difference of Cu is shown among areas. However, when the atomic weight of Cu and O$_2$ is calculated for these areas, the stoichiometry agrees with the CuO phase (Tenorite).

In the same way, a quantification of Y and Ba was performed on those areas previously selected. Figures 9 and 10 show this quantification of both elements, Y and Ba, respectively. It is observed a low quantity of Y for all subareas selected and a relative increment in the quantity of Ba.

An analysis was performed under the area where screen was placed. Figure 11 shows the quantification of elements where steam was deposited and splashing is not present on the surface. Those subareas identified as 3 and 4 show a particular and interesting to be considered as adequate subarea. Table 1 quantifies a regular stoichiometry relationship, where the component 123 of YBCO is 20%.
4. Conclusions

The results show that the morphology of the surface, in thin films grown by PLD, depends mainly on the distance target-substrate. However, it suggests a correlation between the distance and the thermodynamic growing of the thin film. The effects of splashing and outgrowths are decreased at $d_{T-S} = 7$ cm, which in turns may determine specific characteristics on the structure and morphology for engineering applications on nano scale.

The evaporation process at $d_{T-S} = 7$ cm is more congruent than $d_{T-S} = 3$ cm. A homogeneous composition on the thin film is better preserved during the ablation for $d_{B-S} = 7$. The larger the distance between target-substrate, the lower quantity of undesired particles on the surface of a thin film.

The analysis shows four factors that mainly contribute to the lack of a homogeneous composition and the generation of heterogeneous nucleation: the target and the substrate were very close, increasing the probably of deposited particles on the thin film; the lack of an adequate adjustment between the net parameters target-substrate; the set up in the chemical process in the substrate to eliminate all kind of impurity before the growing; and the substrate must not have a monocrystalline surface.

The use of a screen during the growing is another factor that may prevents the effect of “splashing”, which in turns affect an adequate composition. It means that a screen improves both composition and morphology on the surface with a difference of 20% respect to phase 123.

The ablation phenomena and the vaporized material, used as target, are steps that are repeated hundreds of times in a typical deposition, modifying the original target surface since the first laser pulse impacts. After the target-laser interaction, amorphous superficial areas may be observed, more than a crystalline crater upon the film surface. This factor influences the quality in the composition of the thin film.

5. References

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