# Spot-size-dependent bifurcation of laser-ablated plumes

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An ion probe investigation of an excimer-laser-ablated plume from a high-$T_c$ superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) target in an oxygen ambient revealed a significant alteration of the propagating plume as the laser spot size on the target was changed. For larger spot sizes, the time-resolved ion signals showed a bifurcation of the laser plume into two distinct components with increasing spot size. The faster component of the plume showed free expansion behavior, while the slow component corresponded to a highly collisional regime that represented the onset of a shock wave. Similar plume characteristics have been seen for laser-generated plumes expanding in high-pressure ambient gases. The $YBa_2Cu_3O_{7-x}$ films grown under the conditions that produced a high degree of plume bifurcation yielded high-quality superconducting films. Implications of these findings toward superconducting film growth are discussed. © *1995 American Institute of Physics.*

## I. INTRODUCTION

Laser ablation has been shown to be a promising technique for the deposition of high-quality thin films.[1–3] This technique works exceptionally well for the growth of films that require gas phase reaction to incorporate a gaseous constituent into the growing film. It has also been established as the most favorable technique for the growth of high-$T_c$ superconducting films.[4–8] In spite of the considerable amount of research that has been conducted to study the laser ablation process, a complete understanding with respect to the large number of process variables has not been achieved. The extension of this technique to large area film growth at a high deposition rate requires further study at high pulse energies and larger laser spot sizes.

Laser ablation of a composite target and the subsequent film growth on a heated substrate yields three different regimes of interaction. Each of these regimes comprising the laser–target interaction, the laser-plume–ambient-gas interaction, and the plume–substrate interaction plays an important role in determining the quality of the deposited film. In the growth of high-$T_c$ superconducting oxides, where a significant gas phase reaction is desirable to produce *in situ* superconducting films, the interaction of the ambient gas with the expanding plume is important. Typically, high-quality superconducting films are grown at high pressures ($>100$ mT), due to a correspondingly high collision probability that leads to the formation of the oxides in the gas phase.[6–8] However, since the expansion of the plume is considerably suppressed at high pressures, the film growth has to be carried out very close to the target. The kinetic energy of the plume species also decreases rapidly with increasing pressure, requiring high substrate temperatures for film growth.

One possible solution is a reduction in ambient pressure which allows the use of longer target to substrate distances, thereby increasing the area of uniform film growth while facilitating low-temperature growth due to the high species kinetic energy. This benefit is offset by the deleterious effect of insufficient gas phase reaction at low pressure, leading to films with low oxygen content. The determination of the optimum pressure for the growth of large area films at a low substrate temperature, therefore, requires a careful investigation of the plume expansion characteristics. Previous optical emission spectroscopic investigations[9] of $YBa_2Cu_3O_{7-x}$ (YBCO) plumes suggested that different species in the plume expand with different velocities near the target, and attain a common velocity further away from the target. This result indicates that, at a given oxygen pressure, *in situ* superconducting film growth is possible only above a specific substrate-target distance. Kim and Kwok[10] have presented a *P-D* scaling law to make a correlation between the target–substrate distance and the ambient oxygen pressure for the *in situ* growth of superconducting films. This law provides a useful guide to film growth at high pressures where the plume propagation has been shown to follow a "blast wave model." The effect of the ambient oxygen pressure on YBCO plume expansion has also been studied previously by using optical and ion probe techniques.[11,12] These studies have revealed a bifurcation of the laser-generated plume, and have shown an increase in the degree of bifurcation of the plume with increasing pressures that leads to a single slow component above a pressure of 100 mT.

In this article, we report a series of ion-probe experiments to investigate the dependence of the plume dynamics as well as the properties of the deposited films on the laser spot size at the target. A time-of-flight ion probe study of the evolving plume as a function of ambient pressures and laser spot sizes has been carried out at a fixed laser fluence.

## II. EXPERIMENT

The experiment was carried out in a standard laser ablation chamber with the ion probe replacing the substrate. The ion probe was a shielded single circular plate 2 mm in diameter, biased at $-30$ V, and placed along the plume propagation axis. At high pressures a rapid radial change in the plume stoichiometry and the species kinetic energy across the plume is expected.[13] Therefore, the use of a small area probe ensures spatial selectivity of on-axis ion signals exclusively.

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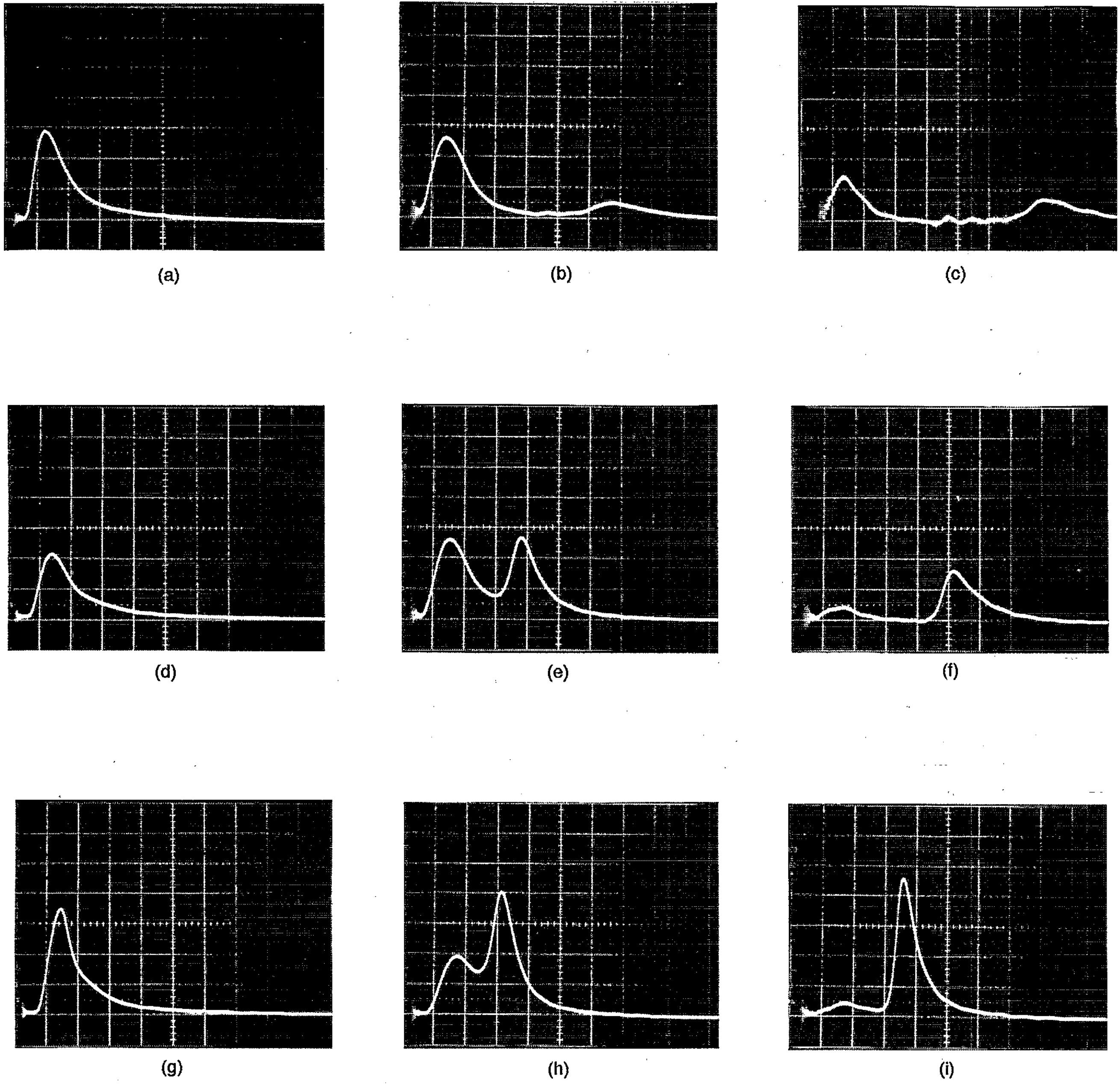

FIG. 1. Time-of-flight ion signals as a function of laser spot size on target and the ambient oxygen pressure. The three rows [(a), (b), (c); (d), (e), (f); and (g), (h), (i)] correspond to laser spot sizes of 3, 6, and 9 $mm^2$ with a laser fluence of 1.8 $J/cm^2$. The three columns [(a), (d), (g); (b), (e), (h); and (c), (f), (i)] were obtained at ambient oxygen pressures of 20, 40, and 60 mTorr, respectively. The target–probe distance was 6.25 cm in each case. Time scale: 5 $\mu$s/div; vertical scale: (d), (g) 0.5 V/div; (a) 0.2 V/div, (h) 0.1 V/div; (e), (i) 50 mV/div; (b), (f) 20 mV/div; and (c) 5 mV/div.

The details of the experimental setup have been described in a previous publication.[14] The KrF excimer laser was focused on to a rotating YBCO target in the vacuum chamber by a 30 cm focal length converging lens placed on a translation stage. The on-target laser spot size was adjusted, as required, by translating the focusing lens while keeping the laser fluence constant. The ion signals were recorded on a fast oscilloscope with a response time of 2 ns, across a 50 $\Omega$ terminator.

YBCO films have been deposited on $ZrO_2$ (100) substrates under similar deposition parameters with different spot sizes, to study the effect of the ablation laser spot size on the superconducting properties. All the films were grown at a substrate temperature of 680 °C.

## III. RESULTS AND DISCUSSION

The time-of-flight ion signals of the plume obtained at oxygen pressures of 20, 40, and 60 mTorr for laser spot sizes of 3, 6, and 9 $mm^2$ on the target are shown in Fig. 1. For these signals the ion probe was placed 6.25 cm from the

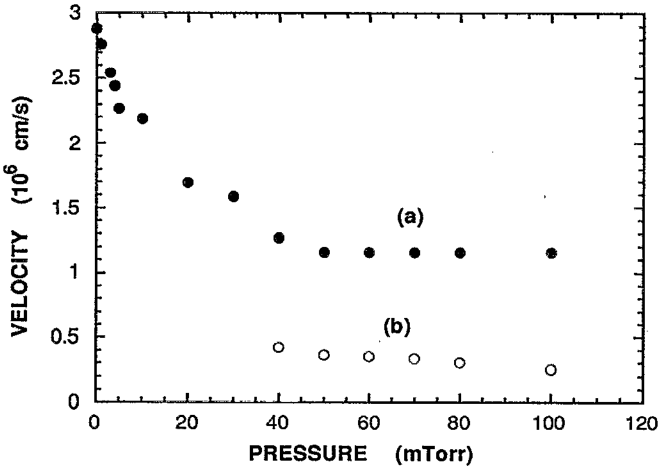

FIG. 2. Dependence of the average velocity on the oxygen pressure for (a) the fast component and (b) the slow component.

target. The laser fluence at all three spot sizes was 1.8 J/cm$^2$. This fluence is above the 0.4 J/cm$^2$ threshold fluence for congruent evaporation of an YBCO target.[15]

Figures 1(a), 1(b), and 1(c) correspond to the ion signals obtained with a focused laser beam (3 mm $^2$ spot size) on the target at 20, 40, and 60 mTorr ambient pressures. At low pressures (<20 mTorr) the ion signal was dominated by the fast component and the development of a weak slow component with increasing pressure was observed. The pressure dependence of the signal at a larger spot size of 6 mm$^2$ is shown in Figs. 1(d), 1(e), and 1(f). At this spot size increasing pressure caused the fast component to become weaker while the slow component was enhanced. As shown in Figs. 1(g), 1(h), and 1(i), a further increase in spot size to 9 mm$^2$ produced a much larger slow component that dominated the ion signal even at the intermediate pressure of 40 mTorr. Notably, the arrival time of the slow component at a given pressure was reduced with increasing spot size, indicating a corresponding increase in the species kinetic energy.

The fast component was rapidly quenched by the increasing pressure, and was not detectable above 80 mTorr. It was also noted that the time of arrival of the fast component at the probe, indicated by the primary peak, increased rapidly with the initial increase in pressure, but attained a steady value above 40 mTorr. The mean velocity of the fast and the slow component of the plume (computed from the peak of the time-of-flight ion signals) as a function of pressure is shown in Fig. 2. As indicated in the figure, after the development of the slow component, the velocity of the fast component remained almost constant.

The effect of the laser fluence on the plume expansion is demonstrated by the ion signals obtained at different fluences for the same spot size and ambient pressure. The signals produced at respective laser energy fluences of 2.5 and 1.8 J/cm$^2$ in a 6 mm$^2$ spot size for an oxygen pressure of 60 mTorr is shown in Fig. 3. In comparing Fig. 3(a) at the higher fluence to its low-fluence counterpart [Fig. 3(b)], it is clear that the increase in fluence has led to an enhancement in the slow component. The earlier arrival of the slow component at the higher fluence is indicative of the correspondingly high plume energy.

The characteristics of the plume expansion at a given pressure were also studied by observing the ion signals at different distances from the target. For a given spot size, the bifurcation of the plume was observed to occur closer to the target at high pressures, whereas at low pressures the onset of the bifurcation was seen only at larger distances from the target. The time of arrival of the fast and the slow components at the probe for different target-probe distances $R$ for a spot size of 4 mm$^2$ is plotted in Fig. 4. In vacuum, at all distances, the plume consisted of only the fast component, and the time of arrival varied linearly with the distance. This observation is consistent with previously reported results.[16] This free expansion behavior corresponded to an expansion velocity of $2\times10^6$ cm/s. The expansion velocity of the fast component reduced with increasing pressure, while the time–distance relationship continued to be linear. Curve (a) in Fig. 4 represents the fast component at an ambient oxygen pressure of 40 mTorr.

In our experiment, where the plume expansion within a 2.5–10 cm distance from the target was observed, the propagation of the slow component followed a functional behavior of the form $R=at^n$, where $a$ is a constant that depends on the laser energy and the ambient oxygen pressure. As indicated by curve (b) in Fig. 4, the slow component assumed the form $R=1.5t^{0.46}$ at 40 mTorr. With increasing pressure the value of $a$ became smaller and the exponent approached a limiting value of 0.4. This agrees with previous observation

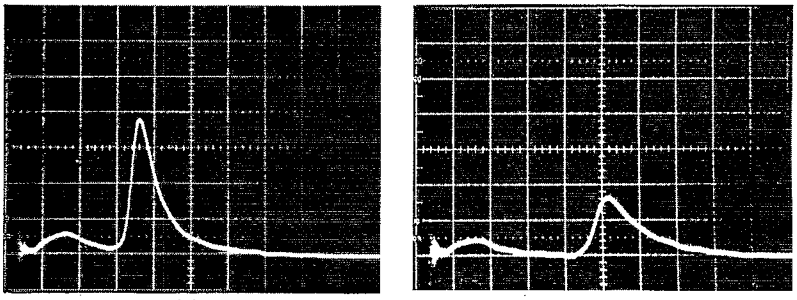
(a)
(b)

FIG. 3. Time-of-flight ion signals for a laser fluence of (a) 2.5 J/cm$^2$ and (b) 1.8 J/cm$^2$ for an oxygen pressure of 60 mT and a spot size of 6 mm$^2$. The target–probe distance is 6.25 cm. Time scale: 5 $\mu$s/div; vertical scale: (a) 50 mV/div and (b) 20 mV/div.

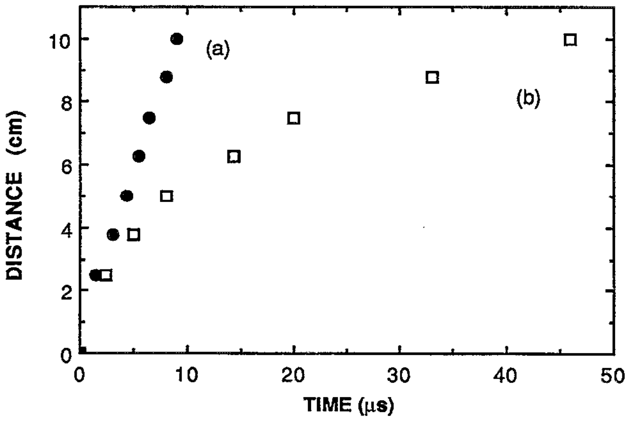

FIG. 4. $R-t$ plot at an oxygen pressure of 40 mT for (a) the fast component and (b) the slow component. The fast component shows a linear variation that corresponds to a $0.9\times10^6$ cm/s velocity. The slow component follows $R=1.5t^{0.46}$.

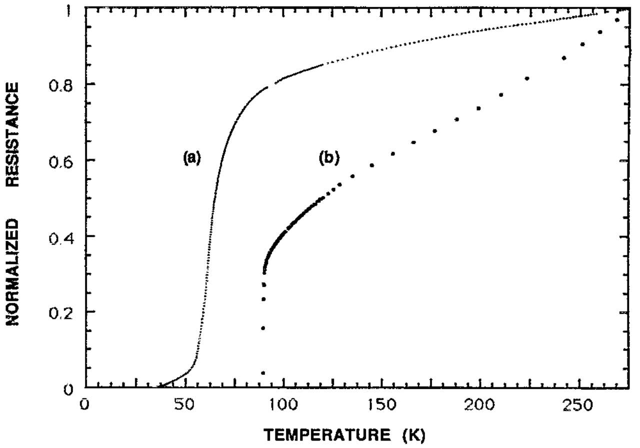

FIG. 5. Normalized resistance vs temperature for YBCO films grown on $ZrO_2$ (100) substrates at a substrate temperature of 680 °C and an ambient oxygen pressure of 80 mTorr, for laser spot sizes of (a) 2 mm$^2$, and (b) 7.5 mm$^2$. The target–substrate distance was 6.25 cm.

at high pressures (>100 mT), where the slow component produced as a result of the hydrodynamic interaction of the plume with the ambient gas has been shown to follow a shock wave behavior of the form $R=\xi_0(E/\rho_0)t^{0.4}$, where $\xi_0$ is a constant, $E$ is the total absorbed energy, and $\rho_0$ is the background gas density.[16–18]

In vacuum, the laser-generated plume expands freely without background gas collisions. In the presence of a relatively low-pressure ambient gas (<20 mT) the plume continues to expand freely, but with a reduced forward velocity due to collisions between the plume and the ambient gas. With increasing pressure the expansion is suppressed as a result of the reduced pressure gradient between the plume and the ambient gas. This may give rise to two different expansion mechanisms for the expansion front and the core of the plume. The expansion front which is mainly subjected to plume–gas collisions would expand freely with a higher velocity than the high density core of the plume which undergoes extensive intraplume collisions. The slow component that represents the core of the plume leads to the formation of a shock front that develops with increasing background pressure.[19]

Our observations of the enhanced plume bifurcation at large laser spot sizes can also be explained by considering the hydrodynamic behavior of the plume. Increasing the spot size at a constant laser fluence on the target will lead to an increase in the vaporized flux and also proportionately higher region of intraplume collisions. Therefore, the slow component, which represents the highly collisional core of the plume, is expected to be enhanced with increasing laser spot size. Furthermore, the increase in the peak velocity of the slow component with increasing laser spot size can be explained by using the time–distance relationship $R=\xi_0(E/\rho_0)t^{0.4}$ for a shock wave. As the spot size is increased at a fixed laser fluence, the total energy imparted to the explosive evaporation ($E$) is increased. This implies a higher velocity for the shock front, as observed in our results.

As far as the YBCO film growth is concerned, increase in collisions leads to increased gas phase reaction, which will in turn enhance the oxygen content of the film. For a high degree of plume bifurcation where the highly collisional regime dominates the plume the gas phase reaction is enhanced. As indicated in our experiments, enhancement in gas phase reaction at low pressures can be obtained by increasing the laser spot size at the target, while keeping the laser fluence above the threshold fluence for congruent evaporation. To validate our hypothesis, two superconducting films were deposited on $ZrO_2$ (100) substrates, using different laser spot sizes. These films were grown at an oxygen pressure of 80 mTorr and a substrate temperature of 680 °C. The target to substrate distance was 6.25 cm, and the two spot sizes used were 2 and 7.5 mm$^2$, respectively. Figure 5 shows the normalized resistance versus temperature characteristics of the two films grown with the two different spot sizes. At this pressure, the plume arriving at the substrate for a 2 mm$^2$ spot size consists mainly of the fast component. Therefore, insufficient gas phase reaction is expected to produce films with low oxygen content. The broad transition and the low critical temperature ($T_c\sim36$ K) shown in Fig. 5(a), for the film grown with a tightly focused 2 mm$^2$ spot size, is a clear indication of the low oxygen content of the film. On the other hand, for a 7.5 mm$^2$ spot size where the plume consists of only the slow component, increased gas phase reaction is expected to produce films with high oxygen content. This is evident in Fig. 5(b) where a high critical temperature ($T_c\sim89$ K) and metallic behavior of the film grown with the 7.5 mm$^2$ spot size is observed.

## IV. CONCLUSION

In conclusion, the propagation characteristics of laser-ablated YBCO plumes have been investigated by an ion probe technique. The plume was shown to bifurcate into a fast and a slow component at high pressures and larger laser spot sizes. The slow component that developed with increasing spot size for a given pressure, was seen to approach a shock wave behavior. Previous studies on the pressure dependence of the plume expansion by others[12,16] have described the early part of the expansion by a drag force model, while the latter stage of the expansion has been shown to follow a blast wave model. In our studies of the laser spot size effect on the plume expansion, which involves only the latter stage of the expansion (distances greater than 2.5 cm from the target), the slow component has also been shown to follow a blast wave model. Similar behavior of the plumes produced by single component targets[20] suggests that the plume bifurcation results from a hydrodynamic effect rather than a mass selective species separation. The formation of the slow component, which represents a high collision regime, has been shown to be preferable for superconducting film growth as it enhances the gas phase reaction. Our results show that at low pressures a significant enhancement in the slow component can be obtained by increasing the size of the laser spot on the target. In a recent report[14] we have pointed out the significance of the slow component in the plasma-assisted laser deposition process for low-temperature film growth, where greater than 100% ionic enhancement of the slow component was obtained in the presence of a plasma.

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