

# PULSED LASER PROCESSING OF ELECTRODEPOSITED $\text{CuInSe}_2$ PHOTOVOLTAIC ABSORBER THIN FILMS

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## ABSTRACT

In this report we investigate the effects of pulsed laser annealing (PLA) on both as-electrodeposited (ED) and electrodeposited-furnace annealed (EDA)  $\text{CuInSe}_2$  (CIS) samples by varying the laser fluence ( $\text{J}/\text{cm}^2$ ) and number of pulses. Results for as-ED samples indicate that liquid CIS-phase formation during PLA with 248 nm laser is to be avoided as liquid CIS dewets on Mo [1] as well as  $\text{MoSe}_2$ . In the case of EDA-PLA samples, scanning electron microscopy (SEM) images suggest no apparent change in surface morphology but photoluminescence (PL) indicates change in PL yield and FWHM after PLA processing, a possible indication of annealing of defect states. The effects of PLA on defects are further explored using deep level transient spectroscopy (DLTS).

## INTRODUCTION

$\text{CuInSe}_2$  (CIS), a derivative of tetragonal chalcopyrite structure offers a number of desirable properties for use in solar cells. For example it is a direct band gap ( $\approx 1$  eV) material with the highest optical absorption coefficient ( $\alpha \approx 10^5$  /cm) amongst known inorganic semiconductors, a low surface recombination velocity etc. Electrochemical deposition coupled with ns-pulsed laser annealing (PLA) represents an entirely non-vacuum process which could be used for fast and cheaper processing of CIS absorber layers. PLA is very different from furnace annealing (FA) and or rapid thermal annealing (RTA), in that the effective heating time in PLA is of the order of hundreds of ns as opposed to furnace annealing ( $\sim 1000$  s) and RTA ( $\sim 10$ - $100$  s). So in principle the annealing parameters realized in PLA can never be achieved using other annealing processes.

Keeping this in mind we are investigating the effects of PLA on both as-electrodeposited (ED) and furnace annealed (EDA) CIS samples by varying fluence ( $\text{J}/\text{cm}^2$ ) and number of pulses. ED and EDA samples were prepared as in [2]. Energy dispersive X-ray spectroscopy (EDS) on the samples indicates that both as-ED and EDA samples are Cu poor with Cu/In ratio being 0.72 and 0.79 respectively.

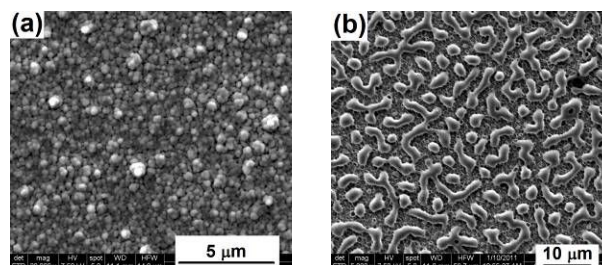
As-ED samples are in the form of nano-crystallites and cannot be used for making solar cells. We attempted to use PLA to improve crystallinity, grow larger grains with less grain boundary area and to synthesize the correct chalcopyrite phase. On the other hand EDA samples have

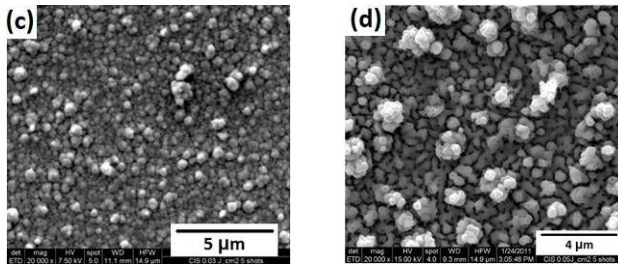
improved crystallinity but because of the low temperature synthesis also have a high density of defect states in the band gap. The high atomic diffusivities during PLA could possibly help in annealing out the defect states via the formation of passivated native defect clusters [3]. Some evidence of improved cell performance after PLA ascribed to reduction of defects at the surface of the CIS layer has been reported earlier. [4]

## RESULTS

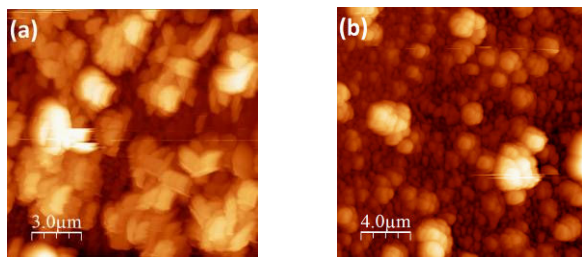
### PLA of As-Electrodeposited (ED) CIS samples

X-Ray diffraction (XRD) results [1] for samples irradiated with 5 shots in the high fluence regime (fluence  $> 0.2$   $\text{J}/\text{cm}^2$ ) for 248 nm laser with 25 ns pulse width indicated increased crystallinity with increasing laser fluence. But scanning electron microscopy (SEM) images demonstrated that the samples dewet in high fluence regime. Furthermore electron back scatter diffraction (EBSD) showed that only the tops of the droplets were responsible for the increased crystallinity seen in XRD. These tops solidified more slowly than the bases (demonstrating that the dominant heat flow was into the substrate) resulting in larger grains. [1]. As liquid phase recrystallization would undoubtedly result in larger grain sizes, an attempt was made to prevent dewetting by introducing a thin  $\text{MoSe}_2$  layer as the back contact instead of Mo. For this the Mo coated glass substrate was annealed in Se atmosphere at  $500^\circ\text{C}$  for 20 min, resulting in a thin  $\text{MoSe}_2$  layer which is known to form an ohmic contact with CIS absorber layer. Unfortunately these samples also dewet (Fig.1 (b)). In the low fluence regime (fluence  $< 0.2$   $\text{J}/\text{cm}^2$ ) there is evidence of surface melting (Fig.1 (d)) which causes reduction in RMS roughness value of the sample (Fig.2). However no improvement in crystallinity is observed in XRD data (not shown).





**Fig. 1:** (a) As-ED sample, (b) sample dewetting observed at  $0.3 \text{ J/cm}^2$ , (c) No change in surface morphology at  $0.03 \text{ J/cm}^2$ , (d) Apparent surface melting at  $0.05 \text{ J/cm}^2$ . All SEM images (b, c, d) for samples processed with 248 nm laser and 5 shots.

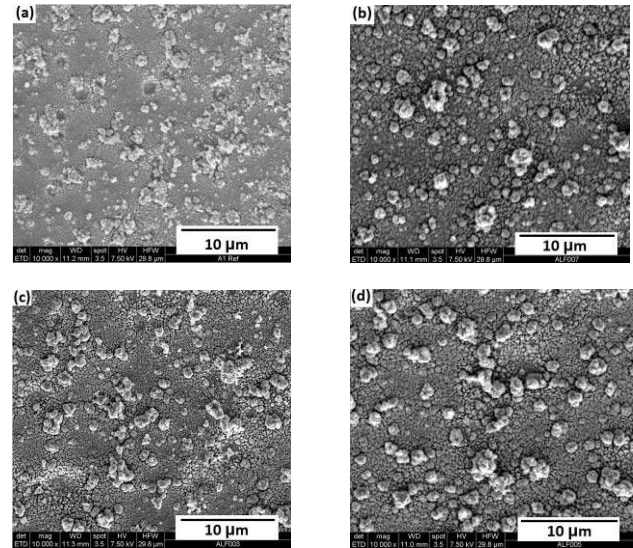


**Fig. 2:** AFM images for (a) As-ED sample (RMS roughness: 205 nm), (b) Sample processed at  $0.05 \text{ J/cm}^2$  (RMS roughness: 160 nm).

Thus we conclude that processes utilizing the laser to drive solid-state diffusion and reaction would offer more possibility. Also by using longer wavelength laser CIS film could be uniformly heated and thus surface melting could be avoided. This is because of the larger optical absorption depth of IR photons (e.g. 500 nm at  $\lambda = 1064 \text{ nm}$ ) as opposed to 248 nm UV photons which have very low optical absorption depth ( $\sim 10 \text{ nm}$ ) and thus deposit all of the pulse energy within the near surface region causing surface melting even at low fluence where the entire film is not heated significantly.

### PLA of electrodeposited-furnace annealed (EDA) CIS samples

EDA samples are processed in low fluence regime (fluence  $< 0.2 \text{ J/cm}^2$ ) using 248 nm laser having 25 ns pulse width. SEM images (Fig.3) suggest no change in surface morphology in low fluence regime. However narrowing of the (112) X-ray diffraction peak was observed after PLA, which is consistent with the results reported elsewhere [4, 5].

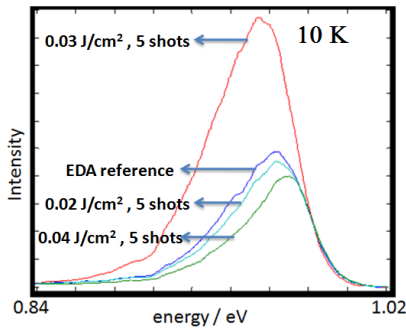


**Fig. 3:** (a) EDA sample, EDA-PLA sample processed at (b)  $0.02 \text{ J/cm}^2$ , (c)  $0.03 \text{ J/cm}^2$ , (d)  $0.04 \text{ J/cm}^2$ . All samples (b, c, d) are processed with 248 nm laser and 5 shots.

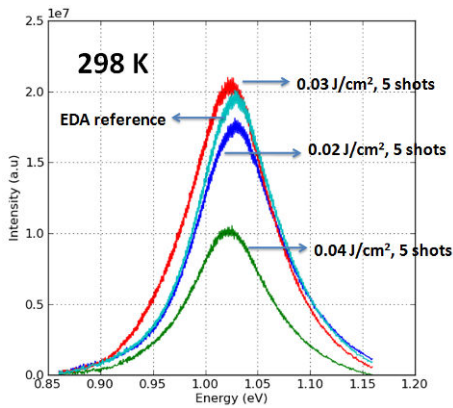
It is known for  $\text{Cu(In,Ga)(S,Se)}_2$  family that surface states are detrimental for device performance as they act as non-radiative recombination centers. Evidence of increased mobility, carrier lifetime and cell efficiency was reported after PLA in [4]. Since we are using 248 nm laser which has a low optical absorption depth it could possibly be annealing out those surface states and help in formation of electrically neutral defect clusters. Photoluminescence (PL) spectroscopy was used to investigate any laser induced changes in defect states. The PL spectrum is a result of all possible radiative transitions; these can be band to band or involve shallow defect states present in the band gap. While the room temperature PL spectra is dominated by band to band (BB) transitions, the low temperature PL spectra results from various transitions taking place between two shallow states such as donor-acceptor-pair (DAP) or band (free) to a bound shallow state (FB) or excitonic transitions. [6]

Fig (4) and Fig (5) show the PL spectra from the samples taken at 10 K and 298 K respectively. Since our samples are polycrystalline we don't expect to see excitonic transitions, so the PL spectra in Fig.(4) is a result of the other radiative transitions taking place at low temperature. As can be seen from Fig.(4), the sample laser annealed at  $0.03 \text{ J/cm}^2$  shows a broader and relatively higher luminescence yield as compared to the EDA and other PLA samples. A broader spectrum is an indication of compensation of the samples possibly because of an increased concentration of shallow defects, while the higher luminescence probably indicates annealing of surface states leading to an overall increase in number of radiative transitions. A similar evidence of reduced surface states is given by an increase in photoconductivity reported for single crystal CdTe samples after PLA using a

694 nm laser. [7] This enhancement was attributed to a decreased surface recombination rate because of removal of oxygen and annealing of structural imperfections. Similarly, X-ray photoelectron spectroscopy (XPS) on our EDA-reference and the sample laser annealed at  $0.03 \text{ J/cm}^2$  suggests removal of oxygen from the surface layer after PLA (data not shown). Fig.(5) shows a similar trend in the PL yield to what we observe at low temperature, the only difference being the data at 298 K is result of BB transitions. In general the higher the luminescence yield, the better the absorber layer. So the data shows evidence that the PLA process can reduce non-radiative recombination in the CIS samples.



**Fig. 4: 10 K PL spectra for EDA samples after PLA at varying fluence.**



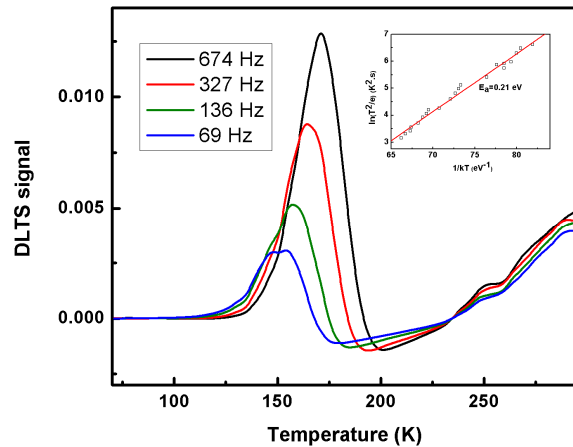
**Fig. 5: 298 K PL spectra for EDA samples after PLA at varying fluence.**

Although we do see changes in PL spectra after PLA more statistics need to be collected and we have begun to investigate the effect of PLA on epitaxial grown CIS samples. Preliminary measurements suggest similar improvement in the optoelectronic quality of the film. The optimum fluence required for absorber improvement depends on the sample quality and its processing history.

Since the PL spectroscopy yields information only about the changes in shallow level defects we need to study the samples using a complementary technique that probes the deep levels which are detrimental for device performance

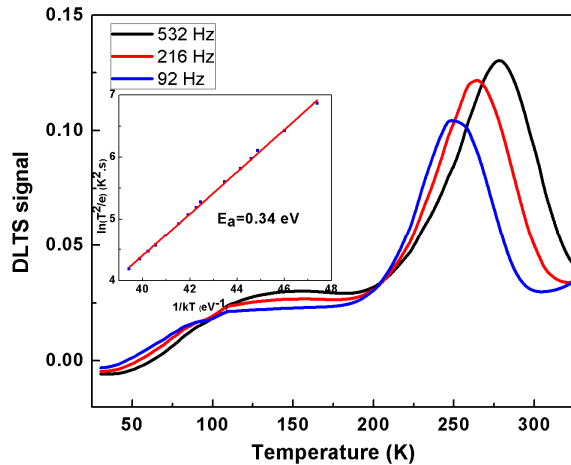
according to Schokley-Read-Hall recombination theory. [8] Deep level transient spectroscopy (DLTS) is a technique that relies on measuring the capacitance transient following a voltage pulse and can identify the activation energy of deep states. [9] The sign of the capacitance transient is very important as it determines whether the signal from majority or a minority carrier trap is being measured. For a properly-measured sample the sign of capacitance transient due to a majority carrier trap will always be negative while the opposite is true for minority carrier trap.

In order to examine our samples we have prepared Schottky barrier diodes by depositing Al-metal (150 nm thick) on CIS absorber films using electron beam evaporator. Before evaporating any Al, all the samples are KCN etched (5% wt. soln.) in order to remove any  $\text{Cu}_x\text{Se}_y$  phases or surface contamination (if present). Fig.6 shows the normalized DLTS signal plot for EDA reference sample. The peak position propagates to different temperature for different rate windows [9]. A linear fit through the maxima of all the peaks yields a straight line, the slope of which determines the activation energy of the trap. In this case the activation energy of the trap as determined from the Arrhenius plot is found to be at 0.21 eV. Since the capacitance transient is negative for the sample it is a majority carrier trap. On the other hand the activation energy for the sample laser annealed at  $0.03 \text{ J/cm}^2$  is determined to be 0.34 eV and is also seen to be a majority carrier trap. In order to make sure we were measuring the signal from the majority carrier trap, a resistor of  $1\text{k}\Omega$  was inserted in series with the samples and the reversal of capacitance transient was observed at the concerned temperatures. [10] Because of large diode leakage currents we were not able to extract meaningful data for the samples annealed at  $0.02 \text{ J/cm}^2$  and  $0.04 \text{ J/cm}^2$ . We are currently further investigating the effects of the laser on the defect states and population.



**Fig. 6: Normalized DLTS signal at different rate windows for the EDA reference sample. Inset shows the Arrhenius plot for determining defect activation energy.**





**Fig. 7: Normalized DLTS signal at different rate windows for the sample annealed at 5 shots of 0.03 J/cm<sup>2</sup>. Inset shows the Arrhenius line plot for determining defect activation energy.**

### SUMMARY

We have found that melting should be avoided during laser processing of as-ED CIS on top of both bare Mo and MoSe<sub>2</sub> because the CIS films dewet. The PL measurements at 10 K and 298 K indicate changes in PL yield and FWHM for PLA samples. This could possibly be an indication of annealing of surface defects which act as non-radiative recombination centers and are detrimental to device performance. DLTS results also suggest changes in defect states after PLA but the physics of the induced changes is not fully understood and a detailed study is under progress to pin down the intricacies of the process.

### ACKNOWLEDGEMENTS

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