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# Pulsed laser deposition of superconducting $REBa_2Cu_3O_{7-x}$ thin films

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## Abstract

Superconducting thin films of $REBa_2Cu_3O_{7-x}$ (RE: Sm, Eu, Gd) (RBCO) were deposited by a pulsed laser ablation technique on strontium titanate substrates at different substrate temperature and reduced oxygen pressure. The resistivity versus temperature measurements show the onset and the offset of the superconducting transition between 95 and 70 K. For all the investigated rare earths, we find a substrate temperature value for which morphological and structural analyses, performed by scanning electron microscopy and X-ray diffraction, are also reported the grown film has the offset of the superconducting transition above 90 K. Morphological and structural analyses, performed by scanning electron microscopy and X-ray diffraction, are also reported and discussed.

*Keywords:* Pulsed laser deposition; Superconducting thin films; Transition temperature

## 1. Introduction

Pulsed laser deposition (PLD) is a well assessed technique for growing thin films of high temperature superconductors (HTS). A lot of work has been done for the $YBa_2Cu_3O_{7-x}$ (YBCO) compound which remains the preferred HTS material for microelectronics and power device applications. Among the components of the $REBa_2Cu_3O_{7-x}$ (RBCO) family the $NdBa_2Cu_3O_{7-x}$ is a good candidate for substituting the YBCO because it exhibits critical temperature and critical current density higher than YBCO in high magnetic fields [1,2]. On the contrary, little attention has been devoted to $SmBa_2Cu_3O_{7-x}$ (SBCO), $EuBa_2Cu_3O_{7-x}$ (EBCO) and $GdBa_2Cu_3O_{7-x}$ (GBCO), probably because of the difficulty of avoiding cation disorder associated with the substitution of the rare earth atom RE for Ba [3,4]. This substitution usually leads to an abruptly lowering of the critical temperature and the overall superconducting behaviour deteriorates [5]. Otherwise, when the substitution is partially controlled, an effective pinning mechanism and subsequently a general improvement of the transport properties, mostly in the presence of high magnetic fields, may result.

By light of the good performance of the SBCO thin films obtained by in-axis PLD [6–9], comparable results are expected by working in off-axis geometry and substituting the rare earth atoms [10].

In the present work, we analyse the effect on the critical temperature of the deposition parameters such as off-axis geometry and substrate holder temperature

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$T_s$, at fixed values of oxygen pressure and fluence of the laser.

## 2. Experimental

The RBCO thin films were grown on strontium titanate(1 0 0) single crystal by off-axis PLD using a Nd:YAG laser operating at $\lambda = 532$ nm and 180 mJ/shot energy in a spot area ($10^{-5}$ m$^2$). The ablation took place from a RBCO commercial high density target in a $O_2$ pressure of $10^{-2}$ Pa. The operating pressure were achieved by filling the vacuum chamber with the right amount of $O_2$ and adding then argon gas up to a total pressure of $10^{-1}$ mbar. The deposition rate was 0.1/0.2 nm/s indicating, for a deposition time of 1000 s and at repetition rate of 10 Hz, a film thickness of 0.1/0.2 μm. After the deposition the films were annealed in situ at $T_s = 450$ °C for 1800 s in $10^5$ Pa of oxygen.

Structural and morphological characterizations were performed by using a Siemens D5000 X-ray diffractometer (XRD) and a Philips 500 scanning electron microscope (SEM). The resistance ($R$) versus temperature ($T$) measurements were performed by the standard four leads configuration with low bias current. The sample temperature was lowered by using a closed cycle refrigerator down to 9 K.

## 3. Results and discussion

Superconducting thin films of SBCO, EBCO and GBCO were grown in the 700–820 °C substrate temperature range. We compare the films grown at 700, 760 and 820 °C. Thin films of SBCO were also deposited at $T_s = 740$ and 785 °C.

The typical surface morphology and the structural characteristics are reported in Figs. 1 and 2, respectively, for a GBCO thin film. A smooth and quite homogeneous surface is observed, with reduced presence of droplets. The X-ray diffraction analysis only shows the (0 0 1) reflections of the superconducting phase indicating that the films are $c$-axis oriented and have no additional crystallographic phases.

In Fig. 3, we report the GBCO resistance versus temperature for the $T_s$ investigated (700, 760 and 820 °C). At $T_s = 760$ °C we have a $T_{c0} = 90$ K and a transition width of 2 K while in the other cases we observe a $T_{c0} \sim 70$ K and a transition width of ~20 K, indicating a deterioration of the superconducting properties, probably due to the oxygen deficiency. The resistivity ratio (RR) decreases approaching a value $RR = 1.89$ for $T_s = 700$ °C and $RR = 1.46$ for $T_s = 820$ °C.

In the EBCO deposition, the parameters reproducibility window is wider and we find high $T_{c0}$ and narrow transitions down to $T_s = 700$ °C. The film

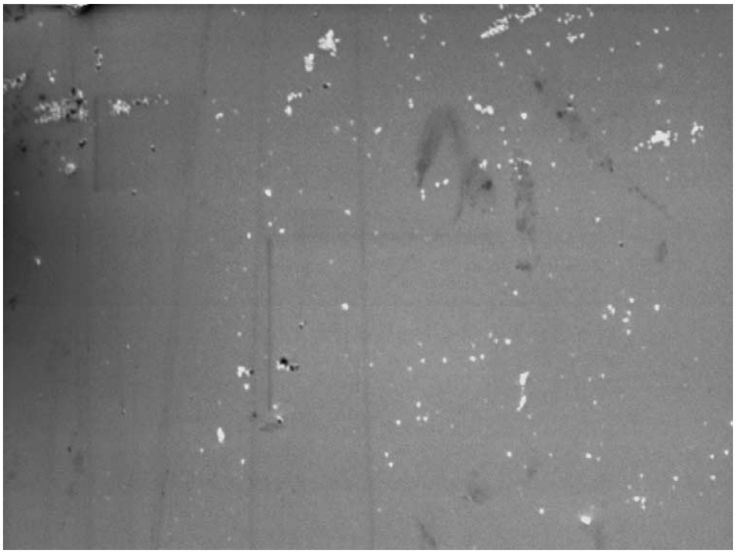

Fig. 1. SEM micrograph of a typical RBCO thin film (GBCO).

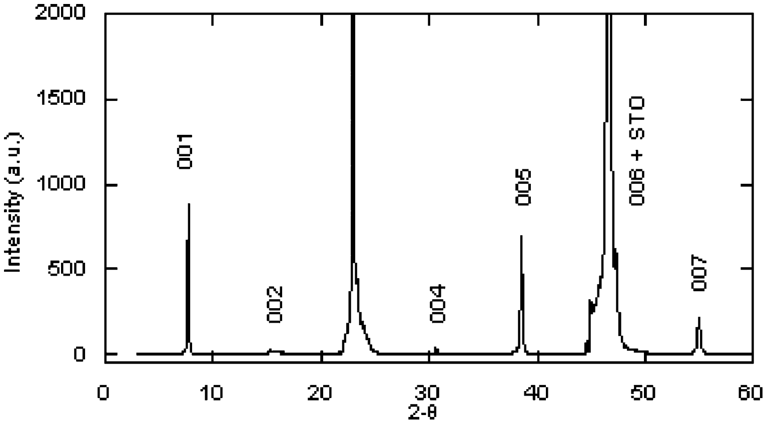

Fig. 2. XRD spectrum of a typical thin film (SBCO).

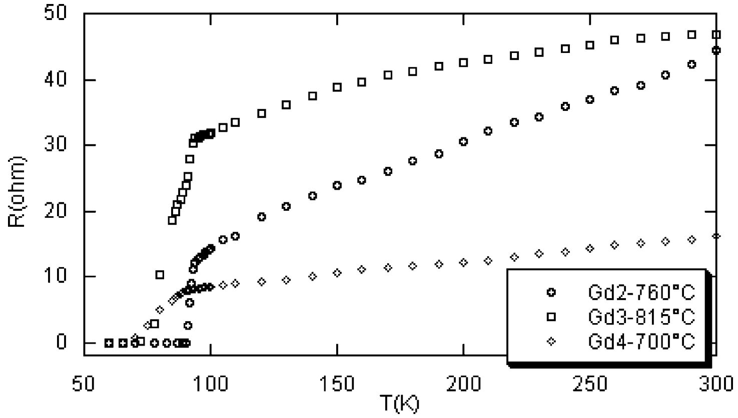

Fig. 3. $R$ vs. $T$ measurements of GBCO deposited at different substrate temperature.

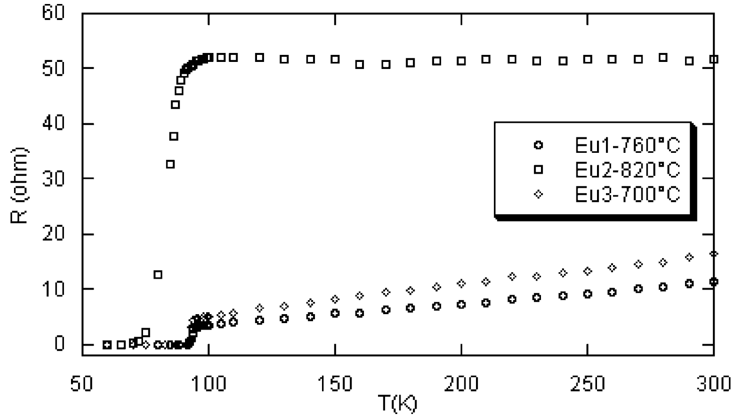

Fig. 4. $R$ vs. $T$ measurements of EBCO deposited at different substrate temperature.

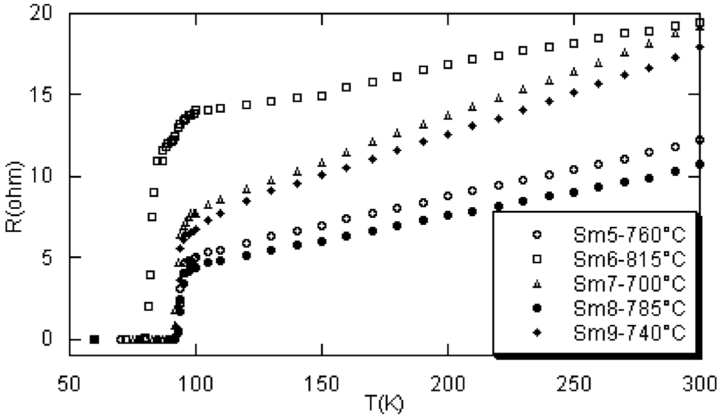

Fig. 5. $R$ vs. $T$ measurements of SBCO deposited at different substrate temperature.

deposited at $T_s = 820\ ^\circ C$ shows the same superconducting transition as that of the GBCO one (Fig. 4). Also RR shows a similar behaviour since it has the same value (≅3.25) at $T_s = 700\ ^\circ C$ and falls down (≅1) at $T_s = 820\ ^\circ C$.

Finally, we have analyzed the SBCO thin films, grown at $T_s = 740$ and 785 °C (Fig. 5). Except for the case $T_s = 820\ ^\circ C$, the transitions are narrow (~2 K), the $T_{c0}$ is in the 90/93 K range and the resistivity ratio is almost constant (≅2.5). On the contrary, the sample grown at $T_s = 820\ ^\circ C$ results in a wider transition width (≅10 K) and in a lower $T_{c0}$ (≅80 K), but, in any case, the result is better than EBCO and GBCO at the same temperature.

At $T_s = 760\ ^\circ C$ (Fig. 6) all the films exhibit the best superconducting transition with $T_{c0} > 90$ K and $\Delta T = 1/2$ K. EBCO and SBCO thin films exhibit resistive transitions with similar resistance values.

At $T_s = 700\ ^\circ C$ (Fig. 7) SBCO and EBCO present a similar behaviour, while GBCO thin films suddenly get worse, showing a lowering of the critical temperature and a broadening of the transition.

At $T_s = 820\ ^\circ C$ (Fig. 8) the superconducting properties of all the thin films get worse. We observe higher resistivity values in the normal state, the broadening of the transition widths and the lowering of the transition temperature. The SBCO is less influenced than EBCO and GBCO by this temperature increase.

We observe that for all the substituted rare earths there is a limited window for the deposition parameters $p$ and $T$, where the thin films are of good quality and reproducible ($T_{c0} = 90/93$ K, $\Delta T \sim 2$ K). Varying the

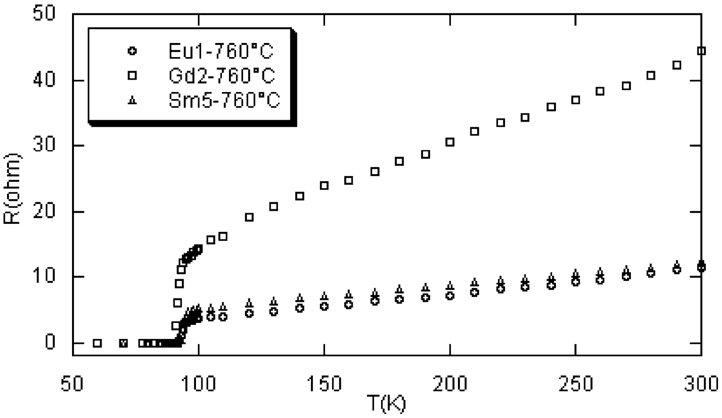

Fig. 6. $R$ vs. $T$ measurements of the RBCO thin films at deposition temperature $T_s = 760\ ^\circ C$.

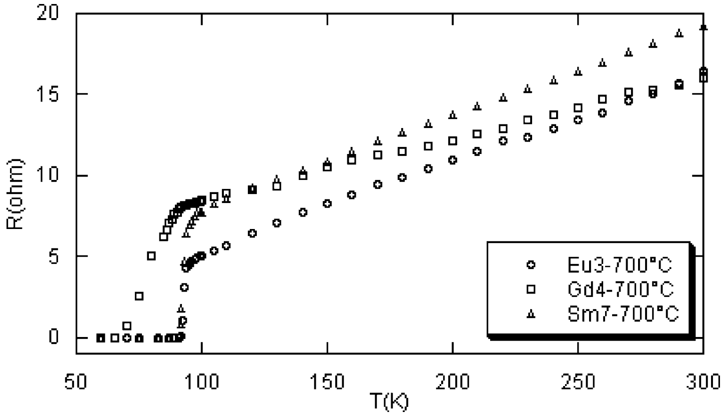

Fig. 7. $R$ vs. $T$ measurements of the RBCO thin films at deposition temperature $T_s = 700$ °C.

substrate temperature, at fixed oxygen pressure [1], the superconducting properties get worse, depending on the rare earth substituted (Sm, Eu or Gd). Among these, the Sm is slowly influenced by temperature deposition variations so that we ever grow superconducting thin films with critical temperature higher than nitrogen boiling point. We can explain this result by thermodynamic considerations [6,7]. The film growth by PLD is a typical non-equilibrium process where the metastable phases can influence the surface and so the superconducting properties. In particular, the SBCO has a wider stability window in the $p$–$T$ phase diagram where the oxygen content and the substitutions of Re for Ba ions are controlled so we can easily grow good thin films even varying the substrate temperature. On the contrary, GBCO has a peritectic temperature lower than SBCO and so a narrower stability window. Out of the thermodynamic stability window, the superconducting properties get worse and we assume [11] that it is due to Re for Ba substitution and oxygen content.

In conclusion, these results suggest that it is possible to deposit high quality SBCO, EBCO and GBCO thin films with the off-axis PLD technique. There are $T_s$ and $p$ $O_2$ values for which the SBCO, EBCO and GBCO thin films have similar superconducting properties, being $T_{c0}$ in the range 90/93 K for all the compounds. The phase diagram window, in which good quality films grow, is wider for the SBCO than

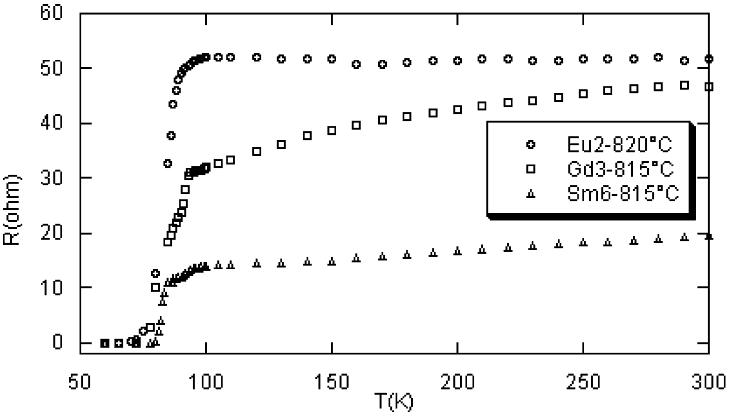

Fig. 8. $R$ vs. $T$ measurements of the RBCO thin films at deposition temperature $T_s = 820$ °C.

EBCO and GBCO indicating a larger thermodynamic stability and a better reproducibility in the deposition process of the thin films.

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