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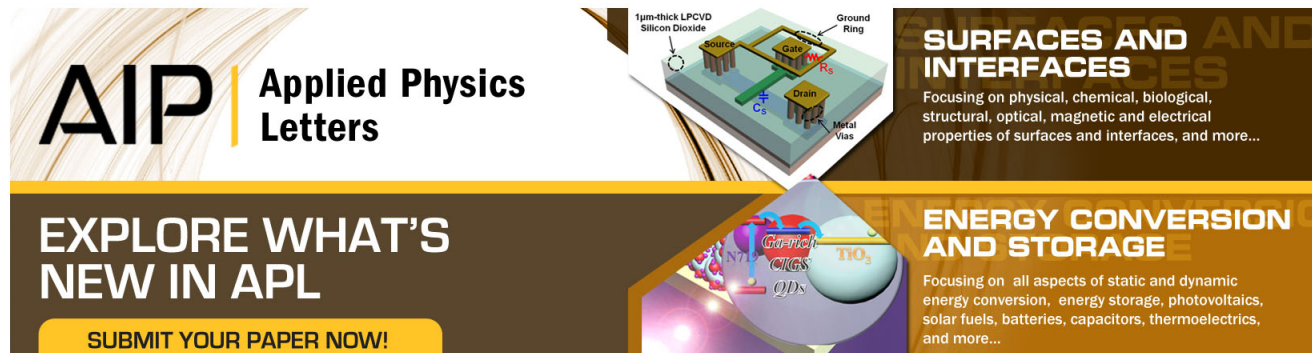
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The role of film re-emission and gas scattering processes on the stoichiometry of laser deposited films

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Laser ablation of a BiSrCaCuO target is performed both in vacuum and in an oxygen pressure of 0.1 mbar. Two substrates are located in the chamber in order to study the role of re-emission processes from the growing film and/or the scattering of the ablated species by an oxygen atmosphere. The results indicate that re-emission processes from the growing film are very weak (they may affect up to 1% of the deposited material at most) and are not related to the re-sputtering of the growing film. Films grown in vacuum are found to have the correct cation composition, whereas those grown in an oxygen environment show significant variations which are clearly related to gas scattering processes. © 1995 American Institute of Physics.

Laser ablation has become a widely used technique to grow high quality thin films of a great variety of materials, most of them being complex oxides.^{1,2,3} The technique has been successfully applied to grow high T_c superconducting films and it has been shown that the quality of the films and the deposition process are very sensitive to the experimental conditions. Thus, good quality films are only obtained in a limited range of laser fluence, gas pressure and substrate temperature.^{4,5,6,7,8}

The interaction processes in the gas phase have been widely studied in order to determine their influence on the composition and structure of the films.^{7,8,9} The study of the interactions at the substrate have received much less attention, although it has been shown in the case of PZT films that they may affect the film composition.⁴ Several mechanisms have been proposed to explain the lack of stoichiometry. The existence of preferential evaporation of the most volatile component from the substrate, or the scattering of species by the substrate due to a sticking coefficient below unity are usually proposed.^{4,6,10} Moreover, it is well known that highly energetic species are produced during ablation, with ions being the most energetic ones.^{11,12} Therefore, ion bombardment of the film during growth can be a third mechanism responsible for compositional changes, due to preferential sputtering of some of the components.^{4,13,14} These three mechanisms related to emission or scattering of species which arrive at the substrate will be referred to hereafter as re-emission processes.

The aim of this letter is to examine the role of re-emission processes in the composition of films grown by laser ablation. Films grown on substrates located at two sites shown in Fig. 1 were studied: substrate S1 is located along the target normal and facing it, and substrate S2 is located shifted upwards and non-facing the target. In this geometrical configuration, substrate S2 faces substrate S1 and therefore it can receive the re-emitted material from the film growing on substrate S1. The experiments are performed with a high- T_c superconducting target. It has been reported

that an oxygen pressure is required to grow good quality films,⁵⁻⁷ therefore the present experiments are performed in an oxygen environment. In the presence of a background gas, the scattering of the ablated species by the gas prior to deposition is another mechanism that can account for compositional changes in the films.^{7,8,9,15} Therefore we will study the films grown onto substrate S2 under two configurations. In the first configuration, substrate S1 is removed and only substrate S2 is present. The material deposited onto substrate S2 can only come from the scattering of the ablated species by the background gas species. This configuration will be referred to hereafter as S2 in the gas scattering configuration (S2GS). In the second configuration, both S1 and S2 sub-

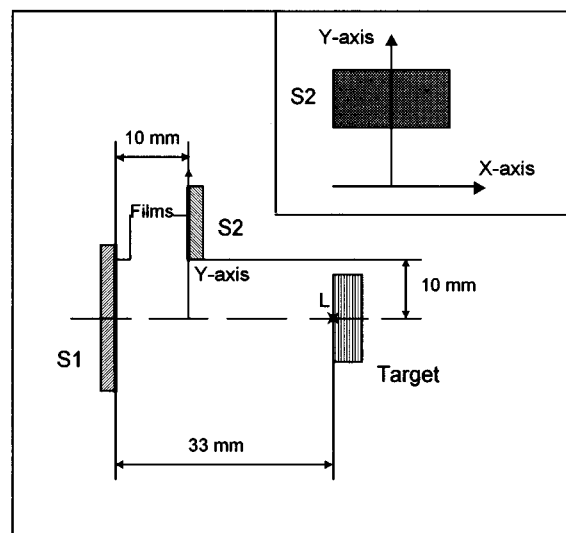


FIG. 1. Target-substrates configuration plotted in a plane perpendicular to the laser incidence plane. S1 faces the target, S2 opposes the target and L is the impact point of the laser beam on the target surface. The inset shows the X and Y axes along which the composition of films deposited on substrate S2 is studied, X and Y being perpendicular and parallel to the plane of the figure, respectively. The plane of incidence is perpendicular to plane of figure and includes the point L.

TABLE I. Total amount of cations ($\times 10^{15}$ atoms/cm²) deposited onto substrates S1 and S2 in the two studied configurations (S2RE, S2GS) both in vacuum and in an oxygen pressure of 0.1 mbar. The values at the maximum of the distribution (maximum thickness) for substrate S1 and the maximum variation along the X and Y axes for substrate S2 are included.

Environment	S1	S2 in S2RE	S2 in S2GS
Vacuum	1400	15	0.5
0.1 mbar O ₂	370	50–150	120–200

strates are present, and it will be referred to hereafter as S2 in the re-emission configuration (S2RE).

The experimental set-up is based in an ArF excimer laser ($\lambda = 193$ nm, $\tau = 12$ ns FWHM) working at a repetition rate of 6 Hz. The laser beam is focused onto a sintered Bi₂Sr₂Ca₁Cu₂O₈ target with an energy density of 2.4 J/cm². The laser incidence plane is perpendicular to the plane of Fig. 1, it includes the laser impact point on the target surface (L) and contains the X axis showed in Fig. 1. Films are grown at room temperature on Si wafers either in vacuum (4×10^{-8} mbar) or in an oxygen pressure of 0.1 mbar, the deposition time being 1400 s in all cases. Nuclear microanalysis, by the direct observation of the backscattered particles, is used to study the composition of the deposited films. The cation content is obtained by Rutherford backscattering spectrometry, using a ⁴He⁺ beam at 2.0 MeV. The backscattered particles are detected at 165° and the RUMP simulation program is used to determine the relative concentrations.¹⁶ The amount of cations is determined at the maximum of the distribution on substrate S1 (maximum thickness), while in the case of S2 it was determined along the two axes (X and Y) shown in Fig. 1, that are parallel and perpendicular to the laser incidence plane.

Table I shows the total amount of cations deposited on the different substrates in the two configurations and environments studied. The interval corresponds to the maximum variation along the two perpendicular axes considered in substrate S2 (X and Y axes shown in Fig. 1). The amount of material deposited onto S2 is small and close to the experimental detection limits when the deposition is carried out in vacuum and S1 is not present (S2GS). When the substrate S1 is present (S2RE), the amount of deposited material is slightly larger, but is still two orders of magnitude lower than the amount of material deposited on substrate S1. In both cases, no significant variations along the X and Y axes are observed. The presence of the oxygen gas produces a dramatic increase in the amount of deposited cations on substrate S2, the amount is now of the same order of magnitude than those of the film on substrate S1. In addition this amount is higher when only substrate S2 is present than when both S1 and S2 are present. This result may be related to the fact that when S1 is present, it acts as a collector of the ejected species from the target, thus decreasing the amount of species in the plume and therefore decreasing the probability of deposition on S2 when both substrates are present. These results allow us to conclude that the process that leads to film growth on substrate S2 is more important in the presence of an oxygen environment and is nearly independent of the presence of a growing film on substrate S1.

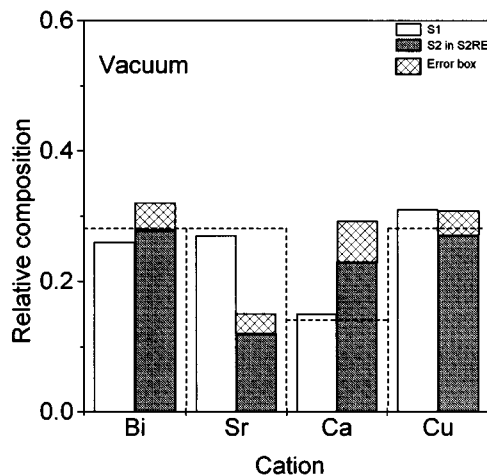


FIG. 2. Relative cation composition (N_x/N_{tot}) of films grown in vacuum on substrate S1 and S2 in the S2RE configuration. The dashed line indicates the composition of the target and the error boxes show the relative composition variation of films on S2 along X and Y axes.

Figure 2 shows the relative composition of cations (N_x/N_{cat}) in the films grown simultaneously in vacuum on substrates S1 and S2 (S2RE). N_x represents the number of $x = \text{Bi, Sr, Ca or Cu}$ atoms and $N_{cat} = N_{\text{Bi}} + N_{\text{Sr}} + N_{\text{Ca}} + N_{\text{Cu}}$ is the total number of cations. For films on substrate S2, the results depend mainly on the position along Y axis and the values are within the interval shown in the figure as an error box. The results show that films grown in vacuum on substrate S1 present a composition very close to that of the target, while the film grown on substrate S2 is clearly deficient in Sr and rich in Ca.

Under vacuum conditions, the only possible mechanisms leading to the growth of a film on substrate S2 are any of the processes previously discussed as re-emission processes, which is consistent with the fact that there was not significant deposition on substrate S2 in the S2GS configuration. Earlier optical studies of the plasma dynamics have shown that the kinetic energy of Ca, Cu, Sr and Ca⁺ species was lower than 50 eV, whereas that of Bi and that of Sr⁺ were close to 100 and 175 eV, respectively.¹² Therefore the most energetic species (Sr⁺ and Bi) arriving at the substrate may produce the sputtering of the species previously deposited. The sputtering yield of the different cations (Bi, Sr, Ca and Cu) under bombardment of Sr⁺ and Bi have been calculated using the equations published elsewhere¹⁷ and following the procedure described by van de Riet.¹³ The results indicate that the re-sputtering probabilities of Bi and Sr are similar and are 2 and 4 times higher than those of Ca and Cu. Since we observe a very low (high) Sr (Ca) content in S2 films, these results suggest that re-sputtering cannot account for the measured composition of films deposited on S2 (S2RE) in vacuum. Therefore, other processes as preferential evaporation of the most volatile component or substrate scattering, should be the most likely mechanism responsible for the deposition observed on substrate S2 in vacuum.

When an oxygen environment is present, the composition of the films changes also dramatically as seen in Fig. 3. The film on substrate S1 becomes richer in Bi, and poorer in the other cations with respect to the target. The film grown

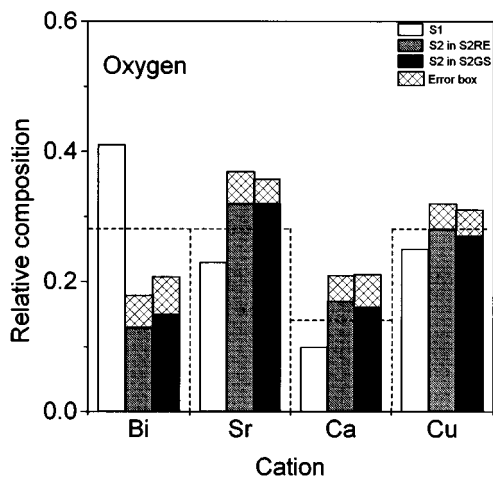


FIG. 3. Relative cation composition (N_x/N_{tot}) of films grown in oxygen on substrate S1 and S2 in the S2RE and S2GS configurations. The dashed line indicates the composition of the target and the error boxes show the relative composition variation of films on S2 along X and Y axes.

on substrate S2 presents the complementary behavior in both configurations (with and without a film growing on substrate S1). These results further support the conclusion that the presence of an oxygen pressure is responsible of the changes in the cation stoichiometry of the growing film. Since the re-emission mechanisms may affect up to 1% of the deposited material, as deduced from the experimental results obtained in vacuum, the interaction processes between the ablated species and the background gas molecules, prior to the film deposition, have to be responsible of this lack of stoichiometry. It is well known that the kinetic energy of the ablated species decrease significantly in the presence of a background gas at pressures above 0.1 mbar.^{12,18} In addition, the species with masses similar to those of the foreign gas atoms/molecules have a much higher probability to suffer significant deviations from their original trajectory than the heavy species.^{7,8,9,15} In our case, the atomic masses are $m_{Bi}=209$, $m_{Sr}=88$, $m_{Cu}=64$, $m_{Ca}=40$, $m_O=32$ and the cross sections of the different atoms in oxygen have been estimated to be in the ratio $\sigma_{Sr}=\sigma_{Ca}=1.3\sigma_{Bi}=1.6\sigma_{Cu}$.¹⁹ These figures suggest that the scattering of Bi species by the oxygen atoms / molecules is much less than that of the other cations as it has been found experimentally.⁹ Bismuth species travel with the lowest angular dispersion, and therefore most of them are deposited on the substrate S1. The other species are expected to have the opposite behavior and the scattering effects should be particularly important for Sr and Ca species; thus, their relative concentration should be higher on S2 films. Finally, although Cu has a small cross section ($0.8\sigma_{Bi}$), its mass is three times lower than that of the Bi and

therefore the effect of the gas scattering should be closer to that of the lighter species. This reasoning, that does not depend on the presence of the substrate S1, is in very good agreement with the results presented in Fig. 3. It can be then concluded that the deviation of cation stoichiometry in films grown by laser ablation in an oxygen pressure is mainly due to the scattering of the ablated species by the foreign oxygen species, this scattering being more important for the lighter species.

In summary, we have shown that the dominant stoichiometry altering mechanism when films are grown in an oxygen pressure is the scattering of the ablated species by the foreign oxygen species and not the re-emission from the growing film. Whereas films grown in vacuum have the stoichiometry of the target, those grown in oxygen have an enriched relative composition of the heaviest element (Bismuth).

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