Study of ion activation in the *in situ* low-temperature laser deposition of superconducting $YBa_2Cu_3O_{7-\delta}$ films

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The presence of a pulsed discharge during the reactive deposition of high T_c thin films allows the lowering of substrate temperatures to ~475 °C for *in situ* superconducting film deposition. We present the first ion probe analysis to study the role of this pulsed discharge on the excimer laser ablated $YBa_2Cu_3O_{7-\delta}$ plume. The ionic enhancement in the laser-ablated plume, during reactive deposition in the presence of a positively biased ring electrode, is studied both in terms of its extent and temporal characteristics. A significant increase in the forward-directed incidence of oxygen ions on the depositing substrate, following in the wake of the highly directional plume, is demonstrated. The dependence of this ionic enhancement on ambient oxygen pressure and the bias voltage on the ring electrode is discussed.

I. INTRODUCTION

Excimer laser ablation for the deposition of thin films,[1] particularly for *in situ* superconducting films of high T_c superconductors, is now a well established technique.[2] In addition to facilitating the stoichiometric reactive deposition of high T_c superconducting films, this technique has been demonstrated to be useful for the growth of epitaxial heterostructures.[3,4] The integration of such *in situ* superconducting film deposition techniques with existing semiconductor technologies, particularly for potential devices incorporating multilayer deposition, requires a reduction of the substrate temperature. Currently, typical substrate temperatures to ensure sufficient adatom mobility for the epitaxial growth of the desired crystalline phase, range from 650 to 720 °C.[5] However, such high temperatures are not conducive to direct deposition on reactive substrates such as Si or GaAs because of the resultant film contamination due to thermal diffusion.[6]

The inclusion of a positively charged ring electrode between the target and the substrate has been shown to allow the reduction of substrate temperatures (for *in situ* superconducting film deposition) to 475 °C.[7] This reduction was also observed to be closely related to an increase in the ion flux at the substrate.[5] Photoluminescence spectra acquired during the deposition indicate an increase in the plasma temperature from 6300 to 6800 K between the ring electrode and the substrate.[8] A measurement of the substrate current, with and without the ring electrode, has been recently reported.[5] In this study, the increase in substrate current in the presence of a ring bias was attributed to ionic enhancement in the plume.

We report the first ion probe analysis of the laser ablated $YBa_2Cu_3O_{7-\delta}$ (YBCO) plume during reactive deposition in an oxygen background in the presence of a ring electrode. Previous experiments have monitored the luminous component of the laser-ablated plume using optical spectroscopy[8–13] or intensified charge-coupled detector (ICCD) imaging of the plume.[14] Our present experiments directly measure the ionic content of the plume. Since any optical measurement is strongly influenced by small amounts of electronically excited radiative species that may not be representative of the actual ionic population in the plume, ion analysis is crucial for assessing the role of the ring electrode. Information on the ionic content is obtained at the expense of species selectivity inherent in optical measurements. Furthermore, in contrast to the recent study of the substrate current, which measures the *net charge* incident on the substrate,[6] our ion-probe experiments are designed to yield the *ionic content* of the laser ablated plume. This distinction is important because the

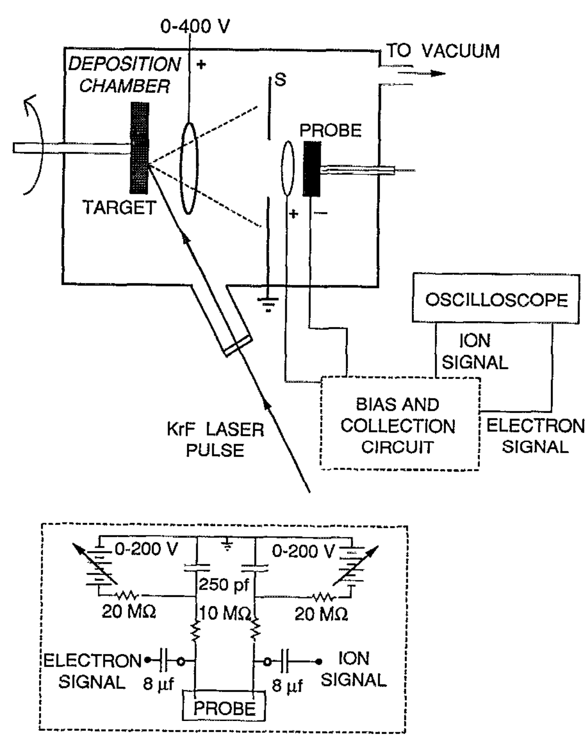

FIG. 1. Schematic diagram of the laser ablation deposition system and the ion probe. The probe bias circuit and the charge collection electronics are shown in the inset.

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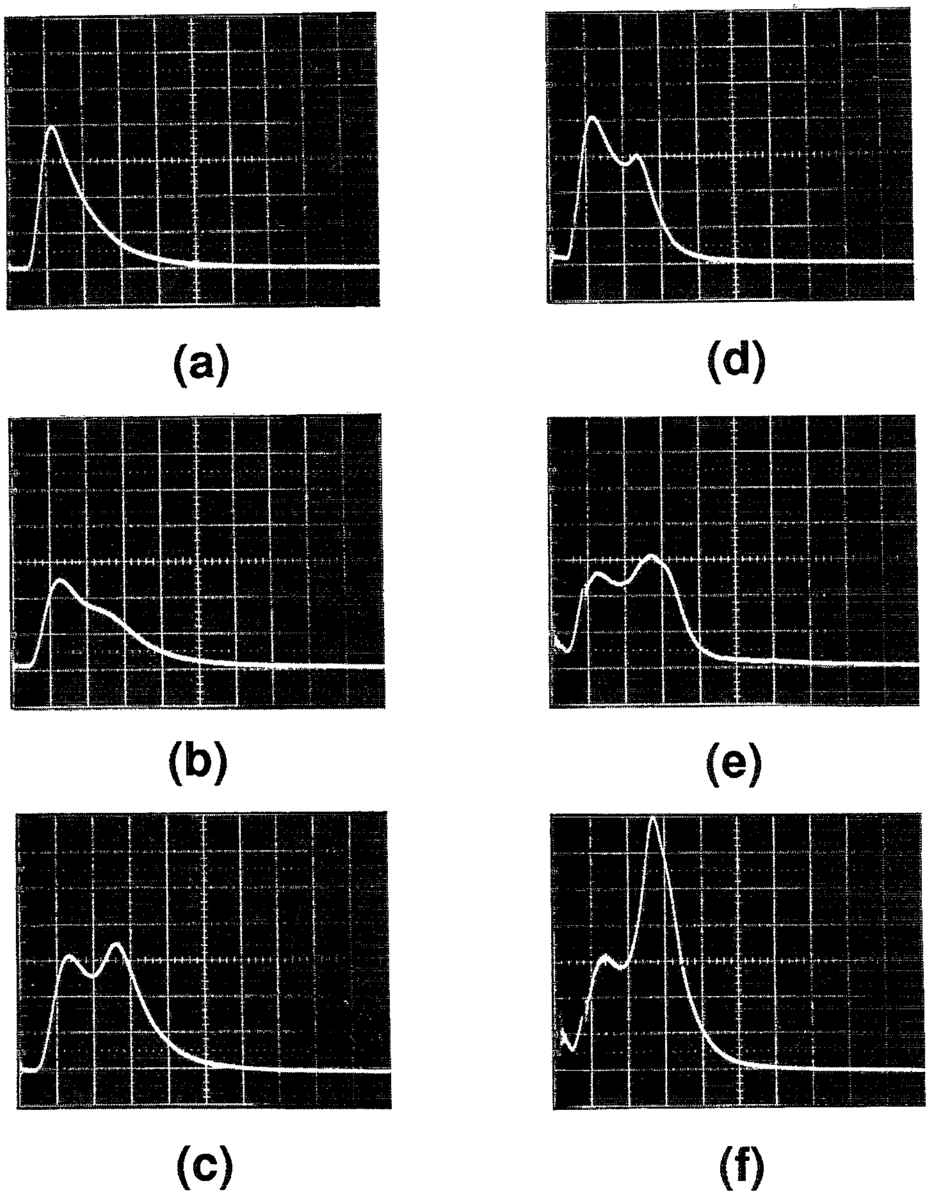

FIG. 2. Time-of-flight ion signals obtained with an on-axis probe 7.5 cm away from the target. (a)–(c) were taken without any ring voltage while (d)–(f) were at a 400 V ring bias. The ambient oxygen deposition pressures were 10 mTorr [(a) and (d)], 20 mTorr [(b) and (e)] and 30 mTorr [(c) and (f)]. The vertical scales are 1 V/div. [(a) and (d)], 0.5 V/div. [(b) and (e)] and 0.2 V/div. [(c) and (f)]. The time scale is 5 μs/div. in each case, with $t=0$ coincident with the arrival of the laser pulse on target.

ionic population in a neutral plasma, consisting of ions and electrons, would be undetectable by a measurement of the net substrate current.

II. EXPERIMENTAL SYSTEM

Figure 1 is a schematic representation of the experimental system. A typical excimer laser ablation system, using 15 ns KrF laser pulses at an energy fluence of 2 J/cm^2 to ablate a rotating YBCO target, was modified by the addition of a positively charged ring electrode in the intertarget-substrate region. The laser-ablated plume, emitted perpendicular to the target, passed through the center of the circular ring electrode of diameter 3.5 cm. In our experiments, the ring electrode was located 2.5 cm away from the target and variably biased in the range 0–400 V. A pulsed discharge occurred between the ring electrode and the grounded shield (S). The grounded shield had a 2.5 cm diameter hole concentric with the axis passing through the center of the ring electrode. The role of the shield was twofold. In addition to providing a grounded termination for the pulsed discharge, it was instrumental in eliminating any residual space-charge effects from affecting the ion probe measurements.

After passing through the aperture in the grounded shield, a portion of the plume was sampled on axis using an ion probe. A variety of dual electrode ion probes were used in our experiments. Biasing the collection electrodes to +150 V and −150 V (using the bias circuit shown as an inset in Fig. 1) allowed effective separation of the electrons and the ions, respectively, in the laser ablated plume. This permitted the simultaneous monitoring of the electron and ion current. For measurements of only the ion content, it was possible to use a single electrode ion probe biased to −100 V. Though the geometry and physical dimensions of the collection electrodes do affect the absolute signals, we observed no difference in the relative trends of the ion signals (presented later in this article) corresponding to changes in the physical configuration of the dual electrodes or shape of the single electrode. The size of the ion collection electrode was restricted to 5 mm in diameter, to avoid artifactual plume perturbation during the measurement. Suitable electrical termination in a 50 Ω resistor was used to acquire temporally resolved time-of-flight ion current signals and consequently dynamic information on the ion content of the plume. Integrated ion signals, on the other hand, allowed a measurement of the total ionic content.

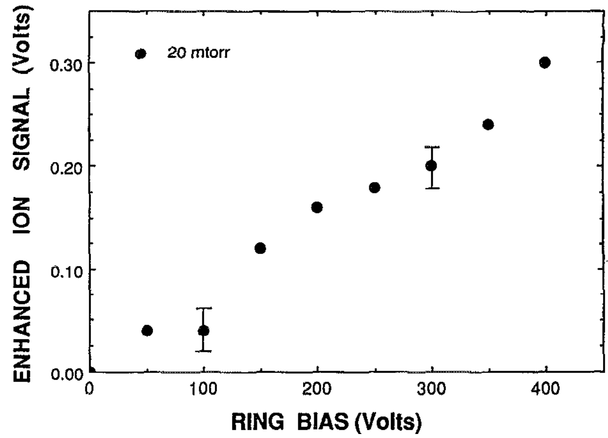

FIG. 3. Ring bias-dependent enhancement in the integrated ion signal at an ambient oxygen pressure of 20 mTorr.

III. RESULTS AND DISCUSSION

The dynamic behavior of the ions in the plume is demonstrated by the time-of-flight signals recorded in Fig. 2 at a temporal resolution of 20 ns. Figures 2(a)–2(c) represent the ion signals obtained without a ring bias at background oxygen pressures of 10, 20, and 30 mTorr, respectively, while Figs. 2(d)–2(f) are their counterparts at a ring bias of 400 V. The ion probe was located on axis in the laser-ablated plume 7.5 cm away from the target. Figure 2(a) indicates a single ion peak with a modal ion velocity of 1.25×10^6 cm/s in the laser-ablated plume, which reduces slightly to 1.15×10^6 cm/s [Fig. 2(b) at 20 mTorr of O_2] and 1.07×10^6 cm/s [the first peak in Fig. 2(c) at 30 mTorr of O_2]. These values are consistent with previously reported velocities for the highly forward directed laser ablated YBCO plume.[5] The sequence of time-of-flight signals in the absence of a ring voltage [Figs. 2(a)–2(c)] shows an increase in the width of the velocity distribution with pressure and the generation of a low velocity tail at 20 mTorr, which develops into a second delayed ion peak at 30 mTorr. The origin of this slow component is an interesting problem currently under investigation and will be discussed in a future publication. For the present study, however, we focus exclusively on the role of the ring electrode as demonstrated by a comparison of Figs. 2(a)–2(c) (in the absence of the ring bias) with their counterparts Figs. 2(d)–2(f) (obtained at a ring bias of 400 V). Visual examination of the plume in the presence of a 400 V ring bias indicated a luminous pulsed discharge consistent with previous optical studies that indicate the formation of O_2^+ ions in the activated plume.[8] The time-of-flight ion signals in the presence of the O_2^+ activation indicate a small delayed ion spike following the main peak at 10 mTorr of O_2 [Fig. 2(d)], with the formation of a dominant secondary peak at 20 mTorr and a pronounced delayed ion peak significantly larger than the primary plume ion signal at the higher O_2 pressure of 30 mTorr. The first ion peak, corresponding to the highly forward directed component of the laser ablated plume, is unaltered by the pulsed discharge throughout the range of ambient oxygen pressures investigated in our study.

There are two alternatives for the origin of the delayed ion signal generated in the presence of the ring bias. One possibility is an enhanced ionization of the slow component of the laser-ablated plume while the other explanation may be the incidence on the probe of forward-directed O_2^+ ions created during the pulsed discharge. Previous optical studies have indicated the absence of further plume ionization while confirming the generation of O_2^+ ions in activated reactive deposition.[8] The second alternative therefore appears to be the likely explanation.

The role of the ring bias on the extent of the ionization may be further assessed by a measurement of the enhancement in total ion content due to the pulsed discharge. The enhancement may be evaluated by the difference between the integrated ion signal at a given ring bias and that without any voltage on the ring electrode. A representative example of the enhancement is shown in Fig. 3 at a background O_2 deposition pressure of 20 mTorr. A rapid increase in the enhanced ion signal with increasing ring bias, specifically beyond 100 V, is clearly evident. Visual examination of the plume indicating observably increasing plume luminosity beyond 100 V is consistent with the trend exhibited by Fig. 3.

The effect of background O_2 pressure is further evidence of the origin of the increased ionization. A comparison of the percentage ionic enhancement as a function of ring bias for ambient oxygen pressures of 40 and 10 mTorr is shown in Fig. 4. At a ring bias of 350 V, the total ion content of the plume has nearly doubled at 40 mTorr in contrast to an increase of ∼50% at 10 mTorr. The higher percentage increase in ionic content at the higher O_2 pressure supports the hypothesis that oxygen ionization rather than ionization of the slow component in the laser-ablated plume is responsible for the enhancement ionic content.

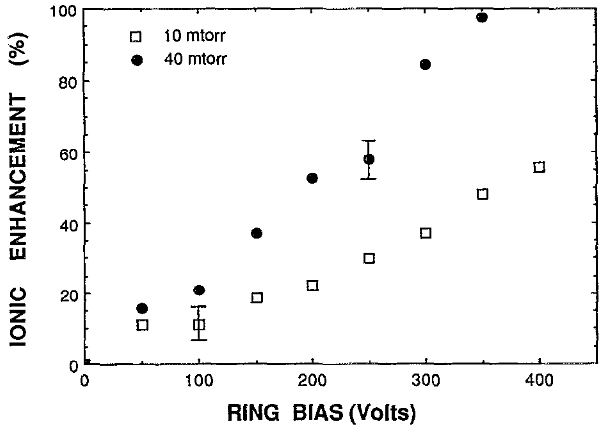

FIG. 4. Variation of percentage ionic enhancement with ring bias at two different ambient oxygen pressures during ablation.

IV. CONCLUSION

In summary, ion measurements in the excimer laser-ablated YBCO plume in the presence of a pulsed discharge reveal a significant increase in ionic content that relates directly to the ambient oxygen pressure during deposition. Time-of-flight ion signals obtained by us indicate that this enhancement results in a delayed ion peak of oxygen ions following in the wake of the highly forward directed laser ablated plume. Since ions are important for columnar growth leading to oriented epitaxy[8] and for efficient oxygen incorporation into the depositing film, the enhanced ionization generated by the ring electrode may be responsible for the observation of oriented superconducting YBCO films on low-temperature substrates.

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