Applied Surface Science 69 (1993) 365–369
North-Holland

applied
surface science

Laser deposition of thin films of high T_c superconductors
In situ analysis of the transient species formed in the plume and surface diagnostics of the deposited material

A. Giardini Guidoni, I. Pettiti
Dipartimento di Chimica, Università La Sapienza, P.le A. Moro 5, 00185 Rome, Italy

A. Morone, V. Marotta, M. Snels, G.P. Parisi and G. Bentivenga
Istituto Materiali Speciali, Area della Ricerca di Potenza, CNR, Via S. Loja loc. Zona Industriale, 85050 Tito (PZ), Italy

Received 2 June 1992; accepted for publication 30 October 1992

The present work reports some results on the laser deposition technique of high T_c superconducting films. In situ analysis of transient species formed in the plume and surface diagnostic of the deposited Bi–Sr–Ca–Cu–O (BSCCO) thin films has been performed. It has been ascertained that mixed oxide cluster ions are produced in the plume together with neutral and ionized atoms of constituent material. The effect of annealing parameters on the structure and quality of deposited thin films of BSCCO is reported and discussed.

1. Introduction

In the last few years many research groups applied different techniques (molecular beam epitaxy, sputtering, etc.) for the production of high T_c superconducting thin films with the aim to optimize the deposition processes and the thin film quality [1]. In our laboratory a systematic study of thin film production by laser ablation is in progress [2]. The interaction of intense laser radiation with solid matter causes several processes to occur: energy transfer, evaporation of solid material, generation of a dense plasma, formation of charged and neutral particles. The study of all these phenomena is rather complicated and theoretical models based on local thermodynamic equilibrium and hydrodynamical equations of motion can give only a qualitative explanation of the processes taking place during laser deposition. Measurements of space and time dependent emission spectra of the species present in the plume provide a key to understand the dynamics and reactivity of the ablated materials in gas phase. Evidence of chemical reactions in the plume has been previously ascertained. In particular it has been shown that the addition of copper oxide to second group elements, Ca, Ba, Sr, oxides leads to the formation of mixed ions at the expenses of pure oxide clusters [3]. The aim of this work is to throw some light on the role played by the transient species in the aggregation process and by the annealing parameters on the structure and quality of films.

2. Experimental

The laser ablation of BSCCO superconducting and nonsuperconducting targets has been performed using 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 [2], is equipped with a quartz laser entrance window and with rotatable support for target and substrate holder. The pressure in the

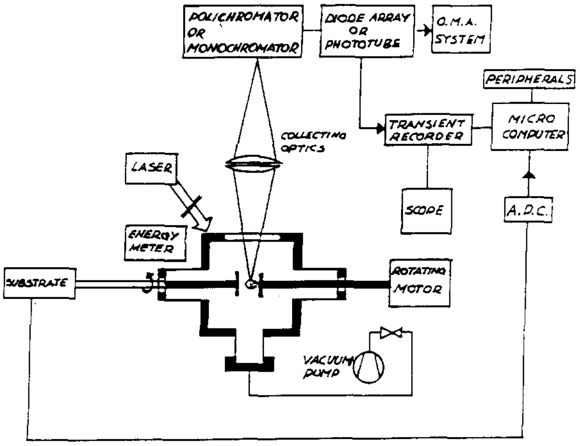

Fig. 1. Scheme of the experimental apparatus for laser ablation and deposition.

chamber is kept at 1.5×10^{-6} mbar during the ablation process. The laser energy is about 2.5–3 J/cm^2, the incidence angle with respect to the target surface is 45° (fig. 1). The ablated material originates a luminous plume which extends about 2 cm from the surface. Time-of-flight mass spectroscopy [3] and luminescence measurements [4] were utilized to obtain information on the intermediate species, neutral and ionized, present in the plume. Emission spectra of the species present have been measured through an optical multichannel analyzer (EG&G OMA 1460) mounted on a small (30 cm) monocromator (Jarrel Ash). The spectral resolution of this detection system is about 0.3 nm, the temporal resolution about 100 ns.

An MgO or $SrTiO_3$ substrate, glued by silver paint to a mechanical support, was positioned in front of the target at a distance of about 2.5 cm and kept at room temperature during the ablation experiment. Thin films of $Bi_2Sr_2CaCu_2O_x$ material were deposited on $SrTiO_3$ (100) or MgO (200) substrates by laser ablation of superconducting target of BSCCO synthesized by calcining mixtures of Bi_2O_3, $CaCO_3$ and CuO at 840°C. Other deposits were produced by laser ablation of stoichiometric 2:2:1:2 nonsuperconducting pellets. A deposition rate of 0.19 nm/s has been measured. The thickness of thin films, measured with an alfa-step profilometer was typically 1 μm after 2 hours of irradiation.

The deposited films were annealed in air in the temperature range between 840 and 880°C, for different duration time. X-ray analysis of the target and deposited films was performed with a Philips diffractometer model PW 1710. Analysis

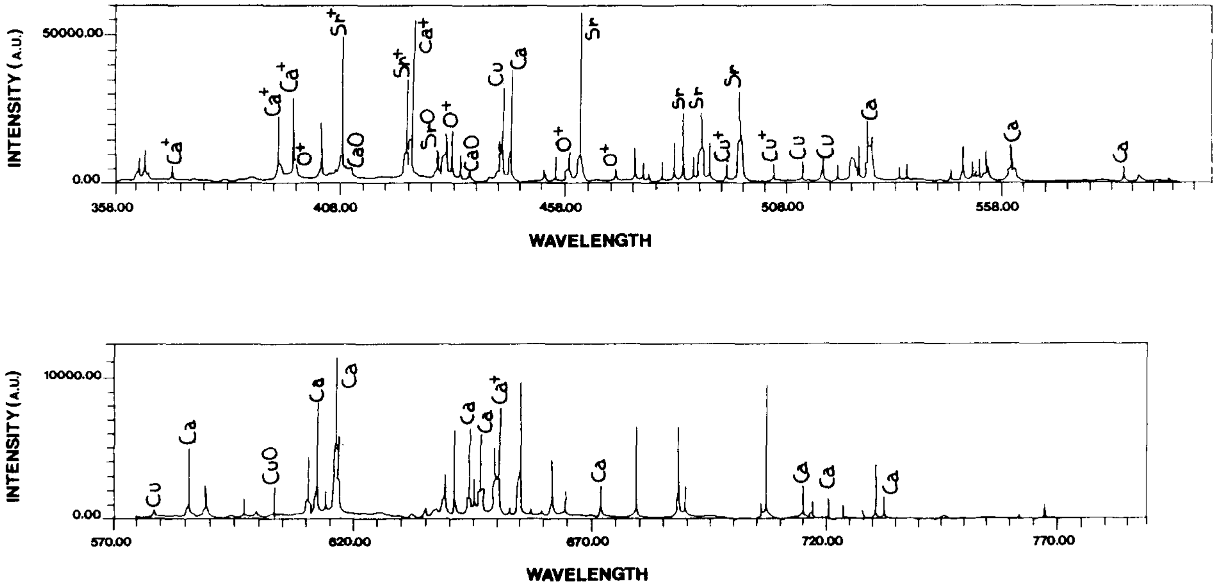

Fig. 2. Optical spectra of laser produced plume from BSCCO target at pressure of 10^{-6} Torr.

of standard pellets and of the produced thin film either "as deposited" and after annealing was performed by SEM and XPS. XPS spectra were collected by an LH XI Leybold spectrometer using unmonochromatized Mg Kα radiation (1253.6 eV). A standard four probe technique was used to measure the resistance of the annealed samples.

3. Results and discussion

Time-of-flight mass analysis of the ionic species produced by laser near the surface (1 mm) in superconducting BSCCO targets have been already reported [4] and the results will be here only summarized. Sr, Bi, Ca, Cu and simple oxide ions predominate in the mass spectrum and masses of simple and mixed positive cluster oxide ions are present. The mass spectra of nonsuperconducting specimens are similar in type of ions and relative intensity. This feature is characteristic also of the other metal oxide mixtures and of oxide mixtures of superconductor precursors [3]. The mass spectrometric plume analysis was performed in the region near to the laser spot on the surface but it cannot be excluded that heavier aggregates are formed at a larger distance from the target. They could eventually reach the substrate and initiate the film growth. The emission spectrum from the laser produced plume in a superconducting target has been already reported [4] and does not essentially differ from that of a superconducting specimen.

The total emission of the plume at the distance of 5 mm from the target is shown in fig. 2. Atom and ion emissions are strongly predominant. Very weak emission features attributable to CuO, CaO and SrO molecules could be present. Time resolved spectra measurements for most of the emission lines show a prompt and delayed emission which have already been attributed to laser and collisional excitation of ablated species, respectively [5]. For example the optical emission as a function of time, of the Sr^{3+} ion ($\lambda = 346.6$ nm) at an observation distance of 5 mm from the target surface, is reported in fig. 3. The delayed emission disappears at 1 μs, is peaked at around

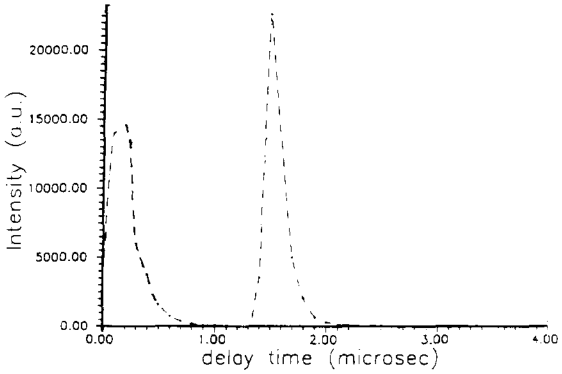

Fig. 3. Time resolved optical emission of Sr^{2+} ions ($\lambda = 346.4$ nm) at 0.5 cm distance from a BSCCO target.

0.2 μs. The low time resolution allowed only an estimation of time-of-flight velocity which is of the order of 10^6 cm/s in qualitative agreement with previous measurements [5]. XPS surface analysis of films obtained from a superconducting target confirmed the presence of all the constituent elements. XPS analysis of the Cu 2p region of the target and deposited film before and after annealing showed that the copper valence is restored after the annealing treatment in the presence of oxygen [6]. Analogous results are obtained also in the case of a nonsuperconducting target. Annealing duration and temperature affect the quality of the deposited thin films. In table 1 the results obtained on some samples originated from a superconducting and nonsuperconducting target in different annealing conditions are reported. The resistivity versus temperature characteristics of the samples A to F of the

Table 1
Results obtained on some examples originated from a superconducting and nonsuperconducting target in different annealing conditions

Sample	Target type	Dep. time (h)	Dep. temperature (K)	Annealing time (h)	T_c (K)	Major phase
A	Superc.	2	855	2	73	2212
B	Superc.	1	855	12	45	2212
C	Superc.	3	840	1	65	2212
D	Superc.	3	855	6	65	2212
E	Superc.	3	880	12	65	2201
F	Nonsuperc.	2	850	4	–	2212

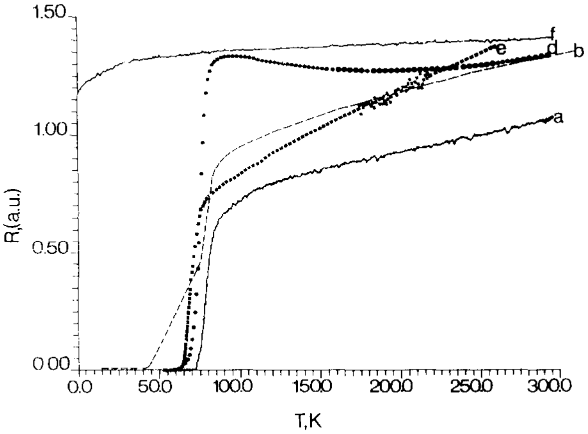

Fig. 4. Thin time $R-T$ curves at different annealing conditions: (a) sample A; (b) sample B; (c) sample D; (e) sample E; (f) sample F.

table 1 are plotted in fig. 4. It can be seen that a long annealing time (sample B) appears to deteriorate the quality of the film.

A higher annealing temperature produces a similar behaviour (sample E) as can be observed in the resistance measurements and in the X-ray diffraction patterns reported in fig. 5. The diffraction patterns of sample A and D show a series of strong peaks at $2\theta = 5.47°$, 29.3° and 35.3°. These peaks are considered to correspond to (001) series of a 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 show that the film is polycrystalline with only a slight preferential c-axis orientation of the grains. When the BSCCO thin film was annealed near the melting point at 880°C the presence of the $2\theta = 7.2°$ and 21.9° peaks indicates a phase change from 2:2:1:2 to 2:2:0:1. A similar behaviour was previously discussed [7]. The attempt to obtain high T_c superconducting film from a nonsuperconducting target of 2:2:1:2 phase gave poor results probably due to the not-optimized heating conditions.

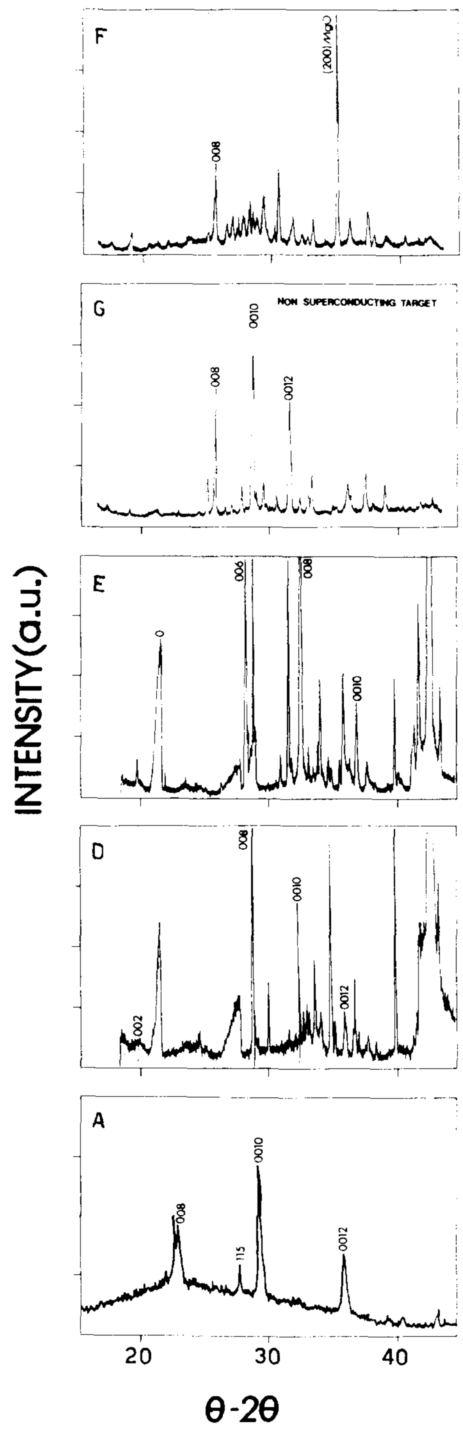

Fig. 5. X-ray diffraction patterns for BSCCO thin film and target at different annealing conditions: (A) sample A; (D) sample D; (E) sample E; (G) nonsuperconducting target; (F) sample F.

In conclusion the present investigation clearly demonstrates that the plume of evaporated material is mainly formed by atoms, ions and few oxide clusters. Its composition appears to be not always representative of the composition of the target, 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 needed.

References

[1] D. Bäuerle, Laser processing and diagnostic (Springer, Berlin, 1984) p. 166.

[2] L. Correra, Ed., High temperature superconductor thin film (Elsevier, Amsterdam, 1991) p. 451.

[3] A. Mele, A. Giardini Guidoni, D. Consalvo, D. Stranges and R. Teghil, Int. J. Mass Spectrom. Ion Processes 91 (1989) 319.

[4] A. Giardini Guidoni, E. Desimoni, A.M. Salvi, R. Teghil, M. Ambrico, S. Piccirillo and M. Snels, Proc. Int. Conf. Laser 90, San Diego (1990) p. 331.

[5] K.L. Saenger, J. Appl. Phys. 66 (1989) 4435;
C. Girault, D. Damiani, J. Aubreton and A. Catherinot, Appl. Phys. Lett. 55 (1989) 2;
H. Fucumera, H. Nakaminami, S. Eura and H. Masuhara, Appl. Phys. Lett. 58 (1991) 22;
J.P. Zheng, Z.Q. Huang, D.T. Shaw and H.S. Kwak, Appl. Phys. Lett. 54 (1989) 3.

[6] A. Giardini Guidoni, A. Morone, M. Snels, E. Desimoni, A.M. Salvi, R. Fantoni, W.C.M. Berden and M. Giorgi, Appl. Surf. Sci. 46 (1990) 321.

[7] M. Knai, T. Kawai, M. Kawai and C. Kawai, Jpn. Appl. Phys. 27 (1988) L1293.