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$Y_1Ba_2Cu_3O_{7-x}$ Laser-Ablation Plume Dynamics Measurement by Nanosecond Response Ion Probe: Comparison With Optical Measurements.

D. N. Mashburn and D. B. Geohegan

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Solid State Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6056
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D. N. Mashburn and D. B. Geohegan

Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6056

ABSTRACT

A family of fast time response ion probes has been developed to study the laser-ablation plume dynamics under $Y_1Ba_2Cu_3O_{7-x}$ film-growth conditions. These probes are useful over a wide range of pressures, distances, laser energies, and energy densities. The ion probe measurements are complemented and corroborated by measurements using spatially and temporally resolved optical emission and absorption spectroscopy. The results confirm a long lived *ionized* component to the plume and a marked slowing of the plasma front at film deposition pressures and distances. Both the ion probe and spectroscopic techniques show promise as sensitive process monitors for film deposition by laser ablation.

1. INTRODUCTION

It is now recognized that thin film high T_c superconductors made by laser ablation with in situ oxidation equal or exceed the quality of those made by any other technique. This has given real impetus to research on the ablation process. Most of this research has been focused on spectroscopically resolving the fluorescence from the ablation plume[1-12] in an effort to identify and obtain expansion velocities[6,7] of the components. Recently, the non-emitting *ground states* of several species in the laser plume were examined by transient optical absorption spectroscopy and found to have velocity distributions which are significantly broadened and extended to much lower velocities than those of the fluorescence in the laser plume[13,14]. This work showed that a significant portion of the plume mass was in the ground states of the atoms and ions and indicated that the fluorescence is more representative of the kinetic processes in the expanding laser plume (such as electron-impact ionization or recombination) than the density of any one species. The combination of optical emission and optical absorption spectroscopy has provided a view of the interrelationships between the ground, excited, and singly ionized states of a species. The recognition of charged particle interactions and transport in the plume emphasized the need to treat it as a *plasma*[15,17]. This view of the plume as an expanding plasma, and a growing suspicion that charged particles have a major effect on film morphology and superconducting properties, prompted the development of the electrical measurement techniques described in this paper.

While a number of electrical techniques for exploring laser ablation plasmas have been developed in the laser fusion field[18,19] they have been applied to much less complex targets than $Y_1Ba_2Cu_3O_{7-x}$, usually at much higher power densities, and at low pressures where ion collisions with background gas molecules are negligible. Our interest here is in techniques that can measure properties of plumes from $Y_1Ba_2Cu_3O_{7-x}$ pellets ablated by 10^7-10^8W/cm^2 40 nsec pulses of 248 nm light in pressures of up to 1 Torr over distances of 2-10 cm. Charge collection at a plane perpendicular to the plume velocity should directly indicate total charge *flux* (minus any neutralization within the probe). However, time response, external field sensitivity, and the need for bias voltages (with possible breakdown at higher pressure) all constrain the physical implementation of such a technique. Gutfeld has reported measurements on copper targets with a bare-wire ion probe at 10^{-5} Torr,[20] but we found a similar open plate probe (Fig. 2a) to be very sensitive to stray inductance between the target and probe

ground, and susceptible to EMI noise pickup when used with a high bandwidth (1 Ghz) oscilloscope. While ion probes used in the laser fusion field may be operated with hundreds of volts bias between grids spaced only millimeters apart, such operation at 200 mTorr oxygen pressure results in electrical breakdown. Attempts to control the problem by increasing the spacing between electrodes introduce another problem. As the plasma particles penetrate background gas at high pressures, collisions with stationary molecules slow and neutralize the plasma. For accurate measurements at high pressure, the travel distance of the plasma inside the probe must be kept small compared to the probe-to-target distance.

In this paper we describe a screened-plate charge collector ion probe useful over a wide range of pressures with a verified time response <3 nanoseconds, and a parallel plate charge deflector ion probe for use at lower pressures. Both probes were used in conjunction with optical absorption[13,14] and emission to study ablation phenomena. These studies confirm the long-lived plume component observed by optical absorption, determine the time of flight (TOF) energies, and show effects of oxygen pressure, distance, and laser power on the plume. The fast time response allowed us to see both the photons and direct electrons from the ablation 'fireball'. Since ion probes measure *flux* and the optical techniques measure *density* , the ion probe techniques described here complement the optical techniques in the ability to directly measure transport of the charged species.

2. EXPERIMENTAL

The laser-ablation plume measurement apparatus is shown schematically in Fig. 1 and described in detail elsewhere.[13] Bulk superconducting $Y_1Ba_2Cu_3O_{7-x}$ pellets were rotated inside a turbopumped stainless steel bell jar at base pressures of $< 2 \times 10^{-6}$ Torr and irradiated at an incident angle of 60° by focused 248 nm pulses from an excimer laser. Energy densities were determined by measuring the energy transmitted through apertures placed at the pellet position and orientation.

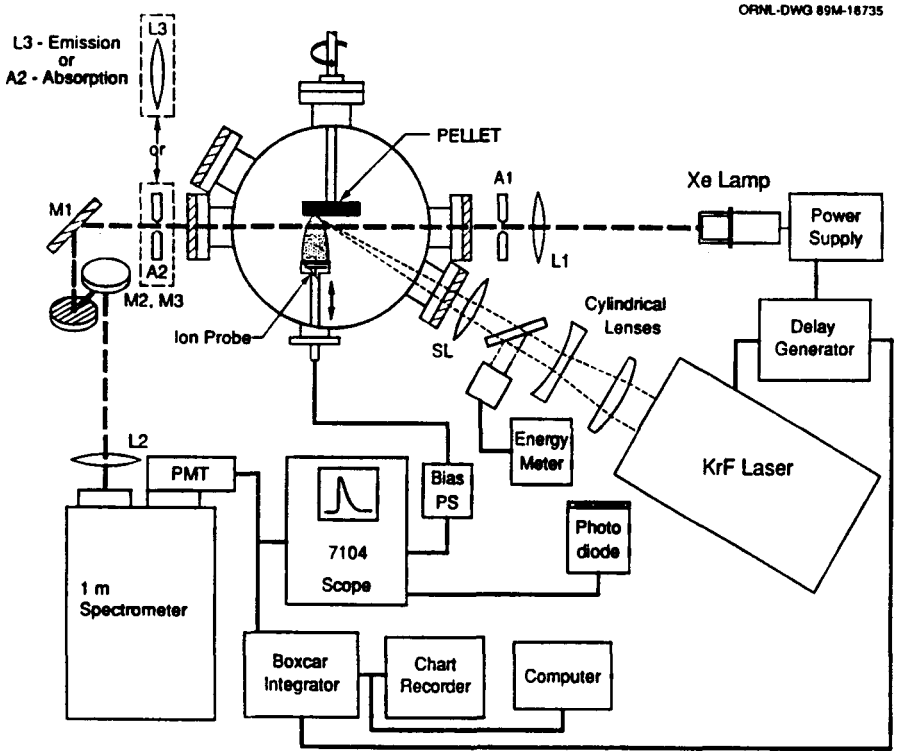

Fig. 1. Schematic diagram of the transient optical absorption, optical emission, and ion probe systems installed on a laser-ablation apparatus.

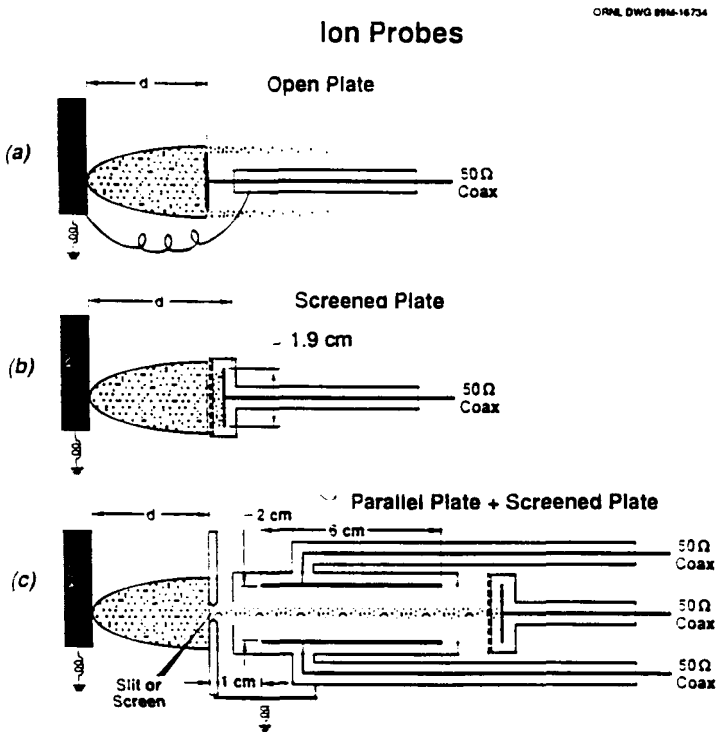

Fig. 2. Three types of ion probes used for laser-ablation studies The ablation target is depicted at the left with inductive coupling to the chamber (ground). The plume is shown expanding across distance d to the respective probes. Probe (a) is a conventional charge collection probe often used in steady state plasma measurements, shown with an uncontrolled inductance between the probe circuit ground and the target. The screened-plate probe (b) consists of a 1.9 cm diameter copper plate recessed 2 mm inside a grounded copper cup which is covered by a 53% open 1.1 mm mesh copper screen giving an effective probe area of 1 cm^2. The plate forms the termination of a 50 ohm coaxial transmission line. The parallel plate probe (c) consists of two 4 × 6 cm copper plates held 2 cm apart within a grounded open-ended box, mounted behind a grounded slit which forms a 'slab' of charged particles aimed midway between the two plates. Bias voltages, applied to the plates through coax cables, electrostatically deflect charged particles. Charged particles which strike a plate induce current in its external circuit. A rear plate, actually probe (b), detects charged particles that get through.

The ion probe of Fig. 1 was placed perpendicular to the pellet to intercept the center of the plume. Probes (a) and (b) of Fig. 2 could be translated from ~1–15 cm without breaking vacuum. Probe (c) was used at a fixed distance. The ion probe bias power supply used for time-resolved measurements was a completely isolated and shielded 1 mfd-capacitor-bypassed 30 V battery and potentiometer in series with the signal line. The bias supply, cables, and ion probe were tested as a system with a time domain reflectometer and verified to give no spurious responses at times >20 nsec for probe (c) and >3 nsec for probe (b). The signal from the open plate probe (a) was so affected by the ground return connection to the pellet that it could not be relied on for precise measurements. The screened-plate probe shown in Fig. 2b with a collecting area of 1 cm^2 was well sized for plume investigation 2–10 cm from the ablation target. This probe was operated at a -6V bias for the measurements in Figs. 4–10. Because this probe is planar it can be operated at pressures up 1 Torr, and because it is well shielded it can operate in high external electromagnetic fields.

The parallel plate probe [19] of Fig. 2c can be used to measure the energy/charge ratio of ions from the plume. For singly charged particles acting independently, the perpendicular E field deflects them into the plate if their kinetic energy in eV is <4.5 times the voltage across the plates, since the plates are 6 cm long and spaced 1 cm to either side of the 'slab' of charged particles passed by the slit. Raising the voltage on the parallel plates until the rear plate signal just disappears gives a measure of the maximum kinetic energy/unit charge. Since the distance from the parallel plate to the target is known, and the circuit has <20 nsec time response, a cross-check on the energy is available from the signal timing if the ion mass is known, or the signal timing can help ascertain the mass/charge ratio. However, because of its length, this probe is not useful at pressures >100 mTorr.

The ion probe is used in conjunction with a high frequency oscilloscope to capture the temporal profiles of the ion currents associated with each laser pulse. The scope is triggered from the same delay generator as the laser, the boxcar, and the light source used in absorption measurements, with individual delays for each device. The currents from the 1 cm^2 area probe are easily detectable in a 50 ohm circuit. The time delay for a known pellet-probe distance gives the flight time (TOF) of the charged particles.

2a. ION PROBE MEASUREMENTS

A fast response ion probe of the charge collector type as in Fig. 2b responds to a flux of three different classes of particles from a laser ablation pulse. First to arrive are scattered and reflected laser photons, photons emitted by the ablation plasma fireball, and fluorescence photons from the plume interacting with the background gas. Second to arrive are the direct electrons from the target, photoejected and 'runaway'. Third to arrive are the plasma ions, of all elements present in the target, singly or multiply charged.

A small negative bias voltage on the collector relative to the screen causes electrons ejected from the probe's collector by photons of energy greater than the material's work function to be captured by the screen generating a *positive* output current. The direct electrons with kinetic energy greater than the bias potential will generate a negative output current. Bias voltage has two effects on the arriving plasma front: First, it repels the plasma electrons if their thermal energy is less than the bias potential. Second it attracts the positive ions once they are closer than the plasma shielding length.[21] For plasmas of the densities studied here this length is <<2 mm (the probe (b) collector-to-screen distance). Any electrons not repelled and any negative ions arriving simultaneously with positive ions will cancel the positive ion signal leading to an underestimate of the true ion density with this type probe.

This probe does not distinguish the type of particle explicitly; however, simultaneous optical measurements show that the detailed shape of the ion current waveform often reveals when a new type of ion arrives. It is certain in the case of the screened probe, operated at negative bias, that positively charged ions are responsible for the current after 2 microseconds. This turn-on time gives the maximum velocity of the ions and an indication of the kinetic energy if the ion is identified. This study used optical techniques to provide that identification. Different bias voltages and polarities can also help to elucidate the situation.

The area under the current vs time curve gives the total charge in each pulse. Since this charge is directly related to the ion density, it allows calibration of the optical absorption of an ion in the case where only a single ion type is present. Furthermore, this charge combined with knowledge of the film growth rate can be used to ascertain the percent ionization or ion-to-neutral ratio and this again can be used to calibrate the optical technique for neutrals. Finally, if all conditions hold constant during a film deposition run, the mass per pulse is expected to remain constant, and the film thickness will be proportional to the total charge collected.

2 b. OPTICAL MEASUREMENTS

The laser-ablation plume was examined spectroscopically by both optical emission and optical absorption techniques which have been described in detail elsewhere.[13,14] A pulsed (500 nsec) Xe arc lamp, spectrometer, and optical arrangement (fig. 1) allowed spatially, temporally, and spectrally resolved optical absorption and emission measurements with 1 mm, 2.2 nsec, and 0.04 Å resolutions.

For investigations of the laser-ablation plume, the spectrometer is tuned to the strongest atomic transitions from the ground state of the selected atom or ion. As the laser plume expands from the pellet, it intersects the optical axis with increasing path length and variations in density. The measured absorbance therefore represents an averaged number density over a given path length. The same considerations also apply to the emission from the traveling plume. Temporal profiles of the number density of ground state Y, Ba, Cu, Y^+, and Ba^+ are made by scanning the laser-lamp delay at a given distance from the pellet.

3. RESULTS

The plume density versus time obtained with the optical absorption technique matches that obtained with the ion probe (c) for ablation of a pure Y metal target when multiply charged ions are not generated. This can be seen in Fig. 3 where the late time character of the curves match very closely. The disparity at earlier times is attributed to Y^{++}. Figure 4 shows both techniques applied simultaneously to $Y_1Ba_2Cu_3O_{7-x}$ ablation at high pressure. The ion probe and optical absorption signals differ markedly in long time behavior from the optical emission signal, although all three techniques give similar early time (highest velocity component) results.

The pressure variation data of Fig. 5 show very strong slowing of the ions, and possibly suppression of multiply charged ions above 125 mTorr at 5 cm. Here is an example of the waveform shape revealing a new ion arrival. Optical emission (not shown) indicates that Ba^+ is responsible for the second hump (≈10 microseconds) in the 100 and 125 mTorr traces. Figure 6 shows a near constant slope in the plasma front TOF data giving a velocity of 2×10^6 cm/sec to >7 cm distance in 100 mTorr oxygen. This is in marked contrast to the data at 200 mTorr (and lower laser energy) shown in fig. 7 where the plasma front velocity seems to be falling at an inverse exponential rate and at 5 cm has slowed to 1.2×10^5 cm/sec. We know from optical measurements at 225 mTorr that Ba^+ contributes significantly to the the signal beyond 3 cm (refer Fig. 4), and optical absorption also fails to find neutrals with higher velocities than the ions at these pressure-distance conditions. Therefore the Fig. 7 measurements place an upper limit on the plume velocity and kinetic energy at these conditions. For Ba^+ this gives a kinetic energy of only 1 eV. For lighter particles the resulting kinetic energy is even lower. The Fig. 7 data is taken at an actual film growth condition that produces high quality films (R = 0 ohms above 90 K).[23]

By measuring the area under a curve (similar to Fig. 5 over a longer time interval) taken by probe (b) at 3.9 J/cm^2, 200 mTorr O_2, and 5 cm spacing, the total ion charge collected was determined to be $+6 \times 10^{12}$ unit charges/cm^2. From film thickness measurements divided by the total pulses per film, assuming 100% sticking factor, we can determine that each pulse contained 1.5×10^{14} atoms/cm^2 along the normal to the target at 5 cm. This gives a minimum ionization of 4% at 5 cm in 200 mTorr oxygen.

Careful study of figures 5, 6, and 7 shows that the pressure-distance product does not have a linear effect on the plasma leading-edge velocity nor on the neutralization rate of the ions. It is expected that the different ionic species would behave differently as they penetrate relatively high density stationary gas. The ionization potentials of the elements involved are: Ba = 5.2 V, Y = 6.4 V, Cu = 7.7 V, and O = 13.6 V. An ion moving through stationary matter tends to become neutralized when its kinetic energy falls below its ionization potential.[22] Accordingly it is reasonable to expect the Ba to remained ionized further out in the plume than copper. Assuming elastic collisions of the $^{63}Cu^+$, $^{89}Y^+$, and $^{137}Ba^+$ ions with the near-stationary background $^{32}O_2$ gas molecules, from momentum considerations one can conclude that the velocity change per collision will vary roughly as the inverse of the atomic weight of the ion and as the inverse exponential of the ion velocity. If we assume, under these conditions, a similar number of collisions per unit distance for all three ions, then we can expect the Ba ion at a given velocity to penetrate 137/63 the Cu penetration, and 137/89 the Y penetration.

This seems to be qualitatively correct according to our observations, but such reasoning ignores the inelastic collisions that generate the plume fluorescence and neutralize the ions, collisions between plume species, and the collision cross section of each ion with oxygen. More detailed measurements are needed to develop a quantitative model.

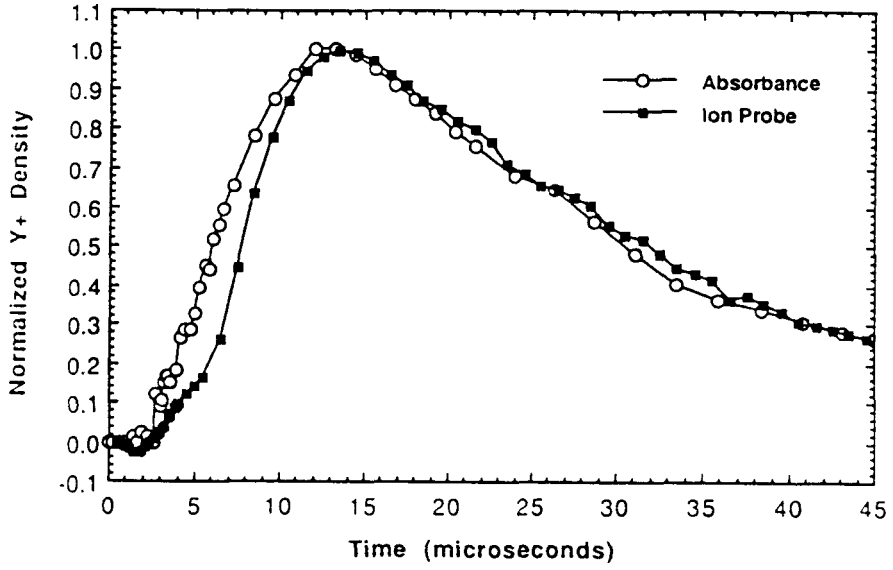

Fig. 3. A comparison between Y^+ ion time dependences as measured by the optical absorption technique and an ion probe following laser ablation of yttrium metal by KrF laser irradiation at 2 J cm^{-2} and 2×10^{-5} Torr. The density-sensitive absorption measurement at d = 3.7 cm and the flux-sensitive ion probe (c) at d = 5.2 cm are TOF-corrected for comparison.

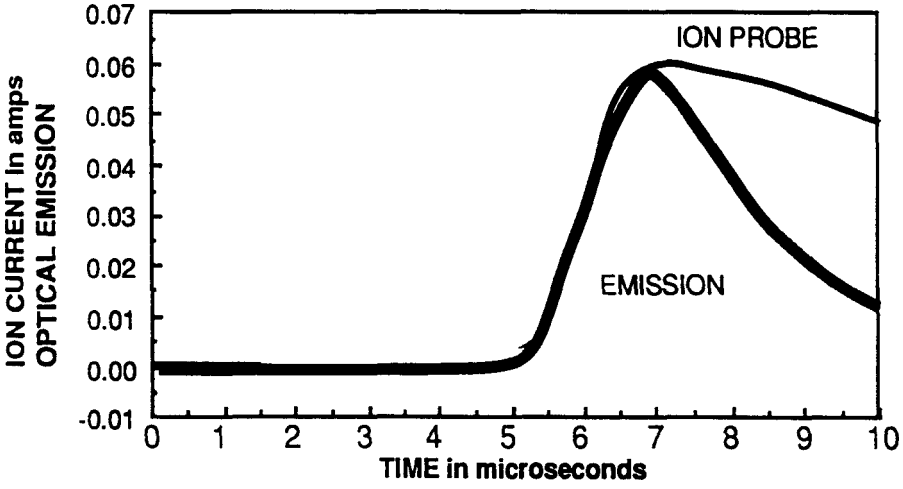

Fig 4. Optical emission at the Ba+ wavelength of 455.42 nm, and screened ion probe (b) signals at 225 mTorr O_2, 3 cm distance, and 2 J/cm^2 laser energy density onto $YBa_2Cu_3O_{7-x}$ target.

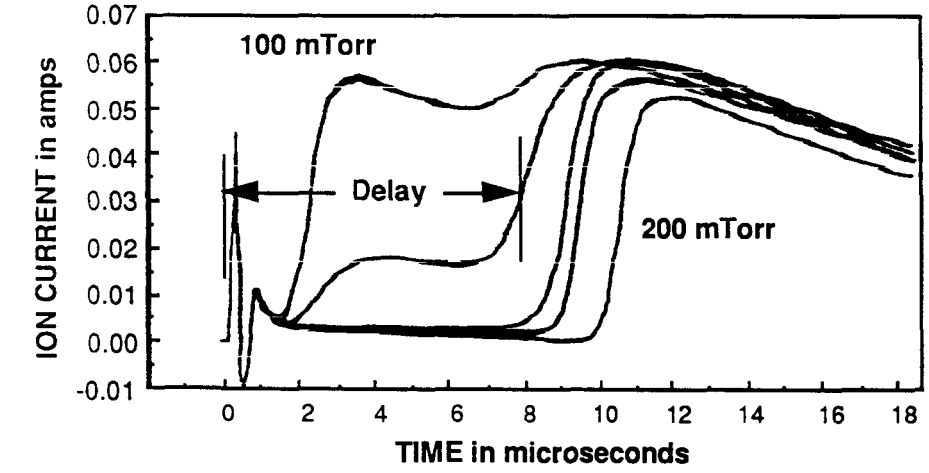

Fig. 5. Ion probe (b) data at 5 cm distance, 3.7 J/cm^2, $Y_1Ba_2Cu_3O_{7-x}$ target and O_2 pressures of 100, 125, 150, 175, and 200 mTorr. The signature of a second ion front at 8 microseconds can be seen at 100–125 mTorr. It is identified optically as Ba^+.

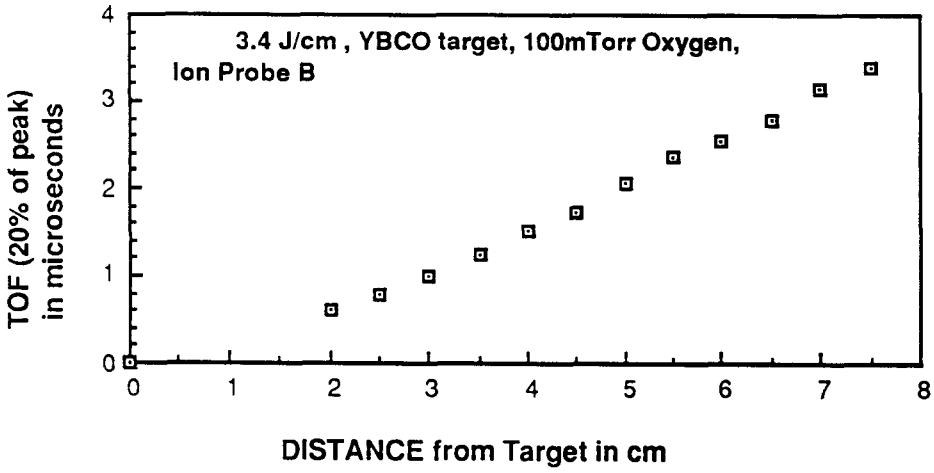

Fig. 6. The plasma front TOF data from ion probe(b) has nearly constant slope to >7 cm, giving a constant velocity of 2 × 10^6 cm/sec .

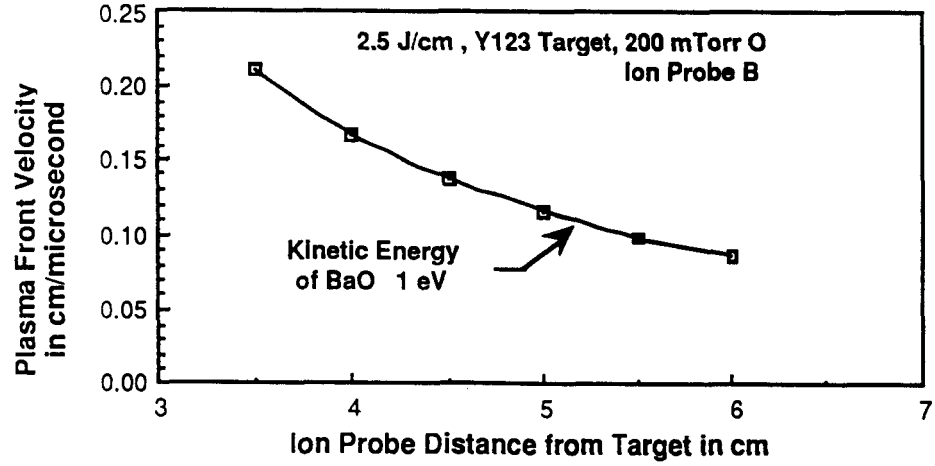

Fig. 7. Plasma front velocities computed for 0.5 cm intervals from ion probe (b) TOF data taken at 200 mTorr oxygen pressure. Delays used in the computations were measured from laser pulse onset to ion current pulse onset at 50% of peak as diagrammed in Fig. 5. Simultaneous ion and optical measurements giving waveforms, not shown but similar to Fig. 4 and 5, verify that this condition selects Ba^+ ions.

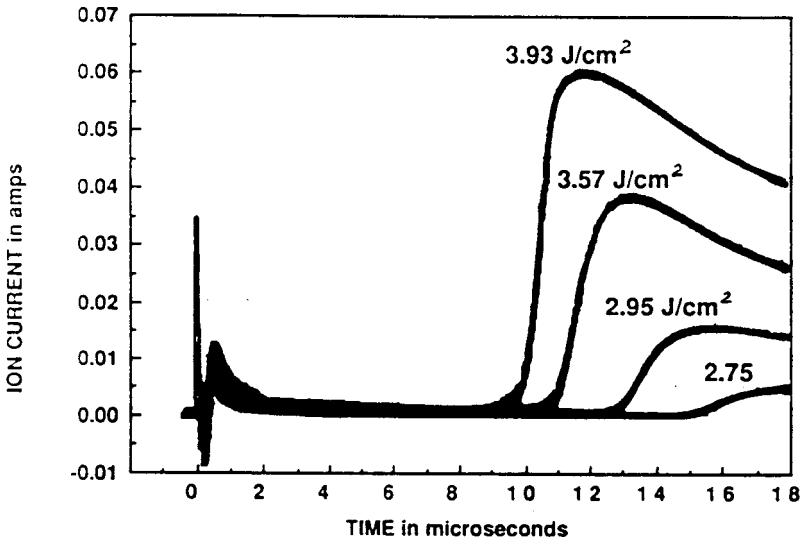

Fig. 8. The laser energy variation data were taken at a distance of 5 cm, a pressure of 200 mTorr oxygen, and varied laser energies at constant focus by attenuating the continuously monitored beam with quartz plates.

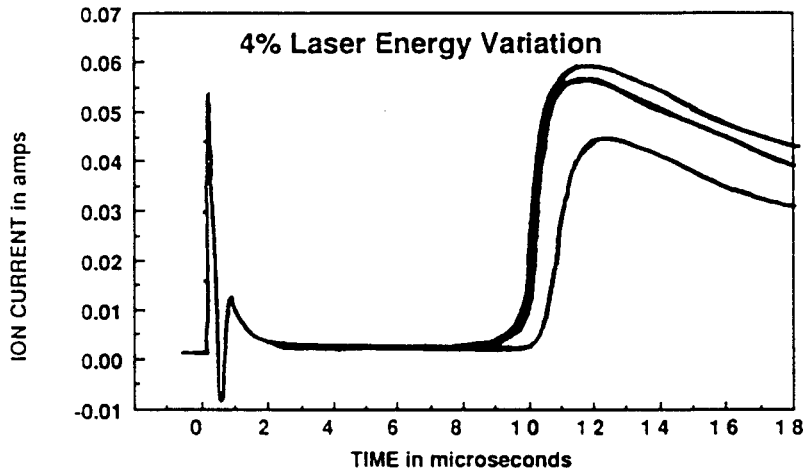

Fig. 9. Shows the effect from a 4 % shot-to-shot variation of the laser energy .

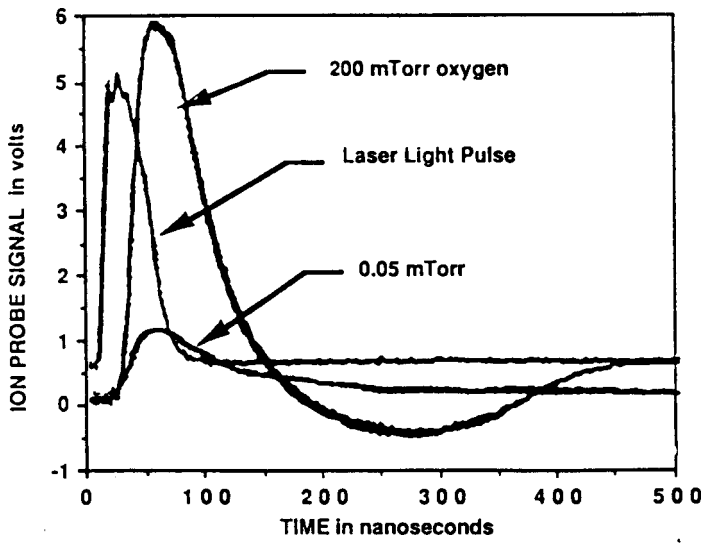

Fig. 10. The photoelectric and direct electron response of the screened ion probe at -6V bias, 5 cm distance, 3.5 J/cm^2 laser energy density, and oxygen pressures of 0.05 and 200 mTorr are compared to the timing reference signal from a 1 nsec rise time vacuum photodiode looking at the KrF laser light reflected from the cylindrical lens closest to the laser. (See Fig. 1.) The 20 nsec offset between the ion probe and photodiode signals is due to instrumental delay and remains constant.

Figures 8 and 9 show how very sensitive the ablation process is to the laser energy and/or the target surface condition. The latter is believed to have remained constant since the target had been ablated >10,000 pulses. This highlights the ion probe's value for ablation mechanism studies. The robust signal from the ion probe, allowing single-shot data acquisition, makes such variation apparent.

The earliest part of the signal in Fig. 10 is generated by photons. This was determined by directing the unfocused laser beam directly into the probe which produced a signal nearly identical to that from the reference photodiode, except for a 20 nsec delay. (All high speed measurements take this delay into account.) In the ablation mode, covering the probe with a quartz plate made little change in the earliest positive pulse while the later features of the signal were completely eliminated. Also it was found that the delay difference between 1 and 15 cm probe-to-target spacing was <1 nsec for this initial positive pulse, implying a velocity approximately that of light. This photoelectric response of the ion probe is useful as an intrinsic zero timing marker for TOF measurement, and as a plume luminosity monitor. Note the tenfold increase in luminosity at 200 mTorr oxygen relative to 0.05 mTorr as shown by comparing the positive areas of the signals.

A clean copper collector plate in probe (b) would only be expected to produce a photoelectric response to light of >4.7 eV/photon or <264 nm wavelength. But since the probe was used in the high density plume where visible deposits occur after a few hundred pulses, we assume that the surface film on the probe includes BaO. The work function of BaO is only 1.4 eV, so that a photoelectric response to light of >800 nm might be possible. Certainly a significant change in the photoelectric response was noted immediately after the coated probe was acid cleaned. More can be learned by making the collector of other materials and coating it with known materials.

The negative part of the signal in Fig. 10 is attributed to direct electrons from the target. The timing variation of this part of the signal is a few hundred nanoseconds for 1–15 cm distance change. The velocity implied by this delay is orders of magnitude less than that of the photons, yet orders of magnitude greater than that of the 'ion' signals of Figs. 5, 8, and 9. It can be seen that the tail of the photon signal and the leading edge of the direct electron signal overlap since the signal does not dwell at zero for any finite time. This overlap confuses attempts to precisely measure maximum electron velocities with this configuration. However , the negative signal peak at 250 nsec indicates a velocity of at least 20 cm/microsecond.

4. CONCLUSIONS

The combination of fast response ion probes and optical absorption or emission measurements allows determination of ion species, velocities, and fluxes. Combining composition and total mass/pulse data from film deposition experience at these conditions, with optical absorption data, allows determination of neutral velocities and fluxes. Thus the charge collection and optical techniques complement each other to produce detailed measurements of the laser ablation transport process. These techniques work up to and beyond the pressures, plasma densities, and distances needed to produce good in situ $Y_1Ba_2Cu_3O_{7-x}$ films, so the results are directly applicable to film deposition work as well to as research on the ablation process. These new measurements show a marked slowing of the plume front and a much longer *non-emitting* but *ionized* tail to the plume under film growth conditions than was heretofore realized.

The simple and inexpensive screened-ion probe gives a robust signal which is sensitive to small changes in laser power, chamber pressure, and target texture, making it a good candidate for process monitoring during film deposition. The optical absorption technique is non-intrusive and can also be used as an in situ monitor during deposition of films by laser ablation.

5. ACKNOWLEDGMENTS

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