DYNAMICS OF IONIC ENHANCEMENT IN THE PLASMA-ASSISTED LASER DEPOSITION OF HIGH T_c SUPERCONDUCTORS

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ABSTRACT

The presence of an oxygen discharge during the laser ablation-deposition of superconducting films has been shown to facilitate low temperature growth. It has been speculated that the increased surface activation via ionic collisions and enhanced oxidation of the film in an oxygen plasma enabled the growth of the superconducting phase at a lower substrate temperature[1]. To understand the effect of the oxygen discharge on the film growth, we have investigated the ionic content of the laser plume as it propagates in the oxygen discharge by utilizing an ion probe technique. The time resolved and integrated ion signals clearly reveal the ionic enhancement of the plume in presence of the oxygen discharge. The role of the background gas and level of excitation in the pulsed discharge on the ionic content of the plume is systematically analyzed.

INTRODUCTION

Laser ablation of a composite target of $YBa_2Cu_3O_{7-\delta}$ (YBCO) in an oxygen back ground is a well developed technique for the growth of in-situ superconducting films. Several deposition parameters such as the laser fluence, ambient oxygen pressure, substrate temperature and substrate to target distance have been shown to determine the quality of the films grown on a given substrate[2]. Substrate temperatures from 400°-720°C and oxygen pressures from 20-200 mT [1-5] have been used in various studies for the growth of high T_c films.

A high adatom mobility for the material impinging on the substrate enhances the crystallinity of the film, which along with sufficient incorporation of oxygen into the growing structure leads to the formation of the superconducting phase. A high substrate temperature enhances both the adatom mobility and the oxidation of the growing film. The role of the background oxygen is more complicated, as increased oxygen clearly enhances its incorporation into the film but has the undesirable consequence of collisionally lowering the effective adatom mobility of the plume species when they impinge on the substrate. An alternative may be the use of high substrate temperatures to compensate for the lower mobility while allowing the use of high oxygen pressure during the growth. However, low temperature growth techniques may be imperative in processes where interfacial diffusion at the film-substrate or heterojunction interface are required to be minimal.

The growth of in-situ high T_c superconducting films below a substrate temperature of 500°C has been reported using the plasma assisted laser deposition technique, where laser ablation-deposition is carried out in the presence of an oxygen plasma[1]. This technique offers several useful advantages towards superconducting film growth for device applications. In addition to the low growth temperature, lower background pressures are achievable without affecting the oxygen incorporation, thereby allowing the target-substrate distance to be increased without a significant reduction in the kinetic energy of the species. Since the target stoichiometry is preserved only within a cone angle of 20° in the forward-directed laser plume[6], an increase in target-substrate distance increases the area of uniform film deposition.

Spectroscopic techniques have been successfully utilized to observe the luminous species in the plume, which include ions, excited atoms and molecules[7-10]. Since the presence of the plasma affects the film growth by increasing the ion density arriving at the substrate, our study exclusively investigates the ionic content of the plume. To understand the role of the oxygen plasma in thin film deposition, we have carried out ion probe measurements under various deposition conditions. The results of this systematic study which elucidate the plasma assisted laser deposition process will be discussed in this presentation.

EXPERIMENTAL PROCEDURE

A schematic representation of the experimental system is shown in Figure 1. The main components include a rotating YBCO target, an excimer laser delivering ablating pulses 15 ns in duration and with a fluence of $2J/cm^2$ at the target, a positively biased ring electrode, a grounded circular shield and the ion probe. We have explored several different probe configurations, including dual electrodes for charge separation, and found the relative trends in the measured ion signals to be independent of the probe configuration. The 2mm diameter single shielded probe used in our experiment detected only the ions when biased at -100 V. Further increase in the probe bias did not cause a significant change in the ion signal. The probe shield minimized any plume perturbations due to the probe bias voltage. As the positive bias

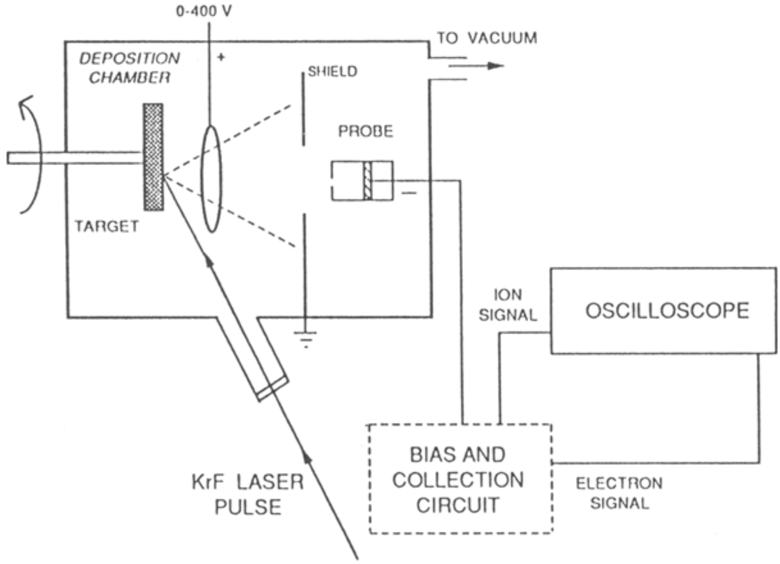


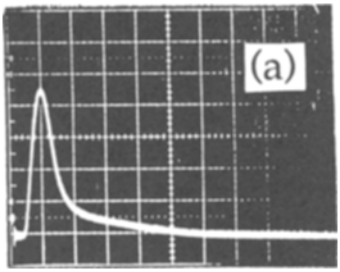
FIG. 1. Schematic diagram of the ion probe and the plasma assisted laser deposition system.

for the ring electrode is turned on, most of the electrons in the plume are removed by the ring, and even at a lower probe bias (-50V) the probe signal corresponds only to the ions. A recent report of the substrate current produced by the net charge incident on the substrate, clearly shows the transformation of an initially neutral plume to an ionic plume as the ring voltage is turned on[11]. The grounded shield has a 2.5 cm diameter hole concentric with the axis passing through the center of the ring electrode and the point of incidence of the laser pulse on the target. The function of this shield is to eliminate space charge effects and also to act as the terminating electrode for the discharge. This aids the production of a uniform, reproducible gas discharge during each laser pulse. In the absence of the grounded shield the ion probe signal is observed to be extremely noisy and non-reproducible.

RESULTS

Laser-Ablated Plume Dynamics

The superconducting properties of the high T_c films grown by laser ablation are largely dependent on the substrate temperature and the ambient oxygen pressure. A substrate temperature of ~ 500°C and an oxygen pressure of 20 mT is sufficient to form the superconducting phase



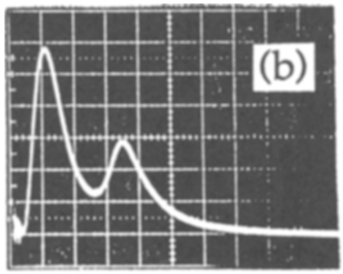
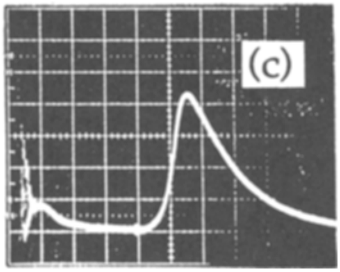


FIG. 2 Time-resolved ion signals due to the laser ablated YBCO plume measured 6.25 cm from the target at background oxygen pressures of (a) 20 mT, (b) 40 mT and (c) 100 mT. Horizontal scale : 5μs/div; vertical scale : (a) 1 V/div, (b) 0.2 V/div and (c) 10 mV/div.



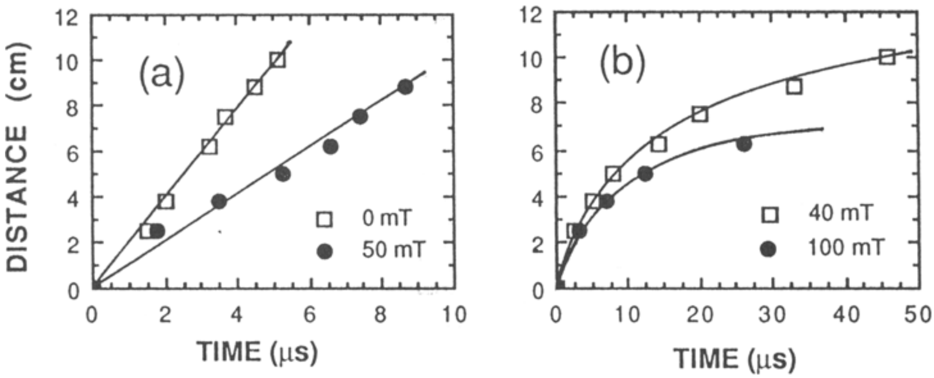


Fig. 3. Plume propagation dynamics derived from time-of-flight ion signals for **a)** the fast component at oxygen pressures of 0 mT and 50 mT and **b)** the slow component at 40 mT and 100 mT of oxygen. The fast component exhibits a linear variation with the slope yielding velocities of 2×10^6 cm/s and 0.9×10^6 cm/s at 0 mT and 50 mT respectively. The slow component follows $R = at^n$, with $R = 1.76t^{0.47}$ at 40 mT and $R = 1.55t^{0.44}$ at 100 mT.

on a single crystal substrate, but exhibits poor superconducting properties as a result of oxygen deficiency.

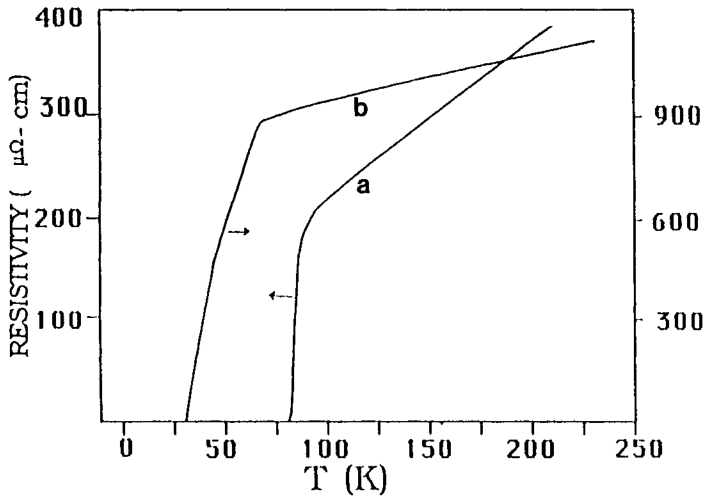
A laser plume propagating in vacuum undergoes free expansion. As the back ground pressure is increased, the plume expansion is governed by the gas phase collisions. At background pressures above 100 mT the formation of a shock wave has been observed[12,13]. In a typical high T_c film growth process, oxygen pressures above 100 mT are used to promote the gas phase reaction by increasing the collisions within the plume. By using an ion probe technique, we have investigated the dynamics of the plume as it evolves from a free expansion regime in vacuum to a highly collisional regime at high pressures. Unlike the species resolved optical spectroscopic techniques, the dynamics of the ionic constituents in the plume observed by the ion probe describe the behaviour of the composite plume. This is an advantage in the investigation of ionic enhancement in a plasma-assisted laser deposition process.

The time-of-flight signals obtained for a target-probe distance of 7.5 cm as the back ground pressure is changed from 0-100 mT is shown in Figure 2. A single peak in the ion signal at low pressure (20 mT) indicates a narrow velocity distribution with an average velocity of $2x10^6$ cm/s , which agrees closely with previously reported values[12,14]. At an oxygen pressure of about 40 mT the formation of a delayed second peak was observed. The intensity of the fast component decreased with increasing pressure while the velocity did not seem to change significantly. At high pressures, the slow component became dominant and the fast component completely disappeared above 100 mT. The velocity of the slow component decreased consistently with increasing pressure. The behavior of the fast and the slow components at different target-probe distances and pressures have been studied and are presented in Figure 3. As shown in Figure 3(a), the velocity of the fast component remains a constant for a given pressure, characteristic of a free expansion. The slow component of the plume approaches a distance-time relation predicted by a blast wave model of the form $R=at^n$, with n approaching 0.4 with increasing pressure[15,16]. Since n=0.4 represents a shock wave, the development of the second peak signifies the transition of the plume from a free expansion regime to a shock wave regime. The coefficient a is dependent on both the oxygen pressure and the laser fluence at the target.

The increase in pressure increases the collisional frequency between the species in the plume and oxygen, which in turn enhances the gas phase reaction. However, the increased collisions will also lead to reduced kinetic energy for the species arriving at the substrate, which has to be compensated by increasing the substrate temperature. Therefore, for the low temperature in-situ growth of films the background pressure becomes a crucial parameter. The pressure has to be high enough to maintain the high collision regime for enhanced gas phase reaction while being low enough to sustain a significant plume kinetic energy. Such an enhancement in the gas phase reaction and the kinetic energy is possible in a plasma assisted laser deposition process.

Plume Dynamics in Plasma-Assisted Laser Deposition

The introduction of a positively biased ring electrode between the target and the substrate produces a luminous oxygen pulsed discharge near the ring as the laser generated plume propagates from the target to the substrate. This oxygen plasma has been shown to improve the superconducting properties of the film. The temperature dependence of the resistivity of two YBCO films grown on ZrO_2 (100) with and without the influence of the plasma (shown in Figure 4) clearly indicates the



(a)	(b)
$T_s = 500\ ^oC$	$T_s = 500\ ^oC$
$V = +400V$	$V = 0$
$T_c = 80K$	$T_c = 30K$
$T_{onset} = 92K$	$T_{onset} = 70K$
$\rho_{100K} = 210\ \mu\ \Omega$-cm	$\rho_{100K} = 870\ \mu\ \Omega$-cm

FIG.4. Effect of the plasma on the temperature-resistivity characteristics for films on ZrO_2 (a) with and (b) without the plasma (Ref. 17).

effectiveness of the plasma in improving superconducting properties of the film. To produce films that are superconducting under these conditions, the plasma-laser plume interaction should not alter the plume stochiometry, while simultaneously providing a sufficient ionic and atomic oxygen flux to enhance the reactivity. Previous spectroscopic studies[18] of the laser plume in the presence of the plasma have shown an increase in both O_2^+ and atomic oxygen near the substrate. By placing an ion probe at the position of the substrate we have investigated the net ionic content of the plasma arriving at the substrate.

The time-of-flight ion signals obtained for 20 mT and 40 mT background pressures of oxygen when the probe is located 7.5 cm from the target on the axis of the laser plume, is shown in Figure 5. At 20 mT the plume is dominated by the fast component as shown in Figure 5(a). When the ring voltage is increased above +100V, formation of a bright

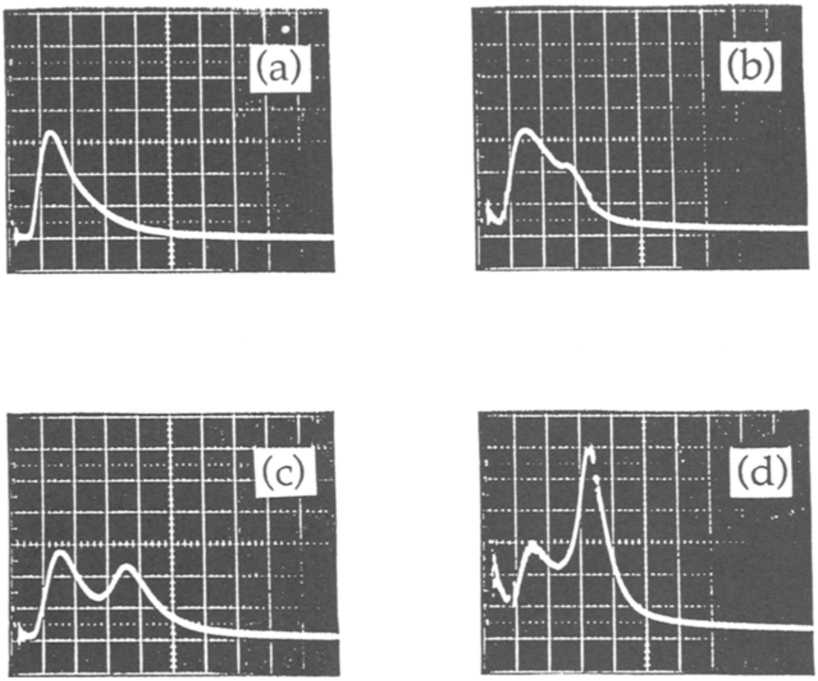


FIG. 5. Time-resolved ion signals measured 7.5 cm away from the target for 20 mT of oxygen with (a) 0 V and (b) 400 V ring bias. Also shown are the corresponding signals for 40 mT of oxygen at (c) 0 V and (d) 400 V ring bias respectively. Horizontal scale : 5 μs/div; vertical scale : 0.5 V/div ((a) & (b)) and 0.1 V/div ((c) & (d))

plasma between the biased ring and the grounded shield was observed. The intensity of the plasma increased with the ring voltage, and lasted only during the laser plume. As shown in Figure 5(b), for a ring bias of 400V, the formation of a slow component is observed while the fast component remains unaltered. Above +400V erratic breakdown of the plasma occurs. When the pressure is increased to 40 mT, the formation of the slow component with zero ring bias is observed (Figure 5(c)). A significant enhancement in the slow component, shown in Figure 5(d), is observed at 400V ring bias, whereas the fast component remains the same. The second forward directed component arrives at the probe ~11μs behind the highly forward directed part of the plume. The ionic enhancement in the slow component increased with increasing oxygen pressure, and with the bias voltage up to 400V.

The change in the plume ionic content with increasing ring bias at different pressures have been studied by integrating the ion probe signals. These results show a steady decrease in the plume ion content with increasing pressure. However, as indicated in Figure 6, the percentage increase in the plume ionic content increases rapidly with pressure at 400V ring bias. An ionic enhancement of over 100% has been obtained at an oxygen pressure of 40 mT with the ring biased at 400V.

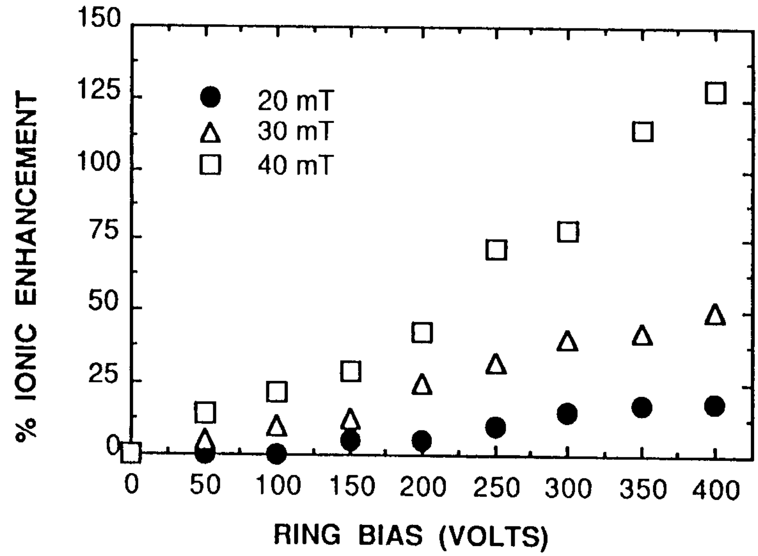


FIG. 6. Variation of percentage ionic enhancement with ring bias at background oxygen pressures of 20, 30 and 40 mT.

DISCUSSION

The time resolved ion signals in vacuum presented in this paper are consistent with the previously reported optical spectroscopic observations[9]. At high pressures (>100 mT), the formation of a shock wave closer to the target has been observed by optical imaging techniques[12]. In our experiments presented here, bifurcation of the plume into a fast and a slow component is seen under two different conditions. The slow component appears at large target-probe distances for low pressures (~40 mT), and at shorter distances for high pressures (>100 mT). Moreover, the expansion behavior of the slow component approaches that of a shock wave with increasing pressure, where as the fast component behaves similar to a free expansion in vacuum. The initiation of a shock wave requires the mass of the ablated plume to be less than the mass of the gas it compresses during its propagation[13,15]. In our experiments, this condition may be satisfied at low pressures and large distances from the target, whereas at high pressures this is easily attained at short distances. It is possible that the bifurcation we observe in the ion signals at a lower pressure than previously reported, indicates an onset of shock wave formation which progressively approaches a well-defined shock wave behavior with increasing pressure. As far as the film growth is concerned, it is advantageous to be in this high collision regime to promote the gas phase reaction.

Our ion probe experiments in the absence of the plasma show that the average kinetic energy of the species in the slow component of the plume, 7.5 cm above the target, changes from about 6 ev at 40 mT to about 1 ev at 80 mT pressure. As far as the low temperature film growth is concerned, the undesirable effect in deposition at high temperature is the drastic reduction in species kinetic energy. Alternatively, if the plume ionic content is significant, the ionic energy at the substrate can be increased by biasing the substrate negatively during the film growth. Therefore, ionic enhancement of the plume in the presence of the plasma will give rise to an appreciable increase in the surface adatom mobility. Furthermore, the formation of atomic and ionic oxygen in the plasma, as observed in previous work[14], will also enhance the gas phase reaction. The enhancement in the gas phase reaction combined with the increased number and energy of the ions in the plume should facilitate the superconducting film growth at a lower temperature.

The characteristics of the slow component and its behavior under the effect of the plasma are currently being studied by optical spectroscopic techniques and will be discussed in a subsequent publication.

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