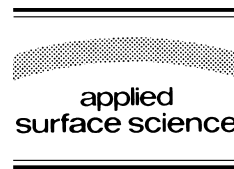




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# Plume expansion and stoichiometry in the growth of multi-component thin films using dual-laser ablation

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## Abstract

The application of dual-laser ablation for the growth of ZnO and multi-component films of  $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$  is presented. Comparison of the optical emission from the ZnO plume under dual-laser and single excimer laser ablation reveals that the coupling of the  $\text{CO}_2$  laser into the excimer laser-ablated plume causes both significant ionic excitation as well as lateral plume expansion. The  $\cos^{21}(\theta)$  thickness profile of the single laser film transforms to a more uniform  $\cos^6(\theta)$  for dual-laser ablation. A comparison of the enhancement of film uniformity at different  $\text{CO}_2$  laser fluences shows that increasing the  $\text{CO}_2$  laser energy leads to greater film uniformity in dual-laser ablation. The advantages of the growth of multi-component materials using dual-laser ablation are demonstrated by optical plume analysis and the deposition of  $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$  films. © 1998 Elsevier Science B.V.

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Keywords: Dual-laser ablation; Stoichiometry; Thin film growth; Solar cells

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## 1. Introduction

Despite the obvious advantages of pulsed laser ablation for thin film growth, it has not been preferred as a manufacturing process primarily because of two limitations. These are (1) a limited area of uniformity in the deposited film, and (2) the deposition of micron and submicron-sized particulates [1,2]. Both these problems were considered to be inherent to the laser ablation process due to the nature of the laser–target interaction, as well as the resultant highly forward-directed plume characteristic of pulsed ex-

cimer laser ablation [3–6]. We have shown that the incorporation of a second  $\text{CO}_2$  laser that is spatially overlapped on the target with the usual excimer laser beam, under conditions of suitable temporal synchronization, leads to the elimination of both the drawbacks associated with single-laser ablation [7]. This dual-laser ablation technique was used to deposit films of  $\text{Y}_2\text{O}_3$ , which exhibited both particulate-free and large-area deposition [7,8]. Even though excellent film quality was obtained in these initial results, two outstanding issues remained to be resolved. These were the applicability of this technique to other materials as well as an investigation of the effects of the inclusion of the second laser on the stoichiometry of multi-component films. In this paper, we report on the extension of our previous

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experiments to the film growth of another oxide material (ZnO) as well as initial results on the application of dual-laser ablation to the growth of multi-component films of  $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$ . Both these materials are of interest in the growth of thin film solar cell devices – the former as a transparent contact, and the latter as a solar radiation absorber.

## 2. Discussion

The dual-laser ablation system used in our experiments has been described in detail elsewhere [7]. Briefly, a 20-ns KrF laser pulse at 248 nm overlapped a 200-ns FWHM  $\text{CO}_2$  laser pulse of wavelength  $10.6 \mu\text{m}$  at the target. The target was a hot-pressed composite comprising the exact stoichiometry desired in the deposited film. Our previous experiments on  $\text{Y}_2\text{O}_3$  have indicated that the following temporal sequence of events took place

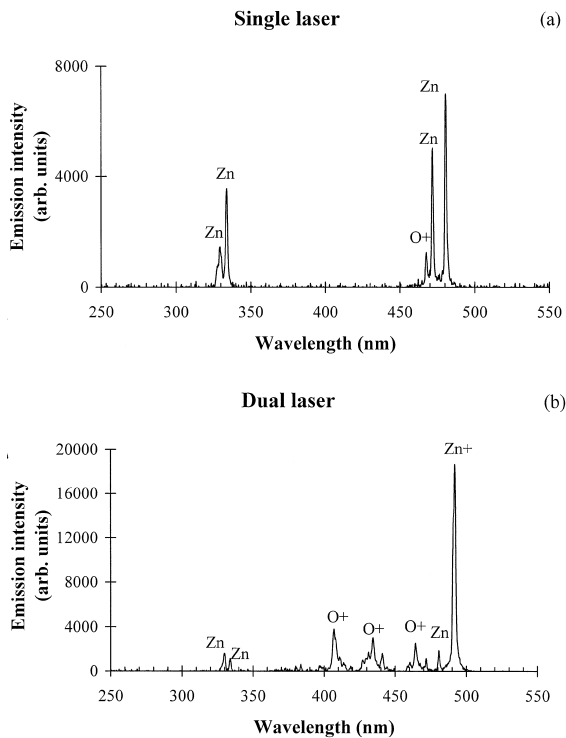


Fig. 1. Time-gated optical emission spectra obtained 3 cm from the ZnO target in vacuum on the axis of the plume for (a) single excimer laser ( $2 \text{ J}/\text{cm}^2$ ) and (b) dual-laser ablation (at a KrF laser fluence of  $2 \text{ J}/\text{cm}^2$  and  $\text{CO}_2$  laser fluence of  $5 \text{ J}/\text{cm}^2$ ).

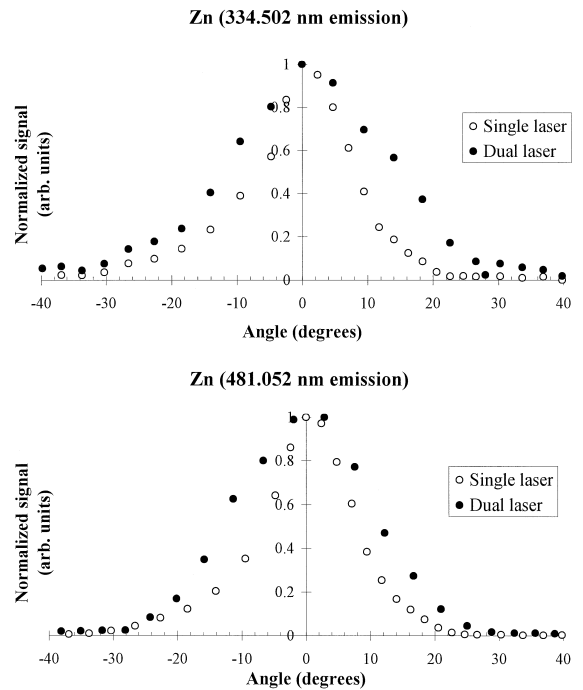


Fig. 2. Angular distribution of two Zn atomic fluorescence intensities from the ZnO target ablated in vacuum using both single- and dual-laser ablation. The distributions are based on radial profiles obtained 6 cm away from the target in an ambient chamber pressure of 10 mTorr of oxygen.

[7–10]. The longer duration  $\text{CO}_2$  laser pulse arrived first on the target surface to locally smoothen the target surface by melting it. The delay between the two laser pulses was controlled in the tens of nanosecond time-scale to ensure the arrival of the excimer laser after  $\text{CO}_2$  laser-induced surface modification of the target followed by optimal coupling of the remaining  $\text{CO}_2$  laser power into the excimer laser-ablated plume. The timing of the pulses on this time-scale should be particularly significant for multi-component targets in order to prevent phase desegregation prior to excimer laser ablation. The dual-laser-ablated plume was incident on a heated substrate to deposit the thin film. In all the experiments reported here, a target–substrate distance of 6.0 cm was used. The  $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$  films were deposited in vacuum while an ambient oxygen pressure of 10 mTorr was used in the deposition chamber for the growth of ZnO films.

The laser-ablated plume was characterized by viewing the optical plume emission perpendicular to

the axis of plume propagation. The plume was imaged onto a translatable optical fiber bundle and spectrally dispersed by a 0.5-m spectrograph prior to incidence on a time-gated optical multi-channel analyzer (OMA) system. Fig. 1 shows time-gated plume spectra obtained on viewing the plume species 3 cm away from the ZnO target along the plume axis. The spectra were obtained using an OMA gate-width of 300 ns at a variety of time delays with respect to the excimer laser. The spectra in Fig. 1 correspond to a time delay of 2  $\mu$ s, at which maximum signal in the 491.162 nm Zn<sup>+</sup> emission was observed for dual-laser ablation. Significantly, no Zn<sup>+</sup> emission is observed in Fig. 1a for the corresponding single laser case. As a matter of fact, no emission from Zn ions was detected for single-laser ablation throughout the 0–25  $\mu$ s range of time delays investigated. The same observation held for the O<sup>+</sup> emissions at 406.990 nm and 434.556 nm. The spectrum in Fig. 1b also indicates the dominant intensity of the ionic zinc emission for dual-laser ablation, which is even more pronounced than evidenced in the depicted spectra when the expansion of the overall dual-laser-ablated plume is taken into account. This plume expansion may be assessed by translating the fiber in the focal plane of the plume image in a direction perpendicular to the plume axis, thereby obtaining radial plume profiles. The 450- $\mu$ m pinhole in front of the fiber combined with the 5:1 reduction in our imaging system provided a plume spatial resolution of  $\pm 1.125$  mm corresponding to an angular resolution of  $\pm 1.07^\circ$  on axis in the radial scan. The OMA gate width was expanded to 25  $\mu$ s to obtain integrated plume intensities. The corresponding angular plume distributions

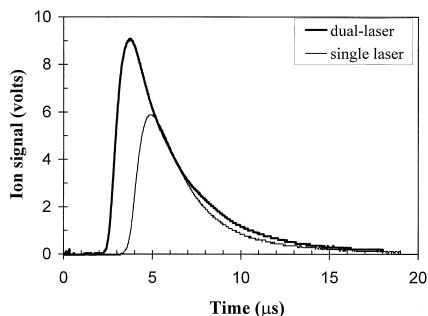


Fig. 3. Time-of-flight (TOF) ion probe signals 6 cm from the ZnO target along the plume axis in vacuum for single and dual-laser ablation.

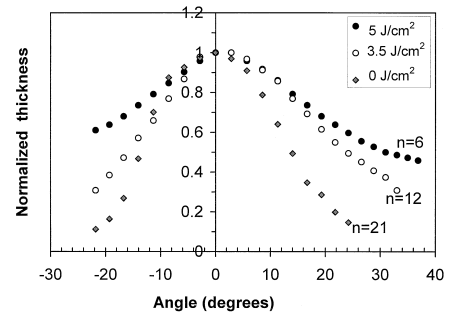


Fig. 4. Ellipsometric thickness profiles for ZnO films deposited in a background oxygen pressure of 10 mTorr at a target–substrate distance of 6 cm for single excimer laser ablation and dual-laser ablation at two different CO<sub>2</sub> laser fluences. The index  $n$  in the  $\cos^n(\theta)$  expansion profile that best fits the data is also indicated in each case.

are indicated in Fig. 2 for two different atomic emissions of Zn. In each case, the single-laser-ablated transverse profile is compared to its dual-laser-ablated counterpart. The distributions in Fig. 2 were obtained at an ambient oxygen pressure of 10 mTorr for comparison with thickness profiles of the deposited films. The radial profiles were obtained by plotting the peak of the corresponding atomic emission signal as a function of transverse position in the plume image. The emission signals recorded include integration of the emission signal along the viewing line-of-sight of the optical fiber. However, at the distances from the target used in our present studies, the plume density is sufficiently low such that reabsorption of the emission within the plume is negligible. The plume expansion for dual-laser ablation is clearly evident – the average cone angle at half-intensity expanding from  $14^\circ$  to  $28^\circ$ . This corresponds to a fractional expansion in area of 4.6. The optical emission from the ZnO plume demonstrates that the coupling of the CO<sub>2</sub> laser into the excimer laser-ablated plume causes both significant ionic excitation as well as lateral plume expansion.

The non-species-resolved ionic content can be investigated by using an ion-probe analysis of the plume. Details of this system have been presented elsewhere [11–13]. Fig. 3 depicts the time-resolved ion probe signals on the axis of the plume 6 cm away from the ZnO target. TOF signals not only confirm the enhanced ionization in dual-laser ablation evidenced in the previously described optical investigations, but also indicate that the bulk of the

enhanced ionization occurs in the leading edge of the TOF signal. This is indicated by the shift of the modal ionic velocity from 1.2 cm/ $\mu$ s for single laser ablation to 1.6 cm/ $\mu$ s under dual-laser excitation. Physically, the TOF signals indicate that the CO<sub>2</sub> laser couples more effectively to the leading edge of the plume.

The efficacy of the dual-laser ablation technique for enhancing the uniformity of the deposited films

is directly assessed by ellipsometric thickness profiles of ZnO films deposited on Si substrates. Films were deposited 6 cm away from the target at an ambient oxygen pressure of 10 mTorr. The three thickness profiles shown in Fig. 4 correspond to the deposition of ZnO films under single excimer laser ablation and dual-laser ablation for CO<sub>2</sub> laser fluences of 5 J/cm<sup>2</sup> and 3.5 J/cm<sup>2</sup>, respectively. In each case, the excimer laser fluence was constant at

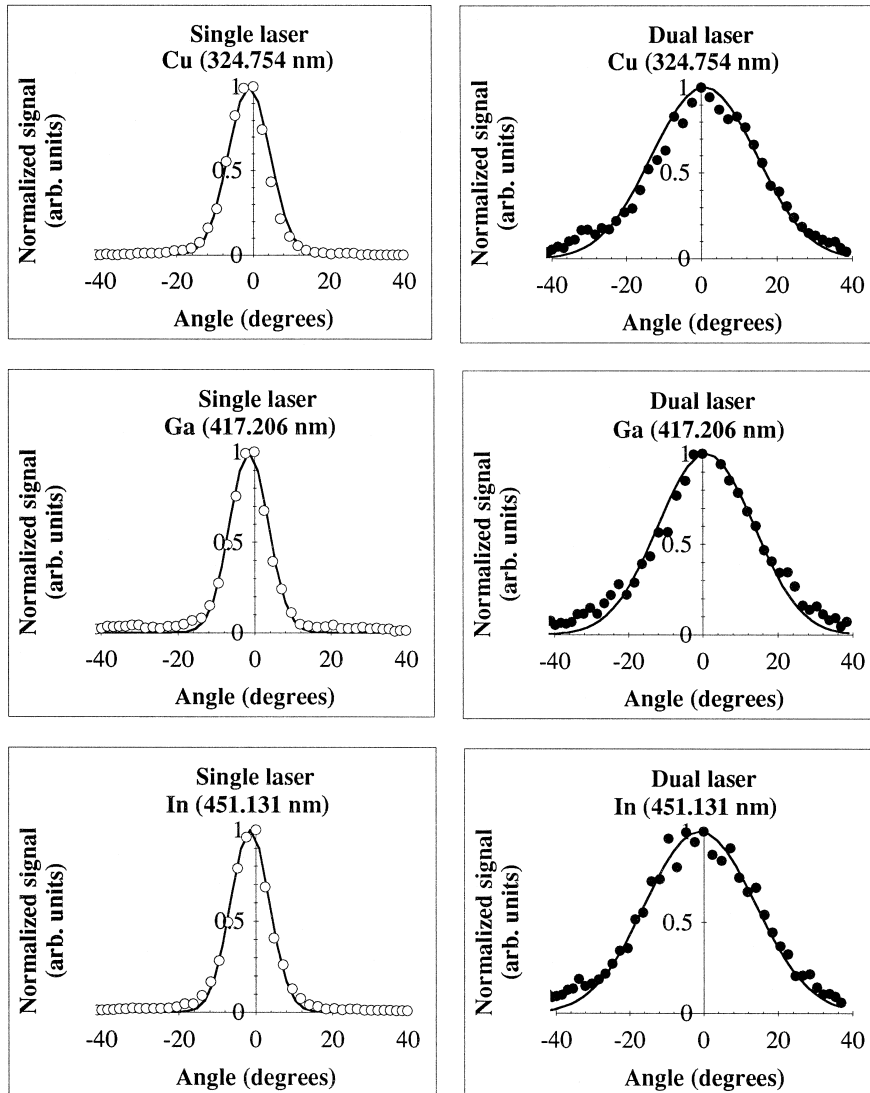


Fig. 5. Angular distribution of Cu, Ga and In atomic fluorescence intensities from the CuIn<sub>0.75</sub>Ga<sub>0.25</sub>Se<sub>2</sub> target ablated in vacuum using both single- and dual-laser ablation. The distributions are based on radial profiles obtained 6 cm away from the target.

2 J/cm<sup>2</sup>. The highly forward-directed  $\cos^{21}(\theta)$  thickness profile of the single laser film transforms to a more uniform  $\cos^6(\theta)$  for dual-laser ablation at the higher CO<sub>2</sub> laser fluence. The corresponding expansion of the area of the film (as assessed by the area over which the thickness reduces to half the value on axis) is a factor of 5.8, even more than the expansion deduced from radial emission profiles of the plume. This suggests that fluorescence expansion profiles underestimate the uniformity of the actually deposited film.

The role of the CO<sub>2</sub> laser energy in the enhancement of film uniformity was investigated by comparing film profiles at two different CO<sub>2</sub> laser fluences. It is obvious from Fig. 4 that increasing the CO<sub>2</sub> laser energy leads to more uniform films. If the plasma density in the excimer laser-ablated plume was above the critical density, increases in CO<sub>2</sub> laser energy would merely result in increased plasma reflection of the excess CO<sub>2</sub> laser energy, thereby not exhibiting any further plume expansion. This is not borne out by our observations implying that the excimer laser-ablated plasma is below the critical density when the CO<sub>2</sub> laser energy is being absorbed. An important operational requirement for enhanced expansion is, therefore, suitable timing of the dual-laser system so that the excimer laser-ablated plume has expanded enough to reduce the plasma density below the critical value prior to the incidence of the peak of the CO<sub>2</sub> laser on the expanding plasma ball. This can be implemented simply by adjusting the inter-pulse time delay to maximize the radial expansion of the visible emission from the laser-ablated plume, as was done in our experiments.

Optical plume analysis and the deposition of CuIn<sub>0.75</sub>Ga<sub>0.25</sub>Se<sub>2</sub> films was used to investigate the application of the dual-laser ablation technique to the growth of multi-component materials. Fig. 5 shows angular plume profiles for three characteristic plume emissions from Cu, Ga and In atoms. The single-laser-ablated plumes show congruent expansion of the three constituents. However, the plume expands significantly in the dual-laser case without compromising the congruency of the expansion – the three atomic emission profiles in Fig. 5 showing almost identical spatial FWHMs. The compositional uniformity of multi-component films deposited by the two techniques was probed directly by EDS analysis

of the films. EDS radial profiles of the ratio of (In + Ga) to Cu indicated that films deposited using single-laser ablation lost stoichiometry rapidly beyond a cone angle of approximately 20°. In contrast, the dual-laser ablation films preserved stoichiometry over a large angular range extending beyond a cone angle of 70°. Since stoichiometric variations were not apparent in the emission profiles, we can conclude that the observed stoichiometric variations in single laser ablation are due to plume–substrate interaction of non-radiating plume species. Presumably, the enhanced radial energy in the dual-laser excitation overcomes this drawback by providing enhanced lateral mobility of atomic species subsequent to incidence on the substrate.

### 3. Conclusion

Our experiments demonstrate that the enhanced plume expansion and ionic excitation previously observed for dual-laser ablation from Y<sub>2</sub>O<sub>3</sub> targets is a universal feature of this technique and generally extendable to other materials. The efficient coupling of CO<sub>2</sub> laser energy to the excimer laser-ablated plume is critically important in effecting this expansion. Specifically for multi-component CuIn<sub>0.75</sub>Ga<sub>0.25</sub>Se<sub>2</sub>, this expansion is observed to promote stoichiometric film growth. These results hold significant promise for the use of dual-laser ablation in the manufacture of large-area, stoichiometric, multi-component films.

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