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Study of laser ablation of BiSrCaCuO

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The formation of BiSrCaCuO thin films by the laser ablation method using a frequency doubled Nd:YAG laser has been investigated. The deposition rate, the angular distribution of the film thickness and of the various constituents, and the surface morphology of the films have been studied by the complementary use of Rutherford backscattering spectrometry, nuclear reaction analysis and scanning electron microscopy. Besides the laser beam parameters, the target density and texture, the oxygen pressure in the evaporation chamber and the substrate temperature were found to widely influence the properties of the deposited films. So, the use of high-density targets yields higher deposition rates and film composition closer to target composition. Substrate temperature and oxygen pressure drastically determine the relative concentrations of the heavier-atomic-mass elements in the films.

1. Introduction

Since the discovery of superconductivity in several copper oxide systems, the pulsed laser ablation method has been widely used to produce thin superconducting BiSrCaCuO films [1]. In this technique, a great number of parameters are expected to influence the film growth. It is therefore important to know what effects the change of these parameters will have, in order to better understand the deposition mechanisms and in turn, to improve the quality of the films. The deposition of thin films by means of this technique can be seen in a simple way as a two-step process: the ablation of the target and the subsequent growth of the film by the material ejected from the target. The influence of the various deposition parameters on each step is not the same. Some of them directly control the ablation process, i.e. the nature of the process. These parameters are related to the laser beam (photon wavelength, laser power density, pulse duration and repetition rate) and also to the target (composition, density and texture). Others determine the growth of the film such as substrate temperature, which determines the surface mobility and sticking coefficient of the ablated species, and the oxygen pressure which determines the composition of the films via some chemical effects.

The effects of the laser beam parameters on the ablation process have recently been discussed [2]. So, we have focused our attention on the other parameters. The dependence of deposition rate, angular distribution of thickness and elemental composition and surface morphology on target density and texture, oxygen pressure and substrate temperature have been investigated.

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2. Experimental

Bulk samples of BiSrCaCu oxides of varying composition and various densities and textures were used as targets for these experiments. These targets were usually mounted on a rotating holder in a chamber evacuated to 10^{-6} mbar, and into which oxygen or argon can be admitted up to controlled pressures. The targets were irradiated under 45° of incidence with a pulsed Nd:YAG laser. The power density was about 200 MW/cm^2. The fundamental laser frequency can be doubled by means of a KDP crystal, and all the irradiations were carried out at 532 nm photon wavelength. The pulse repetition rate was 5 Hz, the substrate–target distance ranging between 2 and 5 cm. The films were grown onto Si or MgO ⟨100⟩ single crystals.

The thickness and the elemental composition of the different elements have been analyzed by the complementary use of Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA). The RUMP simulation program [3] was used to determine the precise depth distributions. The target surface morphology has been studied by scanning electron microscopy (SEM).

3. Results

3.1. Effect of target density and texture

The target nature is expected to be one of the most important parameters among those controlling the first step of the ablation process. Not only the composition but also the density and texture can play an important role in the laser ablation mechanisms, and their effects have to be studied in order to understand and optimize the film growth. Targets of identical composition ($Bi_2Sr_2Ca_1Cu_2$), but with different density and texture have been used for these experiments.

The laser evaporation process is characterized

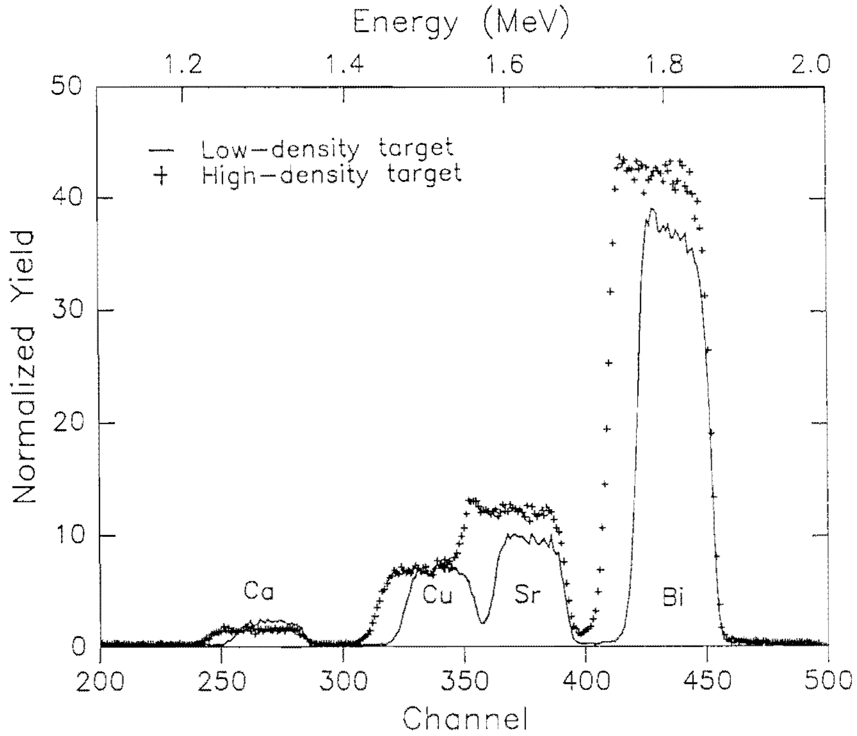

Fig. 1. RBS spectra (2 MeV, $\theta = 165°$, normal incidence) of two samples of BiSrCaCuO deposited under the same experimental conditions using targets of different density and texture but with identical composition ($Bi_2Sr_2Ca_1Cu_2$).

by its very forward-directed nature, i.e. a substantial amount of the evaporated material is deposited in the direction perpendicular to the irradiated area of the target [4]. Fig. 1 shows the RBS spectra recorded in this region for two films deposited under the same experimental conditions using a low density target and a high density target. These spectra evidence large differences between the deposition rates of the films. Both are grown during the same deposition time ($t = 4$ min) however, the higher the target density, the thicker the film, the difference in thickness of each film being about 30%. This result was also observed with the fundamental frequency of the laser, the effect being higher. In the same way, both films are obtained from targets of identical composition, but these RBS spectra show that the elemental composition also differs from one case to the other. Moreover, whatever the target density, the composition in the film differs from that of the target. They always show a Cu enrichment and a Bi depletion with respect to the initial target composition, while the relative concentrations of Ca and Sr seem to depend upon the target: $Bi_2Sr_{2.4}Ca_{1.9}Cu_3$ for the low density target and $Bi_2Sr_{2.5}Ca_{1.1}Cu_{2.5}$ for the high density one. It can be evidenced in a more explicit way looking at the normalized ($C_{Bi} + C_{Sr} + C_{Ca} + C_{Cu} = 1$) cationic concentrations. So, if we compare the normalized concentrations of the films deposited from low and high-density target ($Bi_{0.22}Sr_{0.26}Ca_{0.20}Cu_{0.32}$ and $Bi_{0.24}Sr_{0.31}Ca_{0.13}Cu_{0.31}$, respectively) with the normalized concentration of a $Bi_2Sr_2Ca_1Cu_2$ target ($Bi_{0.28}Sr_{0.28}Ca_{0.14}Cu_{0.28}$) it is clear that there are Bi depletion and Cu enrichment in both cases.

The differences induced by the target properties also appear in the angular distribution of thickness and elemental composition. An elliptical laser spot is formed on the target due to the angular incidence of the incident beam. The evaporated material also forms an elliptical shape, with its center located on the normal to the irradiated target spot. The major axis of the deposited area is found to be perpendicular to the major axis of the irradiated area. Rutherford backscattering spectrometry was used to analyze the spatial distribution of the film thickness and the elemental composition along the minor axis of the elliptical deposit. Whatever the target density, the thickness shows a peaked distribution as a function of the angle (θ) subtended by the radial vector and the normal to the target at the beam impact point. The maximum of the thick-

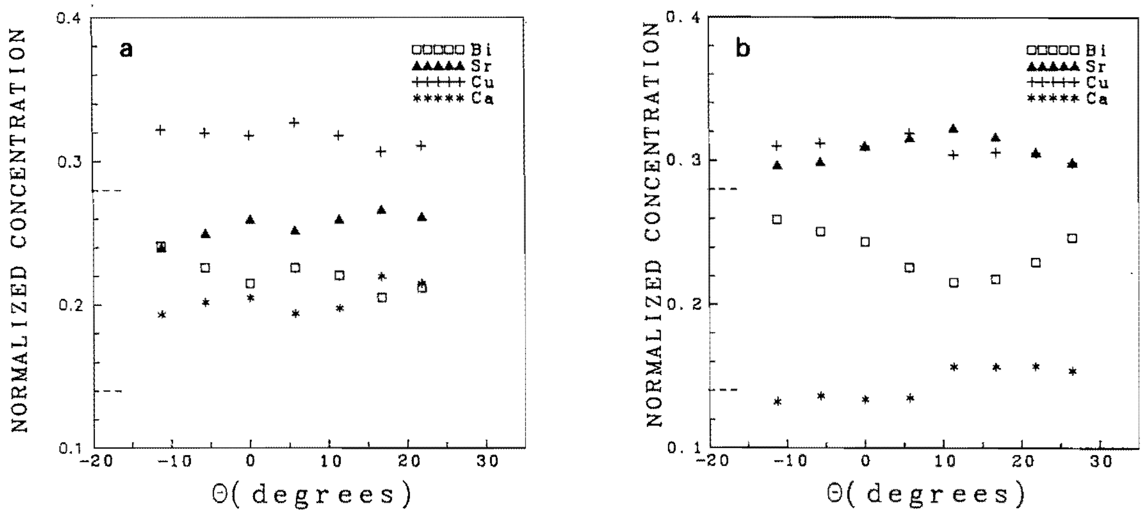

Fig. 2. Normalized concentration of cations as a function of θ for two samples deposited after irradiation of low-density (a) and high-density (b) targets. The horizontal dashed lines show the overall concentration of the elements in the targets.

ness distribution is always centered at $\theta = 0$ and the increase in the target density yields slightly broader distributions.

Figs. 2a and 2b show the normalized concentration of the cations in the films as a function of θ. Films deposited with the low density target present a deficiency of the higher atomic mass species (Bi and Sr), and are enriched in the lower atomic mass cations (Cu and Ca). The increase in the target density yields films with compositions closer to the target composition as it can be observed in fig. 2b. However, there is always a deficiency in the Bi content in the films. Despite this different behaviour, it can be noticed that the relative amounts of the heavier elements (Bi and Sr) are strongly correlated. In fact, whatever the target density, the higher the Bi concentration, the lower the Sr concentration. In the same experimental conditions the oxygen concentration in the film exhibits a behaviour comparable to that of the Sr. This seems to indicate that the variations in concentrations are related to differences in the fixation rate of Bi and Sr in a mixed oxide.

We have also investigated the influence of target irradiation on the resulting target surface morphology and evaporation process. The evolution of the deposition rate as a function of the target irradiation is characterized by a continuous decrease with increasing number of pulses, the deposition rate for laser ablation of the high-density target being greater. Moreover, the thickness distribution always presents a peaked shape form that becomes broader when the number of pulses increases. It can also be observed that the position of the maximum in the distribution of the thickness varies with the number of pulses (fig. 3). The angle (θ_{max}) at which this maximum appears is shifted towards the direction of incidence of the laser beam. This shift occurs in different ways

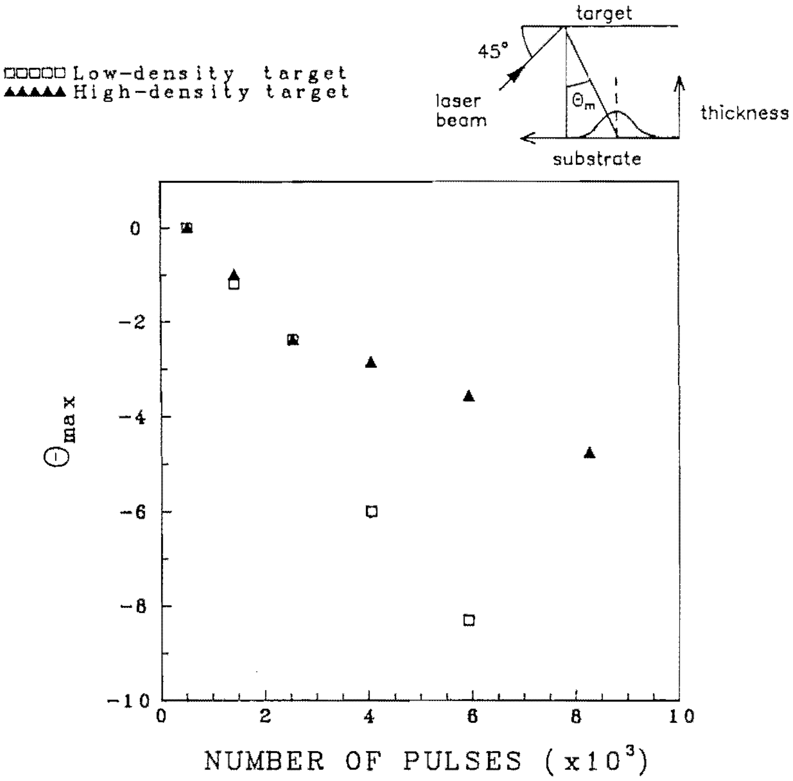

Fig. 3. Evolution of the maximum of the thickness distribution as a function of the target irradiation. Targets of the same composition but of different density and texture are used for these experiments.

depending upon the target nature. Although during the earlier moments of target irradiation θ_{max} is approximately the same for both targets, when the targets are sufficiently irradiated (about 3000 pulses), differences are evidenced in the evolution of θ_{max}. The higher the target density, the slower the shift of the thickness maximum to the direction of the laser beam.

All these modifications induced in the evaporation process are certainly related to surface target modification. After low exposure levels (500 pulses) both targets share similar surface modifications. The irradiated surface shows a quite uniformly eroded region that is populated by closely packed columnar structures of about 15 μm diameter; the column axes are aligned with the laser beam at 45° to the surface normal. These structures have been also observed during the laser ablation of other superconducting materials [5] and they thus seem to be characteristic of the resolidification process which follows surface melting and the ejection of material from the target. Continuous laser irradiation produces different modifications of the surface target morphology depending on target density and texture. After irradiation by 5000 pulses the low density target is more eroded than the high density one. In both cases we still found the columnar structure but the depth of the voids between columns has increased in the case of the low density target. The different erosion rates of the target surface could explain the evolution of θ_{max} with the number of pulses.

3.2. Oxygen pressure and substrate temperature

Once the material is ejected from the target surface, it forms a plasma which expands towards the substrate. The interactions of the ejected material with the molecules that it can meet in the target substrate path are quite important. The number and nature of these molecules can largely determine the energy and the chemical state of the species that arrive at the substrate surface. At this point the substrate temperature will determine the sticking of each one of them. So the oxygen partial pressure and the substrate temperature will be the determining parameters in the deposition process. We have analyzed the deposition rate and the spatial distribution of the elements in oxygen environments in the $10^{-2}-1$ mbar pressure range. The same experiments have also been carried out using an argon environment.

The presence of oxygen during the deposition usually produces more uniform spatial distributions of thickness and elemental composition. The broadening of the distribution is related to the scattering of the species induced by an increase in the number of atomic collisions. The augmentation of the spatial uniformity with pressure is also accompanied by a decrease of the deposition rate. This has been observed whatever the nature of the gas introduced into the chamber (argon or oxygen). However, the presence of oxygen yields a considerable increase in the incorporation rate of the oxygen atoms: the oxygen incorporation rate at 0.3 mbar oxygen pressure is about 1.6 times greater than in argon atmospheres at the same pressure.

The cationic composition of the films also depends on the oxygen pressure in a drastic way. As a matter of fact, fig. 4 shows the normalized concentration of the different cations in the film as a function of the oxygen pressure. The Bi concentration presents a typical behaviour of this

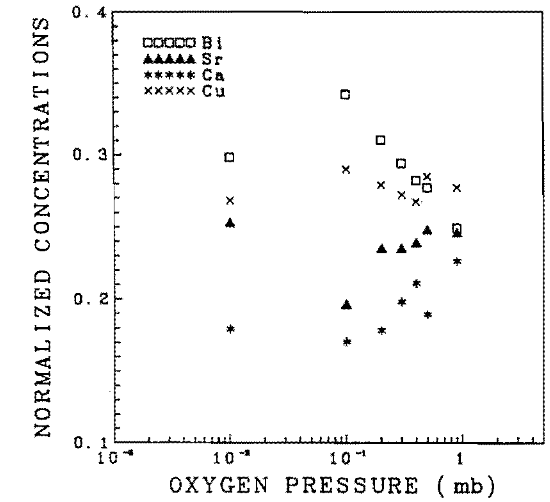

Fig. 4. Normalized cationic composition of BiSrCaCuO thin films as a function of the oxygen pressure during the deposition.

Table 1
Influence of substrate temperature and oxygen pressure on the cationic elemental composition of laser ablated BiSrCaCuO thin films

	Elemental composition	
	Vacuum	Oxygen (0.1 mbar)
Ambient temperature	$Bi_{0.23}Sr_{0.23}Ca_{0.22}Cu_{0.31}$	$Bi_{0.35}Sr_{0.20}Ca_{0.16}Cu_{0.28}$
700 ° C	$Bi_{0.06}Sr_{0.32}Ca_{0.28}Cu_{0.33}$	$Bi_{0.29}Sr_{0.24}Ca_{0.16}Cu_{0.30}$

dependence. The Bi content of the films increases with oxygen pressure until 0.1 mbar; this increase is followed by a rapid decrease for higher pressures. Once again, we can notice that the Sr and Bi variations are correlated and varied in exactly opposite directions. These observations mean that with the same target composition, a wide range of film composition could be obtained. As a result, this will lead to severe complications for the formation of superconducting films since an exact composition is one of the major requirements for the growth of a superconducting phase, especially for in situ growth. In fact, the large differences in fixation rate of the Bi and Sr species with only a slight change in oxygen pressure can be the origin of the formation of an undesirable semiconducting or insulating phase in the films.

The substrate temperature also plays a major role in the composition of the deposited films. Table 1 shows the relative compositions of the cations for films deposited onto MgO substrates heated at about 700°C under vacuum and in oxygen atmosphere (0.1 mbar). The compositions of films grown under the same experimental conditions at ambient temperature are also shown. A quite relevant point is to be noted if we compare the compositions of films deposited under vacuum. Heating of the substrate during the laser deposition process produces films largely deficient in Bi content with respect to the films deposited at ambient temperature. This result does not seem to be an intrinsic property of the laser ablation, since similar phenomena are observed during sputtering or molecular beam epitaxy. But in our case, the diminution of the Bi content is accompanied by the augmentation of the Sr content while the concentrations of the lower atomic mass cations (Cu and Ca) are hardly changed. This great deficiency in Bi can however be minimized if, keeping the substrate at 700°C, the depositions are carried out in oxygen atmosphere. Anyway, the fact of heating the substrate seems to produce a diminution of the Bi concentration of the films both in the presence and in the absence of oxygen environments.

4. Summary

We have investigated the influence of the target density and texture, the oxygen pressure and the substrate temperature in the laser ablation of BiSrCaCuO thin films. The use of high-density targets yields higher deposition rates and film compositions closer to the target composition. The oxygen pressure mainly determines the relative quantities of heavier atomic mass elements. The substrate temperature drastically controls the Bi content of the films. Heating of the substrate produces a decrease of the Bi concentration both under vacuum and in oxygen atmospheres. Contrarily to previous reports which state the importance of laser parameters, these results show that other parameters largely determine the composition and nature of the deposited films, and in turn their quality as superconducting materials. It has been thought that use of the shortest wavelengths possible leads to film compositions closer to the target composition. In fact, besides the pure mechanical effects related to the laser ablation of the target material, chemical effects also play a determining role, since the incorporation of Bi or Sr in the films certainly occurs via oxidized species.

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