

Intense Pulsed Light Processing of Semiconductors for Photovoltaics

T. Druffel* and R. Dharmadasa**

*Conn Center for Renewable Energy Research, University of Louisville,
Louisville, KY, USA thad.druffel@louisville.edu

**Conn Center for Renewable Energy Research, University of Louisville,
Louisville, KY, USA ruvini.dharmadasa@louisville.edu

ABSTRACT

Thin film solar cells typically require post-growth heat treatment to improve the materials properties. In order to manufacture market competitive solar cells, material processing methods with low capital and running costs are required. One method for achieving this goal would be to use atmospheric processing techniques with a high throughput. Here we report the use of Intense Pulsed Light (IPL) to process cadmium sulfide (CdS) and cadmium telluride (CdTe) thin films. IPL is an ultra-fast technique for the heat treatment of materials. Pulses of light from the UV to IR wavelengths are absorbed by the material, leading to localized heating and sintering. IPL has been used to successfully make Cu electrical contacts for use in electronic circuits, however little work exists on the use of IPL in the processing of semiconductor materials. The effect of energy input and the energy density (ED) of the pulse on the films optical, compositional and morphological properties of the films were investigated using UV-Vis spectroscopy, X-ray diffraction, photoluminescence and scanning electron microscopy. These analytical results are supported by computational analysis of the thermal response within the films. IPL sintering resulted in significant improvement to the crystallinity with processing times of less than 2 minutes.

Keywords: intense pulsed light, semiconductors, CdS, CdTe

1 INTRODUCTION

There has been a very strong push in the past decade to deliver solar energy at economically competitive prices. In a large part this has been carried out through unsustainable revenue models that rely on significant reductions in acceptable margins and large government subsidies towards capital equipment. These tactics will ultimately lead to consolidation of the industry in the next few years and stifle innovation as a predominant technology prevails. The industry desperately needs solutions that have manufacturing capabilities more in-line with large area production such as roll-to-roll printing. Devices that can be produced using existing capital equipment offer opportunities to the industry for acceptable margins without the need for huge capital expenditures leading to revenue

positive manufacturing further enabling the cost competitiveness of solar energy.

Roll-to-roll coating typically involves the deposition of liquid inks that may or may not include a solvent that must be removed. Nanoparticles are easily incorporated into these inks especially to impart optical, electrical, chemical and mechanical properties to the deposited films. A variety of techniques exist for manufacturing nanoparticles (liquid and gas phase) and making stable ink dispersions using surfactants and surface ligands. However, for photovoltaic (PV) applications small grain sizes and organic molecules will lead to poor performance. Thus the deposition of inorganic nanoparticle thin films for PV using traditional printing techniques often requires downstream high temperatures as well as other processes, such as noxious or inert environments. These often counteract the cost savings of utilizing printing techniques, and usually cannot be accomplished with polymer substrates.

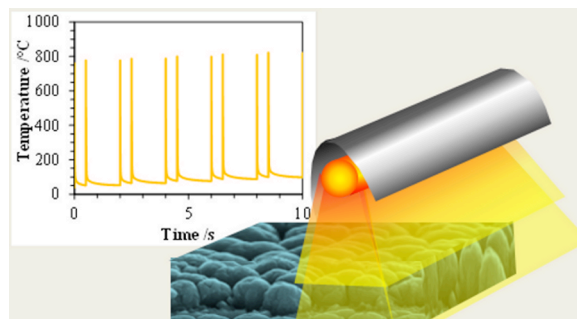


Figure 1. Schematic of the proposed IPL process in which intense light pulses over a large area induces localized temperature rises.

To overcome these we have been studying an intense pulsed light technique to process the nanoparticle thin films for PV. The IPL technique delivers high-energy light in a very short duration over a large processing area, heating thin films containing photosensitive NPs. Sufficient heat is produced within the thin film for consolidation of NPs (Figure 1). The method is analogous to additive manufacturing techniques that utilize infrared lasers to locally sinter powders; however, IPL uses a broader spectrum of light and the processing area is far larger thus is simpler to apply toward economically feasible

manufacturing. Furthermore, the production of NPs can be accomplished in upstream processes that are simpler to scale up and deposit onto substrates using traditional solution printing techniques. The outcome for large-scale PV manufacturing will be reduced capex and O&M costs, which are critical for achieving cost parity while returning manufacturers to profitability.

2 RESULTS

We have investigated the use of the IPL technique using CdS¹ and CdTe² semiconductors. In this paper we will discuss the results of this processing using several tools such as UV-Vis spectroscopy, X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM) and photoluminescence (PL). We have validated that the IPL process is capable of imparting a morphology change to the deposited nanoparticle films.

2.1 CdS

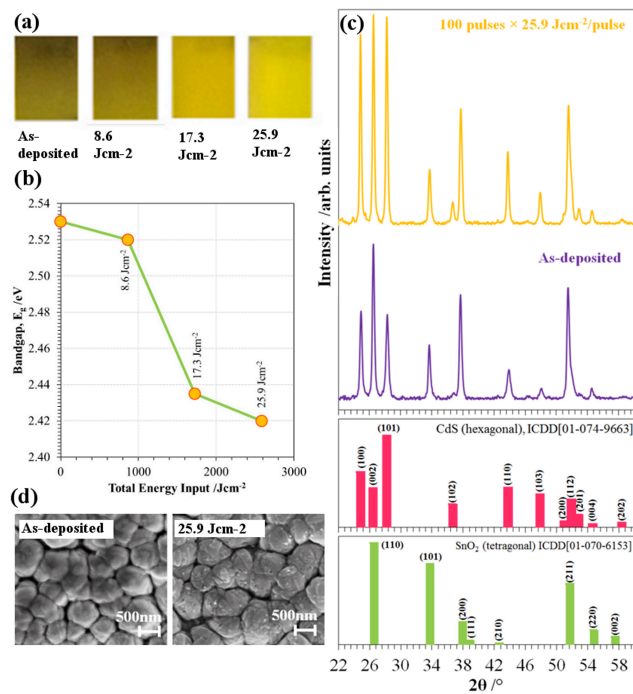


Figure 2. (a) Photos, (b) bandgap, (c) XRD patterns and (d) SEM images of CdS thin films.

Our preliminary studies using IPL processing of CdS has focused on thin films (500 nm) of CdS grown using cathodic electrochemical deposition from aqueous baths.³ (Although a PV device requires ~ 50 nm film, a thicker film was chosen for this study) This study concentrated on the response of CdS NP films using different ED varied from 8.6 to 25.9 Jcm⁻² at a prescribed frequency (1 pulse per second) and pulse duration (1 ms) over 100 s. Figure 2 shows the effect of IPL on the optical properties. The as-deposited films initially appeared a dark green-yellow due

to unreacted cadmium in the films and displayed a relatively small light transmittance. In traditional heat treatment, unreacted cadmium and sulfur in the film are thought to react to form CdS, and the cadmium is also believed to form CdO when the film is treated in air.³ Figure 2 shows that a pulse energy of 8.6 Jcm⁻², was insufficient to raise the temperature high enough for the unreacted elements to be completely converted to CdS as evidenced by the lack of change in the coloration or the E_g of the samples. Increasing the pulse ED to 25.9 Jcm⁻² resulted in a change in the film color (Fig 2(a)) and shift in the E_g (Fig. 2(b)). The decrease in E_g and an increase in the optical absorption is an indication of an increase in both the lattice constants and grain size.⁴⁻⁵ XRD was used to determine the phase and crystallinity of the CdS (Fig. 2(c)). The XRD patterns show that IPL treatment improved the crystallinity of the films; with significant growth in the (100) and (101) crystalline planes and a decrease in their full width at half maximum (FWHM) values. This result indicates that IPL treatment is inducing lateral particle growth. The samples treated with an ED of 8.6 Jcm⁻² pulses showed little improvement in the crystallinity. In IPL, the initial absorption of light by the material creates localized heating and melting. This effect initially leads to disorder within the crystal lattice, before the atoms rearrange into more crystalline structures. If the energy supplied to the material is too low, the sample will cool before it has time to reorganize. Therefore, the observation of un-reacted cadmium in the samples and the small changes to crystallinity indicates that an ED of 8.6 Jcm⁻² per pulse is close to the minimum energy required to treat CdS. The SEM images of the as-deposited and IPL treated CdS film using pulses with an ED of 25.9 Jcm⁻² show that the aggregates in the film appear to have grown laterally and merged with neighbors (Fig. 2(d)). However, the film also shows small bright and dark areas on the surface, as a result of the surface temperature becoming too high during processing, which changed the stoichiometry of the film. Reducing the IPL process to 26 seconds at an ED of 25.9 Jcm⁻², total energy input of 860 Jcm⁻², resulted in similar changes to the morphology of the CdS films treated for 100 s at 17.6 Jcm⁻², total energy input of 1760 Jcm⁻². Further work needs to be done to understand and optimize this process for a thinner CdS film, in order to reduce defects in the film using shorter process times.

2.2 CdTe

Our preliminary studies using IPL processing of CdTe has focused on thin films (400 nm) grown using cathodic electrochemical deposition from aqueous baths.³ (Thin film PV requires films up to 2 microns; however, a thinner film was chosen for this study) The optical E_g of the films was found from Tauc plots of (ahv)² vs. hv. The as-deposited films showed a E_g of 1.47 eV and demonstrate a very slight decrease to 1.46 eV after pulses with an ED of 25.9 Jcm⁻² were applied, which was close to the literature reported E_g

for bulk CdTe.⁶ The as-deposited CdTe film has a good match to the crystalline planes of cubic CdTe (ICDD 01-015-0770). These films also displayed a preferential orientation towards the (111) crystal plane. Figure 3 (top left) shows the plot of the $(111)_{\text{IPL}}/(111)_{\text{as-deposited}}$ ratio vs. the total energy input during IPL treatment. Similarly to the CdS results, XRD showed that when pulses with an ED of 8.6 Jcm^{-2} were applied to the film, the crystallinity of the films decreased slightly. A significant increase in crystallinity of the CdTe and decrease to FWHM values were observed for the reflections treated with an ED of 21.6 Jcm^{-2} . Increasing the ED of the pulses further resulted in a decline in the crystallinity. This effect is an indication that the temperature in the films became high enough to initiate the loss of Cd from the film. The films continued to demonstrate a high preferential orientation towards the (111) crystal plane after IPL treatment.

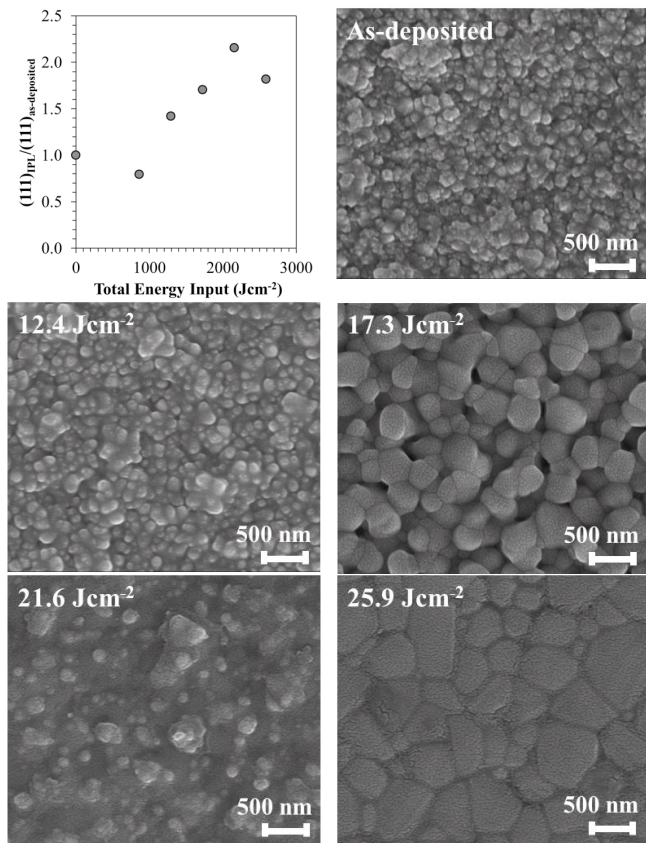


Figure 3. (top left) Ratio of peak intensity $(111)_{\text{IPL}}/(111)_{\text{as-deposited}}$ vs. total energy input and SEM topographical images of as-deposited and IPL treated CdTe film using 100 pulses with an energy densities of 12.9, 17.3, 21.6 and 25.9 Jcm^{-2} .

Figure 3 also shows the SEM topographical images of as-deposited and IPL treated CdTe at varying ED from 12.4 to 25.9 Jcm^{-2} . During IPL, pulses with low EDs less than or equal to 12.9 Jcm^{-2} generate sufficient energy for the recrystallization process to begin. Under these conditions, a

small degree of particle growth was also observed, where the smaller particles undergo solid state surface diffusion. The results show that when the total energy input exceeds 1290 Jcm^{-2} , a sharp increase in the particle size was observed. At this point, melting of the particles was observed. Interestingly, when an ED of 21.6 Jcm^{-2} was used, the surface appears to have melted into an almost continuous surface, making it difficult to calculate the particles size. CdTe in its bulk form is known to have a melting point of approximately 1100°C .⁷ The unique features observed in Figure 3 are an important development for thin film solar cells. The film appeared to have formed a continuous layer on the surface that embeds smaller particles within the film. This is the first reported IPL processing of CdTe and significant due to the formation of a continuous layer. Further study is required to understand how thicker films of CdTe will behave and to optimize parameters for manufacturability and application in PV field.

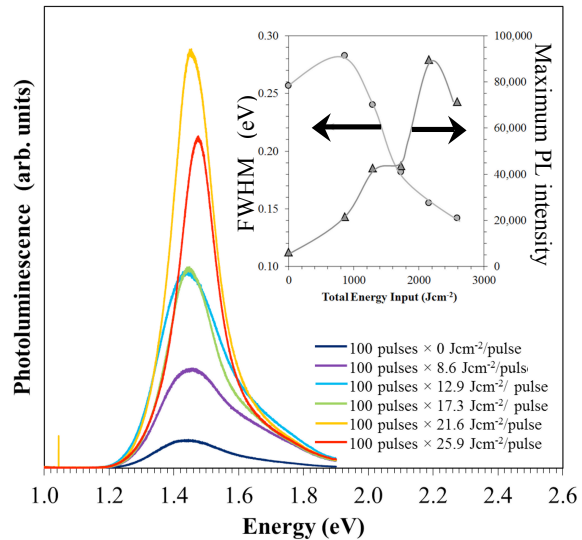


Figure 4. Room temperature photoluminescence (PL) of as-deposited and IPL treated CdTe.

Figure 4 shows the room temperature PL spectra for the as-deposited and IPL treated electrodeposited CdTe layers in the energy range of 1.0 to 1.9 eV. The signal observed for the as-deposited layer has broad peak with a low intensity. This indicates the presence of a large number of shallow donor and acceptor type defects in the material. As a result, the band to band emissions showing the E_g are low, and both high and low energy photons are emitted producing a weak and broad signal. As the layers are IPL treated, the band to band emissions were also observed to increase. The FWHM also reduced showing the best results an ED of 21.6 Jcm^{-2} (Fig. 4 inset). Photon emissions below the E_g are reduced due to the reduction of donor and acceptor like defects in the material. Photons emitted with energy greater than the E_g decreased due to coalescence of nano-sized particles into large grains, thereby reducing the quantum effects. Treatment with higher energy pulses (25.9

Jcm⁻²) displayed a reduction in band to band emissions reducing the peak intensity and a slight shift to higher energies. These PL results are important to understand how IPL impacts the defects; however, more investigation is required.

3 CONCLUSIONS

We have shown that the IPL process can be used to change the morphology of deposited nanocomposite film of CdS and CdTe. The process is extremely fast and can be incorporated into roll-to-roll schemes using polymer substrates. We have noticed very little sublimation of species during the processing.

REFERENCES

1. Dharmadasa, R.; Dharmadasa, I. M.; Druffel, T., *Advanced Engineering Materials* **2014**.
2. Dharmadasa, R.; Lavery, B.; Dharmadasa, I. M.; Druffel, T., *ACS Appl Mater Interfaces* **2014**, *6* (7), 5034-40.
3. Diso, D.; Muftah, G.; Patel, V.; Dharmadasa, I., *J Electrochem Soc* **2010**, *157* (6), H647-H651.
4. Cortes, A.; Gómez, H.; Marotti, R. E.; Riveros, G.; Dalchiele, E. A., *Solar Energy Materials and Solar Cells* **2004**, *82* (1-2), 21-34.
5. Narayanan, K. L.; Vijayakumar, K. P.; Nair, K. G. M.; Thampi, N. S.; Krishan, K., *J Mater Sci* **1997**, *32* (18), 4837-4840.
6. Wu, X., *Solar Energy* **2004**, *77* (6), 803-814.
7. Franc, J.; Höschl, P.; Grill, R.; Turjanska, L.; Belas, E.; Moravec, P., *J. Electron. Mater.* **2001**, *30* (6), 595-602.