Role of temporal delay in dual-laser ablated plumes

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A novel laser ablation process using two lasers of different wavelengths has demonstrated the capacity to grow essentially particulate-free thin films without compromising the ionic excitation and kinetic energy of the plume species. We demonstrate in this article, the critical role of the interpulse delay when a pulsed CO_2 laser spatially overlaps an excimer (KrF) laser on the ablation target during this dual-laser ablation process. At the optimum delay, the excitation and the ionization of the plume were significantly enhanced. The time-of-flight ion probe studies indicate more than a fourfold increase in the ion kinetic energies for this optimized process in comparison to the single-laser ablated plumes. The choice of a suitable delay also facilitates an optimization of elimination of particulate ejection that is typical of single-laser ablation. The morphology of the dual-laser ablated Er-doped Y_2O_3 films deposited on Si substrates as a function of interpulse delay is also discussed.

I. INTRODUCTION

The importance of the laser ablation technique as a method of film growth specially in a reactive ambient environment has been confirmed in its remarkable success in the high critical temperature superconductor film growth.[1–5] In fact, pulsed excimer laser deposition (PLD) outperformed all the other conventional vapor deposition techniques in the fabrication of *in situ* high T_c films. The unique features of congruent evaporation and the production of high energy species that are characteristics of PLD have led to the growth of more than 100 different materials in the thin film form by this technique.[6] Congruent evaporation that takes place under high energy pulsed laser irradiation of materials[7] allows the stoichiometric transfer of the composition of a multicomponent target to the depositing film. Also, the high energy plasma plume produced in PLD, especially by short pulse excimer lasers, improves film crystallinity and allows a reduction of the substrate temperature for epitaxial film growth, while enhancing the gas phase reaction that is essential for most of the nitride and oxide film growth. Experimentally, this is the simplest method available for multicomponent film growth. The fact that a high pressure reactive gas ambient can be tolerated during film growth makes PLD a very attractive method for the growth of films that require the incorporation of a gaseous species into the structure.

However, PLD is not without its shortcomings. Several drawbacks inherent to this technique impede its development as a manufacturing process. During the pulsed laser–target interaction the rapid heating and surface evaporation causes superheating of a subsurface layer that leads to explosive evaporation.[8] The micron and submicron molten particulates ejected from the target are deposited on the substrate leading to defects in the growing film. These particulates are specially detrimental to multilayer structures and for applications as optical films for waveguides and waveguide lasers. This splashing effect is particularly acute in optical film growth as the low absorption coefficient of most of the optical materials at the short excimer laser wavelengths causes a larger sublayer to be superheated. Several particulate removal schemes have been reported.[9] These techniques include the use of mechanical velocity filters,[10] as well as conditioning of a target prior to film growth by resolidifying a 1–2 mm surface layer of the target with a cw CO_2 laser.[11] Although these schemes have shown reduction in particulate deposition, complete particulate removal has not been possible. Additionally, the latter method[11] has been successful only for targets that are highly absorbing at excimer wavelengths. An alternative approach is the reduction of pulse energy to a value just above the ablation threshold.[12] Though beneficial in particulate reduction, this leads to diminished plume excitation.

Furthermore, if the evaporation is carried out in a high ambient gas pressure to increase the gas phase reaction, the decreased pressure gradient across the plume boundary will suppress the plume expansion, while increased collisions will diminish the species energy and thus limit the propagation distance of the plume. These effects will lead to nonuniform film growth and also require high substrate temperatures for epitaxial film growth. We have recently presented a novel dual-laser ablation method that has been successful in overcoming all the drawbacks in the standard single-laser ablation method.[13] The spatial overlap of a CO_2 laser pulse and a KrF laser pulse on the target to be ablated with a temporal delay of 50 ns between the onset of the two pulses produced essentially particulate free films on a substrate without decreasing the desired kinetic energy and ionic excitation of the plume. We present, in this article, the results of experiments that demonstrate the critical role of the interpulse delay in the dual-laser process. The effect of delay is examined both from the point of view of the laser-ablated plume characteristics as well as the morphology of the deposited films.

II. EXPERIMENT

The experimental setup (Fig. 1) is a standard turbopumped excimer laser ablation system with the addition of a pulsed CO_2 laser operated at a wavelength of 10.6 μm. The 248 nm KrF laser pulse had a pulse width of 20 ns, while the CO_2 laser pulse had a duration of 500 ns and a rise time of 125 ns. The two lasers were focused and spatially overlapped on a rotating Er-doped Y_2O_3 target. For the results presented

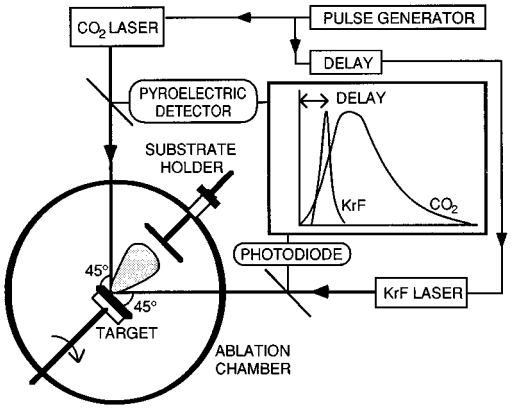

FIG. 1. Schematic diagram of the dual-laser ablation system. The pulse delay between the CO_2 laser and the excimer laser is shown in the inset.

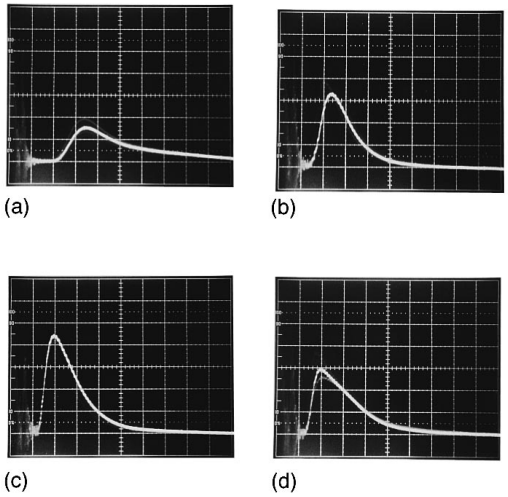

FIG. 2. On axis time-of-flight ion signals of the ablated plume with a target-probe distance of 6.25 cm and 20 mTorr ambient oxygen pressure for (a) single KrF laser alone, (b) dual laser with delay 0 (synchronized at the onset), (c) dual laser with delay 1 (at the rising edge of the CO_2 pulse), (d) dual laser with delay 2 (peaks overlapped). Horizontal scale: 2 μs/div; vertical scale: 0.5 V/div.

in this article the laser spot size used at the target was 9 mm^2, and the laser fluence of the KrF and CO_2 lasers were 1.2 and 3.4 J/cm^2, respectively. The ablation target was prepared by mixing high purity Er_2O_3 and Y_2O_3 powder to obtain 1 at. % Er doping, and subsequently pressing and sintering at 1500 °C for 48 h. The two lasers were triggered through a delay generator with a resolution of 5 ns and an interpulse delay adjustable in the 0–200 ns range. The temporal profiles of the two pulses were directly observed on a fast oscilloscope through a photodiode and a pyroelectric detector, thereby allowing a precise adjustment of the required interpulse delay. The lasers interacted with the rotating target and formed a material plume that propagated normal to the target in a forward-directed manner.

The goal of this work was to study the characteristics of the dual-laser ablated plume as a function of the interpulse delay and to arrive at the optimum conditions for particulate free film growth. The behavior of the plume ionic species were studied by a time-of-flight ion probe experiment. The 2 mm diam shielded ion probe placed on the axis of the plume was biased at −30 V, and the signals were observed on a fast oscilloscope across a 50 Ω terminator. Details of similar ion probe measurements have been previously published.[14] In our experiments, the ionization of the dual-laser ablated plume at different interpulse delays and ambient pressures are compared with that of the single excimer laser ablated plume. Moreover, the enhancement of the emitting excited species under dual laser ablation has been observed by emission spectroscopy. The plume emission was collected normal to the propagation direction and imaged on to an optical fiber of 1.5 mm in diameter. The fiber transmitted the light to a 0.5 m spectrometer equipped with a optical multichanal analyzer (OMA) to detect the spectrally resolved emission. The influence of the dual-laser process on the film morphology, and the role of the interpulse delay in controlling the particulate deposition, was also investigated by depositing the Er-doped Y_2O_3 film on Si substrates. All the depositions were carried out at room temperature, and the film surface morphology was observed using scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

The material plume produced by only the excimer laser at the moderate laser fluences used in our experiment appear to be less excited and more confined in comparison to plumes at high laser fluences. Typically, laser fluences of 2–5 J/cm^2 are used in the single excimer laser ablation of materials to obtain high energy plumes that are conducive to epitaxial film growth. Such film growth is also accompanied by a high density of particulates. However, in the presence of both lasers, the plume excitation and the expansion increased significantly. This increase was noted to be highly sensitive to the interpulse delay between the two lasers. The time-of-flight ion probe signals obtained on the plume axis 6.25 cm from the target at 30 mTorr ambient oxygen pressure are shown in Fig. 2. From Fig. 2(a), which corresponds to the plume produced by the excimer laser alone, the velocity of the leading edge of the expanding plasma is computed to be 0.8×10^6 cm/s. For the dual-laser ablated plume with the onset of the two pulses synchronized in time (delay 0), the peak ion velocity increased to 1.3×10^6 cm/s, accompanied by a 116% increase in the peak ion signal [Fig. 2(b)]. This indicates a coupling of the CO_2 laser energy into the excimer-ablated plume with a resultant increase in the initial plasma temperature that also contributes to an increase in the ion density. As shown in Fig. 2(c), the highest enhancement in the ion velocity and the ion density occurred when the excimer pulse arrived at the target about 50 ns after the onset of the CO_2 laser pulse (delay 1). This corresponds to a triggering of the excimer laser on the rising edge of the CO_2 pulse. The peak ion velocity increased to 1.56×10^6 cm/s with a 200% enhancement in the peak ion density, corresponding to the maximum observed coupling of the CO_2 laser energy into the plasma plume. A further increase in the delay to where the peaks of the two laser pulses are overlapped (delay 2)

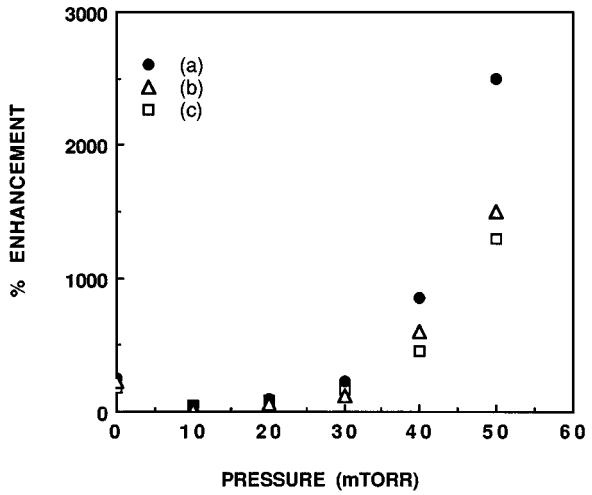

FIG. 3. The peak ion enhancement at different oxygen pressures for (a) delay 1, (b) delay 2, (c) delay 0.

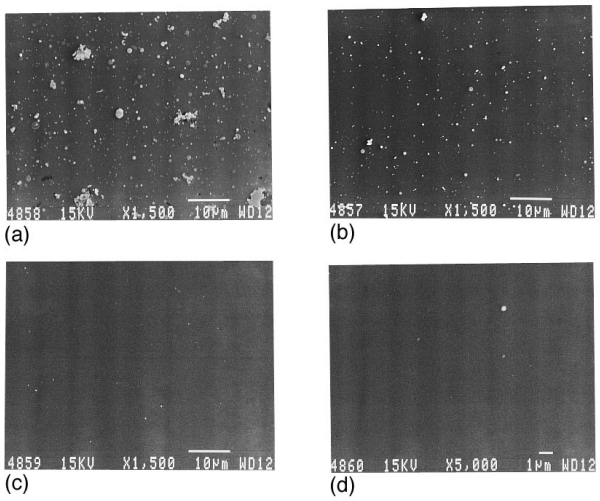

FIG. 5. Surface SEM micrographs of Er-doped films deposited on room temperature Si substrates for (a) single excimer laser, (b) dual laser with delay 2, (c) dual laser with delay 1, and (d) same film in (c) at a higher magnification. The substrate-to-target distance was 6.25 cm and the oxygen pressure was 20 mTorr. All the films are of comparable thickness.

produced similar ion velocities, but the ionic enhancement decreased to 100%, suggesting a reduced coupling of the CO_2 laser into the plasma plume.

The effect of delay on the peak ionic enhancement in the dual-laser ablated plume with respect to its single excimer laser counterpart as a function of the ambient oxygen pressure is shown in Fig. 3 for the three different delays. As shown in this figure, the percent ionic enhancements at all three delays do not differ much up to about 20 mTorr pressure. However, at high pressures the enhancement is much larger for delay 1 than the other delays. The peak ion enhancement for delay 1 reached about 2500% at 50 mTorr pressure. The maximum coupling of the CO_2 laser energy into the plasma takes place at delay 1. As the plume expansion is suppressed with increasing ambient pressure, the collisional ionization within the plume also increases with pressure. Along with the ionic enhancement, the density of the excited species have also been observed to increase under dual-laser ablation. Figure 4 compares the emission spectra of an excimer only plume to a dual-laser generated plume in the spectral range 300 to 500 nm. These spectra correspond to plume emission 1 mm above the target. A significant increase in the emission for some species in the dual-laser process can be observed.

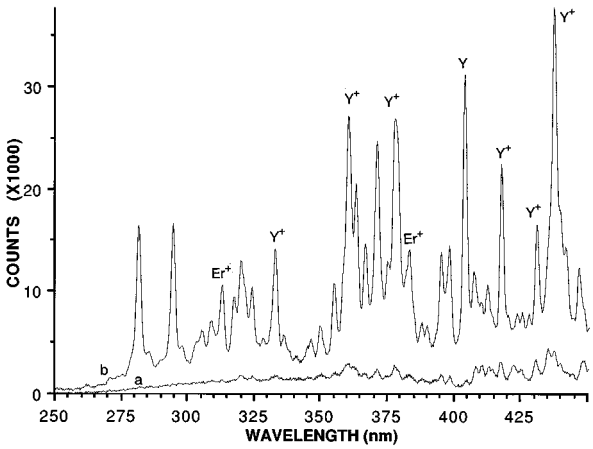

FIG. 4. The emission spectra of the plume 1 mm above the target at an oxygen pressure of 20 mTorr for (a) single excimer laser alone, (b) dual laser with delay 1.

The surface scanning electron micrographs of the films deposited with excimer laser only and with dual lasers are shown in Fig. 5. All the films were deposited under 20 mTorr oxygen pressure and a 6.25 cm substrate-to-target distance, and are of comparable thickness. The film deposited with only the excimer laser [Fig. 5(a)] contains a high density of particulates that is typical of excimer laser ablated films. With the dual lasers at delay 2, where the peaks of the two laser pulses are overlapped, a reduction in the particulate density was observed [Fig. 5(b)]. However, as shown in Fig. 5(c), the film grown under delay 1, where the maximum coupling of the CO_2 laser into the plume was observed, is essentially particulate free. The micrograph in Fig. 5(d) is a magnified image around one of the very few submicron particles in Fig. 5(c). It is clear that the elimination of particulates and the increase in the plume energy as well as the expansion result from effective coupling of the CO_2 laser into the excimer generated plume that occurs at delay 1.

Our experimental result can be explained by dividing the dual-laser ablation into two consecutive regimes. The particulate ejection in PLD result from two mechanisms. The large particulates result from microcracks, pits, and loosely attached particles on the target surface caused by repeated laser pulses.[11] The submicron particulates result from the superheating of a subsurface layer that leads to an explosive evaporation.[12] Particulate ejection by this mechanism is largely dependent on the thermal and optical properties of the target. In the first regime of the dual laser process, the early part of the CO_2 pulse heats the spot on the target. If the excimer pulse arrives after the spot is heated above the melting point but before any ablation by the CO_2 laser (as we have observed[15] for delay 1), the excimer pulse interacts with a molten pool of the material which lack any cracks and pits

that are responsible for the formation of large particulates. In the second regime, the rest of the CO_2 pulse is absorbed into the excimer laser produced plasma by the inverse bremsstrahlung process and screens the target. Since the inverse bremsstrahlung absorption is stronger at longer wavelengths,[16] the CO_2 laser couples into the plume more effectively. Furthermore, intense heating of the plasma by the CO_2 laser tends to reevaporate the submicron particulates in the plasma and at the same time enhance the kinetic energies of the plume species. The enhancement of lateral kinetic energy also results in the observed expansion of the plume under dual-laser ablation.

IV. CONCLUSION

We have developed a novel dual-laser ablation process that overcomes all the major drawbacks in a standard laser ablation method of film growth. In this article we have demonstrated that the dual-laser ablation under the optimum conditions will produce highly excited and ionized plumes with moderate laser fluences. In addition, the plume goes through a rapid expansion that allows large area uniform film growth even at high ambient pressures. A detailed discussion of the plume expansion will be presented in a future publication. To summarize, the dual-laser ablation process under optimum temporal delay facilitates the elimination of the undesirable particulates in the laser ablation process. Furthermore, the enhanced plume excitation and expansion should allow the growth of uniform, large area, high quality films. These features make dual-laser ablation more viable as a manufacturing process.

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