Pulsed-laser ablation and deposition of superconducting BiSrCaCuO thin films

A GIARDINI-GUIDONI^{*1}, T M DI PALMA², V MAROTTA²,
R MARTINO², A MORONE², G P PARISI² and S ORLANDO²

¹ Università degli Studi "La Sapienza", P.le A Moro, 5 Roma, Italy

² Istituto per i Materiali Speciali– C N R, Zona Industriale di Tito Scalo, P O Box 27 Tito Scalo (Pz), Italy

Abstract. The present work reports some results obtained using the laser deposition technique to produce superconducting thin films. *In situ* analysis of transients formed in the plume and surface diagnostics of deposited Bi-Sr-Ca-Cu-O (BSCCO) thin films have been performed. It has been ascertained that mixed-oxide cluster ions are produced in the plume, together with neutral and ionized atoms of the constituent material. The effect of annealing parameters on the structure and quality of pellets and deposited thin films of BSCCO are reported and discussed.

Keywords. Pulsed-laser ablation; BiSrCaCuO thin films; thin-film deposition; superconducting thin films.

1. Introduction

The discovery of a superconducting phase in LaBaCuO compounds constituted a breakthrough in the search for superconducting materials with high transition temperatures (Bednorz and Muller 1986). The worldwide effort has led to the production of a number of superconductors mainly formed of ceramic composite materials, whose common structural feature is the presence of CuO₂ planes in which the copper atoms form a square lattice with the oxygen placed between nearest-neighbour copper atoms (Maeda *et al* 1988). The production of high-quality powder and superconducting thin films from these materials is very important for practical applications as well as for basic studies. The fabrication of high-quality thin films by the pulsed-laser deposition technique (PLD), successfully demonstrated in the late eighties (Venkatesan *et al* 1988), has recently experienced an explosive growth (Beech and Boyd 1992). The advantage of this technique over other deposition methods such as sputtering or molecular beam epitaxy, is the simplicity of the deposition scheme, since the laser source is placed outside the vacuum deposition chamber. Laser rays enter through a window into a vacuum chamber and impinge on the material to be deposited. Laser removal of matter produces a plume in which electrons, ions and neutral species are present. The ablated material can be collected on a substrate placed at a suitable distance. After appropriate heat treatment, the thin films deposited (of BSCCO material)

---

*For correspondence

Figure 1. Experimental apparatus.

become superconducting. The main interest was focussed on studies aimed at understanding the interrelationship between the chemistry, laser ablation processes and the resulting microstructural properties of the thin films deposited. Initially, in our laboratory, we were interested in elucidating the interaction between laser beams and matter (Giardini Guidoni *et al* 1990). Measurements of space- and time-dependent emission spectra of the species present in the plume provide a key to understanding the dynamics and reactivity of the ablated materials in the gas phase (Giardini Guidoni *et al* 1990). Evidence of chemical reactions in the plume has been ascertained; in particular it has been shown that the copper ion reacts with second-group oxides, CaO, BaO, SrO, leading to the formation of mixed ions at the expense of pure oxide clusters (Mele *et al* 1990). Studies aimed at clarifying the role played by the annealing parameters in the structure and quality of deposited thin films are reported here. Some information on pellet sintering is also given. A schematic of the deposition apparatus is shown in figure 1.

2. Experimental

The laser system is a frequency doubled ($\lambda = 532$ nm, pulse duration 10 ns) or quadrupled ($\lambda = 266$ nm) Nd-YAG laser (Quantel 581). The vacuum chamber for ablation and deposition, already described (Giardini Guidoni *et al* 1990) is equipped with a quartz laser entrance window and with a rotatable multi-target support and a substrate holder. The pressure in the chamber is kept at 1.5×10^{-6} mbar during the ablation process. The laser energy is about $2.5 - 3$ J/cm², the incidence angle with respect to

the target surface is 45° . The ablated material originates a luminous plume which extends about 2.5 cm from the surface. Time-of-flight mass spectrometry and luminescence measurements have already been employed to obtain information on the intermediate species, neutral and ionized, present in the plume and the results (Giardini Guidoni *et al* 1990; Mele *et al* 1990) are only summarized here. Sr, Bi, Ca, Cu and simple oxide ions predominated in the mass spectrum and masses of simple and mixed positive cluster oxide ions were present. The mass spectrometric plume analysis was performed in the region near the laser spot on the surface, so it does not exclude heavier aggregates being formed at a greater distance from the target. They could in the end reach the substrate and initiate film growth. In the total emission of the plume, taken at a distance of 0.5 mm from the target, atom and ion emissions were strongly predominant. Very weak emission features attributable to CuO, CaO and SrO molecules were also observed. Time-resolved spectrum measurements for most of the emission lines show a prompt and delayed emission, which has already been attributed to laser and collisional excitation of ablated species, respectively (Saenger

Figure 2. Temperature-dependence of electrical resistivities of two samples sintered in air at 845°C for two different periods of time: sample 1 – 20 h and sample 2 – 100 h.

Figure 3. X-ray CuKa pellet diffraction patterns of samples 1 and 2.

et al 1989). On the holder, different substrates glued by silver paint can be positioned in front of the target, at a distance of 2.5 cm. Thin films were deposited on SrTiO_3 (100) or MgO (200) substrates by laser ablation of sintered BSCCO pellets obtained by calcining mixtures of Bi_2O_3 , CaCO_3 , SrCO_3 and CuO , doped with lead in some cases. Initial attempts to form the superconducting phases, although following the standard fabrication route of sintering in air at 845°C after repeated cycles of grinding and pelletizing, failed to obtain good quality pellets. This could be attributed to segregation of molten material during the calcination stage. The effects of the calcination and sintering time in the furnace are shown, as an example, in figures 2 and 3, where the temperature dependence of electric resistivity and X-ray diffraction spectra of two typical samples are reported.

3. Results and discussion

The data show that superconducting phases are obtained after a longer sintering time (figure 2). The X-ray diffraction pattern confirms this behaviour. In fact, at a longer sintering time (100 h) the 4.8° peak related to the 2223 phase increases with respect to the 5.7° peak related to the 2212 phase (Hitoshi *et al* 1988). The presence of both these peaks indicates that multiphase pellets are formed. Thin-film deposits were produced by laser ablation of multiphase superconducting pellets. A deposition rate of 0.19 mm/s has been measured. The thickness of thin films, measured with an α -step profilometer, was typically $1 \mu\text{m}$ after 2 hours of irradiation. The deposited films were annealed in air in the temperature range between 840 and 880°C , for different durations. Analysis of standard pellets and the thin films produced either "as deposited" or after annealing was performed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction. XPS surface analysis of films deposited by a superconducting target confirmed the presence of all the constituent elements. Moreover, the analysis of the Cu_{2p} region of the target and deposited film showed that the copper valence is restored after the annealing treatment in the presence of oxygen (Giardini Guidoni *et al* 1990). Annealing duration and temperature affect the quality of the deposited thin films. In table 1 results obtained on some samples originating from a superconducting BSCCO target in different annealing conditions are reported. Resistance vs temperature characteristics of the samples of table 1 are plotted in figure 4.

It can be seen that a long annealing time (sample a) appears to deteriorate the quality of the film. A higher annealing temperature produces similar behaviour (sample b), as can be observed in the resistance measurements. X-ray diffraction

Table 1. Results obtained on samples under different annealing conditions.

Sample	Deposition (time) (h)	$T_c(\text{K})$	Annealing temperature	Annealing time	Predominant phase
a	1	45	855	12 h	2212
b	3	65	880	12 h	2201
c	3	65	855	6 h	2212
d	2	73	855	2 h	2212

Figure 4. Electrical resistivity vs temperature of four thin films annealed in different conditions as reported in the table 1.

Figure 5. Total external reflection of superconducting and nonsuperconducting films measured by the high-resolution synchrotron radiation powder diffraction station at Adone.

patterns of the samples, not reported here for the sake of brevity, were performed by a Siemens diffractometer D5000 and by a high-resolution powder diffractometer mounted on a beam line of the Adone storage ring (Burattini *et al* 1992).

In these spectra, peaks were observed at $2\Theta = 5.47^\circ$, 29.3° and 35.3° . These peaks are considered to correspond to (001) series of unit cell with its long axis perpendicular to the substrate. The observed peaks are related to the 2:2:1:2 phase ($T_c = 85$ K). However, the spectra indicate that the films are polycrystalline with only a slight preferential *c*-axis orientation of the grains. When the BSCCO thin film was annealed near its melting point, 880°C , the presence of the $2\Theta = 7.2^\circ$ and 21.9° peaks indicated a phase change from 2:2:1:2 to 2:2:0:1. Figure 5 shows the total external reflection of nonsuperconducting and superconducting thin films obtained by synchrotron radiation at the Adone storage ring in the range 0.1° – 1° (2Θ).

These measurements will permit some information to be obtained on the physical properties of the thin films, such as refractive index, density and thickness. In conclusion, the present investigation clearly demonstrates that the plume of evaporated material is mainly formed by atoms, ions and a few oxide clusters. Its composition does not always appear to be representative of target composition; however, the net result of deposition is stoichiometric. To obtain high-quality thin films, not only a suitable target but also a good choice of post-annealing treatment is required.

Acknowledgements

The authors gratefully acknowledge Dr U Gambardella, Dr C Alvani and Dr M Penna for valuable discussions and constructive criticism.

References

- Beech F and Boyd I W 1992 *Photochemical processing of electronic materials* (London: Academic Press) p. 387
- Bednorz J G and Muller K B 1986 *Z. Phys.* **B64** 189
- Burattini E, Simeoni S, Cappuccio G and Maistrelli P 1992 *Rev. Sci. Instrum.* **63** 1002
- Giardini Guidoni A, Desimoni E, Salvi A M, Teghil R, Ambrico M, Morone A, Piccirillo S and Snels M 1990a *Proc. Int. Conf. Lasers* p. 331
- Giardini Guidoni A, Morone A, Snels M, Desimoni E, Salvi A M, Fantoni R, Berden W C M and Giorgi M 1990b *Appl. Surf. Sci.* **46** 321
- Girault C, Damiani D, Aubreton J and Catherinot A 1989 *Appl. Phys. Lett.* **55** 2
- Hitoshi N, Kazuharu S, Yukishige K and Tomoj K 1988 *Jpn. J. Appl. Phys.* **27** 1864
- Maeda H, Tamaka Y, Fukutomi M and Asano T 1988 *Jpn. J. Appl. Phys.* **27** L209
- Mele A, Consalvo D, Stranges D and Giardini-Guidoni A 1990 *Int. J. Mass. Spectrosc. Ion Process.* **95** 359
- Saenger K L 1989 *J. Appl. Phys.* **66** 4435
- Venkatesan T, Wu X D, Inam A and Wachtma J B 1988 *Appl. Phys. Lett.* **52** 2293