Dual-laser ablation for particulate-free film growth

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A novel dual laser ablation process that leads to particulate-free film growth is presented. A pulsed CO_2 laser and an excimer (KrF) laser have been spatially overlapped on a Y_2O_3 target with a temporal delay between the pulses. The particulate density of the films grown by this method are at least three orders of magnitude smaller than the particulate density of a single excimer laser ablated film of similar thickness. In addition, a time-of-flight ion probe study indicates a sixfold enhancement of the plume species kinetic energies under dual-laser ablation. The degree of the plume excitation is observed to depend strongly on the delay between the laser pulses. © *1995 American Institute of Physics.*

Excimer laser ablation of materials for film growth has gained considerable prominence as a result of the unique advantages offered by this technique over other processes.[1–3] Even though this method has been used predominantly in film growth for electronic applications, its usefulness has also been shown in reactive deposition of multicomponent optical films.[4,5] However, the wide use of this technique in optical device fabrication awaits solutions to some significant drawbacks. One major problem has been the ejection of molten particulates during the laser-target interaction, which is inherent to all pulsed laser ablation processes.[6] These particulates are generally undesirable for multilayer structures and fine line patterning for electronic applications. The optical losses produced by these particulates are of specific concern in optical films for waveguide lasers and optical couplers where the presence of particulates leads to an unacceptable scattering mechanism. Several particulate removal schemes have been reported.[7] These techniques include the use of mechanical velocity filters,[8] as well as conditioning of a target prior to laser ablation by resolidifying a 1–2 mm surface layer of the target with a cw CO_2 laser.[9] Although these schemes have shown reduction in particulate deposition, complete particulate removal has not been possible. Excimer laser heating of the plume produced by a 1.06 μm Nd:YAG laser beam about 2 mm away from the target has demonstrated some reduction in particulate deposition,[7] but the quality of the deposited films using this approach is inferior to that achievable by simple excimer laser ablation. An alternative approach is the reduction of pulse energy to a value just above the ablation threshold.[10] Though beneficial in particulate reduction, this leads to diminished plume excitation. A high degree of excitation in the depositing species is desirable as it leads to enhanced gas phase reaction and better film morphology and crystallinity.[1]

In this letter we report a novel dual laser ablation process that significantly reduces the particulate density on the deposited films, while simultaneously increasing the plume species kinetic energy. This allows the growth of smooth films that are suitable for optical applications.

The dual laser ablation system is schematically depicted in Fig. 1. It comprises a KrF laser and a CO_2 laser that are focused and spatially overlapped on the target. The interpulse delay between the two lasers is adjustable in the 0–200 ns range with a temporal resolution of 5 ns. The 248 nm KrF laser pulse has a pulse width of 20 ns while the CO_2 laser is tuned to the 10.6 μm transition with a pulse duration of 500 ns and a rise time of 125 ns. The spatial overlap of the two laser pulses on the target was adjusted to ensure complete containment of the excimer laser spot within the CO_2 beam profile. The stability of the interpulse delay was monitored using a fast oscilloscope and revealed a temporal jitter of ±10 ns during a typical film deposition.

A Y_2O_3 target was used in our experiments as a representative example of optical materials, characterized by a typically low absorption coefficient at excimer laser wavelengths. The targets were prepared by pressing Y_2O_3 powder and sintering at 1500 °C for 48 h. When the two laser pulses interacted at the target, a significant enhancement in the visible emission as well as an increase in the spatial extent compared to the single excimer laser ablated plume was observed. Since the dynamic behavior of the ions is representative of the species in the plume, an ion probe (in the time-of-flight mode) was used to study the laser-generated plume. The temporal resolution solution of the ion probe signals was 20 ns. Details of similar ion probe measurements have been published previously.[11] The ion signals obtained on the axis of the plume at a distance of 6.25 cm from the target in a 10 mT oxygen ambient are presented in Fig. 2. The signal in Fig. 2(a) corresponds to a plume produced by the excimer laser alone with a laser fluence of 3 J/cm^2 at the target. The peak ion velocity of the plume is $\sim 1.6\times 10^6$ cm/s. When the excimer fluence is dropped to 1 J/cm^2, still above the ablation threshold for Y_2O_3, the peak ion velocity dropped to about 9.7×10^5 cm/s and produced a broader ion energy distribution [Fig. 2(b)]. In the presence of both lasers, the coupling of CO_2 energy into the excimer-produced plasma increases the ion energy. The optimum coupling, indicated by the maximum ion energy, occurred with the excimer pulse arriving at the target about 50 ns after the onset of the CO_2 pulse. Figure 2(c) shows the ion signal when the excimer pulse with a fluence of 1 J/cm^2 is triggered on the rising edge of the CO_2 pulse with a 50 ns delay. The ion distribution is narrower and the peak ion velocity increases to 2.4×10^6 cm/s. This corresponds to a sixfold increase in the plume kinetic energy due to the effect of the CO_2 laser coupling in comparison with the excimer alone.

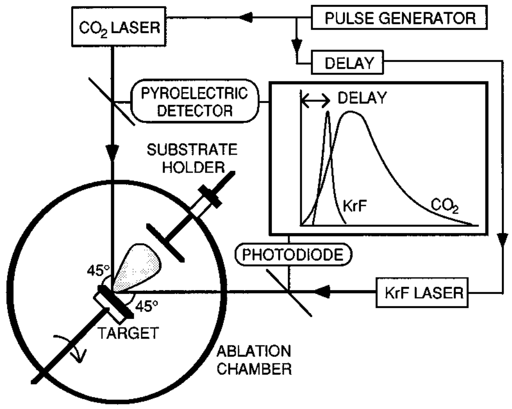

FIG. 1. Schematic diagram of the dual-laser ablation system. The interpulse delay is shown in the inset.

To study the effect of the CO$_2$ laser on the particulate ejection, films of Y$_2$O$_3$ have been grown on Si substrates under the three conditions investigated in the ion probe study, simply by substituting the substrate at the location of the ion probe. Figure 3 presents the SEM surface scans of the Y$_2$O$_3$ films grown under the three conditions. A film grown by only the excimer laser with a fluence of 3 J/cm^2 is shown in Fig. 3(a). In addition to a large number of submicron particles, particulates as large as 2–3 μm are present. When the fluence of the excimer laser was dropped to 1 J/cm^2, a significant reduction in submicron particulates was observed [Fig. 3(b)]. However, as shown in Fig. 3(c), the films deposited with the excimer pulse triggered on the rising edge of the CO$_2$ pulse tend to be extremely smooth with only a few submicron particles present. Figure 3(d) is a low magnification micrograph of the film taken around the same particle in Fig. 3(c). As indicated by this figure, the film contains less than 10^3 particles/cm^2, in comparison to more than 10^6 particles/cm^2 for the single KrF laser ablated film shown in Fig. 3(a). All the films are approximately 0.1 μm thick.

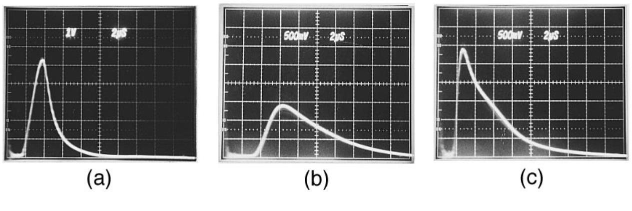

FIG. 2. On axis time-of-flight ion signals of the ablated plume with a probe-target distance of 6.25 cm and 10 mT ambient oxygen pressure for: (a) only KrF laser with a fluence of 3 J/cm^2, (b) only KrF laser with a fluence of 1 J/cm^2, and (c) dual-laser ablation (1 J/cm^2 KrF laser; 3.5 J/cm^2 CO$_2$ laser and 50 ns interpulse delay).

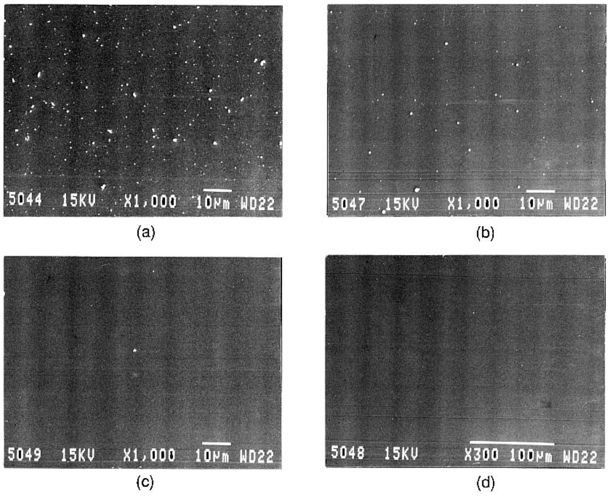

FIG. 3. Scanning electron micrographs of the surface of Y$_2$O$_3$ films on Si substrates, deposited at room temperature and 10 mT ambient oxygen pressure under the following ablation conditions: (a) only KrF laser with a fluence of 3 J/cm^2, (b) only KrF laser with a fluence of 1 J/cm^2, (c) dual-laser ablation (1 J/cm^2 KrF laser; 3.5 J/cm^2 CO$_2$ laser, and 50 ns interpulse delay), and (d) low magnification view around the particle in (c). The thicknesses of all the films are ~0.1 μm.

Our results demonstrate that dual-laser ablation under a suitable choice of inter-pulse delay can produce high energy plumes as well as particulate free films. Ejection of microscopic particulates stems from two mechanisms. Larger particles result from microcracks, pits, and loosely attached particles on the target surface caused by repeated laser pulses.[12] The submicron particulates result from the superheating of a subsurface layer that leads to an explosive evaporation.[13] Particulate ejection by this mechanism is largely dependent on the thermal and optical properties of the target. In the ablation of optical materials the ejection of particulates is more severe due to the poor absorption at excimer wavelengths.

A self-consistent explanation of the dual-laser process is obtained by considering two consecutive regimes for the laser-target interaction. In the first regime, 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 in our experiment), 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 absorption coefficient for this process is proportional to $(Z^3 n_i^2/T^{1/2}\nu^3)\ [1-\exp(-h\nu/kT)]$ where n_i is the ion density, Z the average charge in the plasma, T the plasma temperature, and ν the laser frequency;[14] the absorption is much stronger for the longer wavelength CO$_2$ laser than the excimer laser radiation. 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. The consequent large area uniformity is obtained at a lower deposition rate of about 0.1 Å/pulse compared to the single excimer laser deposition rate of 0.4 Å/pulse.

The dual-laser ablation process facilitates the elimination of undesirable particulates in the laser ablation process, and in addition, the enhanced plume excitation and expansion allows the growth of uniform, large area, high quality films. Since the temporal melt characteristics depend on the temporal profile of the CO$_2$ laser and the interpulse delay, a suitable choice of these parameters should extend this technique to a wide range of materials; thereby, making laser ablation more viable as a manufacturing process.

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[1] J. T. Cheung and H. Sankur, CRC Crit. Rev. Solid State Mater. Sci. **15**, 63 (1988).
[2] R. K. Singh and J. Narayan, Phys. Rev. B **41**, 8843 (1990).
[3] S. Witanachchi, H. S. Kwok, X. W. Wang, and D. T. Shaw, Appl. Phys. Lett. **35**, 234 (1988).
[4] K. E. Youden, R. W. Eason, M. C. Gower, and N. A. Vainos, Appl. Phys. Lett. **59**, 1929 (1991).
[5] S. Witanachchi and P. J. Wolf, J. Appl. Phys. **76**, 2185 (1994).
[6] G. Koren, A. Gupta, R. J. Baseman, M. I. Lutwyche, and R. B. Laibowitz, Appl. Phys. Lett. **55**, 2450 (1989).
[7] G. Koren, R. J. Baseman, A. Gupta, M. I. Lutwyche, and R. B. Laibowitz, Appl. Phys. Lett. **56**, 2144 (1990).
[8] W. P. Barr, J. Plasma Phys. E **2**, 2 (1969).
[9] R. K. Singh, D. Bhattacharya, and J. Narayan, Appl. Phys. Lett. **61**, 483 (1992).
[10] J. T. Cheung, Appl. Phys. Lett. **43**, 255 (1983).
[11] P. Mukherjee, P. Sakthivel, K. Ahmed, and S. Witanachchi, J. Appl. Phys. **74**, 1205 (1993).
[12] D. Lubben, S. A. Barnett, K. Suzuki, S. Gorbatkin, and J. E. Green, J. Vac. Sci. Technol. B **3**, 968 (1985).
[13] R. K. Singh, D. Bhattacharya, and J. Narayan, Appl. Phys. Lett. **57**, 2022 (1990).
[14] J. F. Ready, *Effect of High Power Laser Radiation* (Academic, New York, 1971).