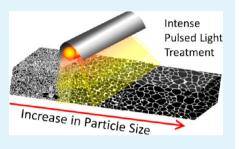
Intense Pulsed Light Treatment of Cadmium Telluride Nanoparticle-Based Thin Films

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ABSTRACT: The search for low-cost growth techniques and processing methods for semiconductor thin films continues to be a growing area of research; particularly in photovoltaics. In this study, electrochemical deposition was used to grow CdTe nanoparticulate based thin films on conducting glass substrates. After material characterization, the films were thermally sintered using a rapid thermal annealing technique called intense pulsed light (IPL). IPL is an ultrafast technique which can reduce thermal processing times down to a few minutes, thereby cutting production times and increasing throughput. The pulses of light create localized heating lasting less than 1 ms, allowing films to be processed under atmospheric conditions, avoiding the need for inert or vacuum environments. For the first time, we report



the use of IPL treatment on CdTe thin films. X-ray diffraction (XRD), optical absorption spectroscopy (UV–Vis), scanning electron microscopy (SEM) and room temperature photoluminescence (PL) were used to study the effects of the IPL processing parameters on the CdTe films. The results found that optimum recrystallization and a decrease in defects occurred when pulses of light with an energy density of 21.6 J cm⁻² were applied. SEM images also show a unique feature of IPL treatment: the formation of a continuous melted layer of CdTe, removing holes and voids from a nanoparticle-based thin film.

KEYWORDS: CdTe, intense pulsed light, rapid thermal annealing, II-VI semiconductors

1. INTRODUCTION

Reducing the size of a semiconductor to the nanoparticle regime is known to produce significant physical and chemical changes to a materials behavior. Within this size range, quantum confinement effects created by these extremely small sizes results in a rise in the optical bandgap of the semiconductors,¹ whereas the enhanced surface area can improve the materials photocatalytic properties.² Increasing the surface to volume ratio of the semiconductor particle can also yield a substantial depression in the melting point temperature.³ This effect is caused by the relatively smaller cohesive energy of atoms positioned at the surface of a film or particle compared to the atoms in the bulk. Consequently the temperature needed to melt the surface is lower than for the bulk of the material. Typically, a particle size less than 20 nm in diameter is needed to produce a decrease in the melting point temperature by a few hundred degrees.^{4,5} This characteristic is beginning to be employed in the printed electronic industry in order to produce conductive metal patterns on low temperature substrates for metal nanoparticulate inks.⁶ However, this development has yet to be fully exploited in the semiconductor manufacturing industry.

Although large grains are thermodynamically more favorable because of their relatively smaller boundary area, a certain amount of energy (i.e., activation energy) is needed to drive grain growth. As a result semiconductors produced through low-temperature routes typically yield significantly smaller particles than their high-temperature counterparts. Consequently, films deposited at low temperatures result in an increase in defects such as pin holes and grain boundaries. If used in thin film photovoltaic (PV) devices, these defects will result in lower fill factors (low shunt resistance) and current densities (high recombination), leading to a drop in efficiency. Thermal processing of these semiconductors following deposition to improve optical, morphological, and electrical characteristics has become standard, defeating the potential benefits of realizing a low temperature thin film deposition scheme. Even materials grown at high temperatures with techniques, such as close spaced sublimation (CSS) have been subjected to further heat treatment in order to improve performance.⁷ Adding to the complexity, many materials including the chalcogenides also require either a vacuum, inert or toxic (e.g., H₂S) environment to produce high-quality materials.⁸ This can add both capital and operational costs to the manufacturing stage.

The nanoparticle films deposited at low temperatures with a suppressed melting point offer an opportunity for alternative equipment and processes to thermally sinter these materials. One such technique, which is being investigated for use in the printed electronics industry, is intense pulsed light (IPL). IPL irradiates the surface of the film with pulses of incoherent light from a Xenon lamp. The lamps can be designed for large area exposure to pulsed light radiation (up to 580 cm²) and the response times are extremely fast (microseconds) making this

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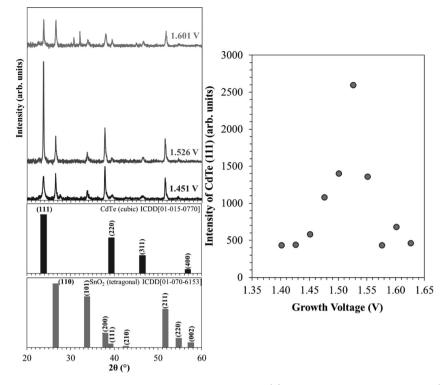


Figure 1. (a) XRD patterns of as-deposited CdTe at 1.451, 1.526, and 1.601 V. (b) Intensity of as-deposited CdTe (111) reflection vs. growth voltage, V_{e} . The XRD patterns were normalized to the SnO₂ reflection at 26.7° of the FTO substrate.

technique highly scalable. Semiconductors, absorb photons with energy greater than or equal to the materials optical bandgap; exciting electrons from the valence to the conduction band. Upon relaxation, phonons are produced in the crystal lattice creating a rise in the lattice temperature. The excitation and relaxation of the electrons, is considered to be an instantaneous mechanism and the fast kinetics can thermally process the material in ambient conditions, without oxidation.⁹ The temperature rise in the semiconductor can be controlled by varying the spectrum, energy density of the pulses, as well as the number and interval time of the pulses. Unlike laser sintering technology, IPL can irradiate the entire surface of the film; therefore, a temperature gradient is only expected in the vertical direction corresponding to the film depth, and not in the lateral direction.

To develop the IPL processing technique for photovoltaic devices, we conducted initial studies on a well-known absorber material. CdTe in particular with its narrow and direct bandgap transition of 1.45 eV draws considerable attention in its ability to produce high efficiency solar cells.¹⁰ Therefore, CdTe was selected for this study. To the best of our knowledge, the use of IPL processing on CdTe thin films has yet to be investigated. In this article, we use a low-temperature technique, electrochemical deposition, to fabricate nanoparticluate CdTe thin films on conducting glass substrates followed by IPL treatment to change the morphology of the deposited nanoparticle films. This study provides a detailed exploration of the light-induced thermal phenomena on CdTe nanoparticles.

2. EXPERIMENTAL SECTION

CdTe films were grown by two-electrode cathodic electrochemical deposition on to TEC-8 fluorinated tin oxide glass substrates (FTO, Hartford Glass Co. Inc.). The FTO was used as the cathode and a graphite rod was used as the anode. The 6.0×4.5 cm² substrates were placed in a Teflon vessel holding an 1400 mL aqueous solution of 0.5

M CdSO₄ (Sigma Aldrich) and the pH was lowered to 1.44 using 1 M H₂SO₄ (Sigma Aldrich). The deposition was carried out at 85°C, and the films were deposited for 2 h. The cathodic growth voltage (V_{α}) applied using a Keithley 2400 source-meter was varied from 1.401 V to 1.626 V. The deposition current density was maintained at ~125 μA $\rm cm^{-2}$, by adjusting the stirring rate and adding TeO₂ (Sigma Aldrich) dissolved in 1 M H₂SO₄. Once the films were grown, CdTe was IPL sintered in air using a Sinteron 2000 (Xenon Corporation). The system delivered rapid pulses of light with wavelengths ranging from the UV to IR region. In this case, CdTe was treated with pulses lasting 1.0 ms. The system was set so that the lamp cycled between its "ON" and "OFF" conditions. During the ON segment, the lamp pulsed/ flashed twice, whereas no flashes occurred during the OFF segment. Each segment lasted 1.0 s, with a 0.5 s gap between pulses. The total energy input to the films was varied by changing the energy density (ED) of each pulse from 8.6 to 25.9 J cm⁻². The number of pulses applied to the films was fixed to 100 pulses; this corresponded to a total processing time of 100 s.

The materials crystallinity and phases were studied using a Bruker AXS D8 X-ray Diffractometer. The equipment was operated with Xray source of CuK_{α} (λ = 0.1548 nm), a position sensitive detector (PCD), a scan speed of 0.5 s/step and step size of 0.02°. XRD patterns were measured using the $\theta - 2\theta$ method in the 2θ range of $20-60^{\circ}$. Optical properties of the CdTe thin films were measured using a Perkin Elmer Lambda 950 UV/Vis/NIR spectrometer. The thicknesses of the films were measured using a Technor Instruments Alpha-Step 500 surface profiler. An FEI Nova NanoSEM 600 was used to study the morphology of the surfaces with an accelerating voltage of 15 kV and a working distance of 5-6 mm. A thin layer of gold was sputtered on the surface of the samples before being studied by the SEM to avoid charging effects. Cross-sectional images of the asdeposited and IPL-treated films were performed by mechanically breaking the sample and charging effects were reduced by covering the surface with a platinum and iridium coating. The images were taken using a Zeiss Supra 35VP SEM with an accelerating voltage of 3.0 kV and a working distance of 6-7 mm. The images were taken at a tilt of 45°. The SEM topographical images were analyzed to find the particle diameter using the imageJ software. The average maximum and

minimum Feret diameters were measured by excluding the particles touching the edge of the image. Photoluminesence measurements were carried out using a Renishaw inVia Raman microscope, with a CCD detector and a 632 nm He–Ne laser as the excitation source. Photoelectrochemical measurements were conducted in a three-electrode setup to investigate the photovoltaic properties of the films. The samples were measured in an aqueous 0.1 M Na₂S solution, using a Ag/AgCl reference and a platinum counter electrode. The potential was scanned with an eDAQ potentiostat using a scan rate of 20 mV s⁻¹. The films were illuminated from the front side using AM 1.5 simulated light from a Newport 300 W Xenon Arc lamp.

3. RESULTS AND DISCUSSION

The deposition method has a strong bearing on the conductivity of CdTe films. High temperature methods, such as closed spaced sublimation (CSS) commonly produce p-type conductivity, as a result of Cd deficiencies within the film. Whereas lower temperature techniques are able to create an excess of Cd; creating n-type conductivity. The low-temperature method of electrochemical deposition (ED) allows films to be specifically tailored n- or p-type by varying the growth voltage (V_g) .¹² Altering the V_g results in changes to the Cd:Te ratio. At high V_{g} , excess Cd is present in the film, yielding ntype films. Lower V_g values produce p-type films due to excess Te in the film. When the Cd:Te ratio is 1:1 the film is considered to be stoichiometric and intrinsic. Figure 1a shows the XRD patterns of as-deposited CdTe grown at 1.451, 1.526, and 1.601 V. The films demonstrate a good match to the (111), (220), (311), and (400) crystalline planes of cubic CdTe (ICDD 01-015-0770). All the films demonstrated preferential orientation towards the (111) crystal plane. Figure 1b shows the intensity of the (111) reflection of CdTe vs. the $V_{\rm g}$. Under the conditions described in the Experimental Section, the intrinsic point where the material is stoichiometric and had the highest intensity for the (111) reflection was observed at 1.526 V.

Thermally treating the as-deposited CdTe is known to affect the conductivity type, as unreacted Cd and Te in the film form CdTe. At very high temperatures the formation of Cd vacancies can also occur, due to the higher vapor pressure of Cd compared to Te.¹³ In addition significant crystalline and morphological changes are also expected depending on the processing conditions. Figure 2 shows the plot of the (111)_{IPL}/ (111)_{as-deposited} ratio vs. the total energy input during IPL treatment. The number of pulses applied to the films was kept constant at 100, whereas the total energy input to the films was

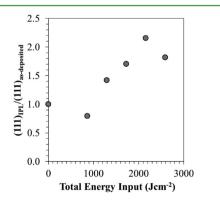


Figure 2. $(111)_{\rm IPL}/(111)_{\rm as-deposited}$ ratio of CdTe vs. total energy input during the IPL treatment. The films were treated using 100 pulses of light with an energy density of 8.6, 12.9, 17.3, 21.6, and 25.9 J cm⁻².

varied by changing the energy density (ED) of the light pulses. The results show that when pulses with an ED of 8.6 J cm^{-2} were applied to the film the crystallinity of the films decreased slightly. It would appear that the temperature rise generated by the pulses is sufficient to begin the rearrangement of atoms in the film, creating disorder in the film. However, the cooling rate appears to be too fast for the atoms to rearrange into more crystalline structures. As the ED of the pulses was increased the film showed an increase in the intensity of the (111) reflection. A significant increase in crystallinity of the CdTe and decrease to the full width at half maximum (FWHM) values was observed for the reflections treated with an ED of 21.6 J cm $^{-2}$. 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 or CdTe from the film. The films continued to demonstrate a high preferential orientation towards the (111) crystal plane after IPL treatment. The lattice parameter a was calculated to be 6.479 Å for the as-deposited CdTe films. Upon IPL treatment using pulses with an ED of 21.6 J cm⁻², a was calculated to be 6.476 Å. Increasing the ED of the pulses to 25.9 J cm⁻², further decreased *a* to 6.472 Å. This reduction in *a* with increasing energy input indicates a relaxation of the stress within the lattice.

UV-Vis-IR transmittance spectra of the as-deposited films show that the CdTe films have a large amount of transmittance in the visible region (Figure 3). This is due to the films only

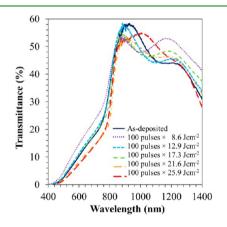


Figure 3. UV–Vis–IR transmittance spectra of CdTe IPL treated without CdCl₂. The films were treated with a total energy input of 0 (i.e. as-deposited), 863, 1294, 1726, 2157, and 2588 J cm⁻².

being approx. 400–600 nm thick. Device quality CdTe films are typically greater than 1 μ m in thickness, in order for the films to efficiently absorb sun light. However, in electrochemical deposition, the lattice mismatch between CdTe and the FTO substrate does not favor the growth of thick films. Consequently it was decided to tune the IPL sintering process on the thinner films. The optical bandgap (E_g) of the films was found from Tauc plots of $(\alpha h\nu)^2$ vs. $h\nu$. The as-deposited films showed a E_g of 1.47 eV. IPL sintering resulted in a decrease in transmittance in the visible light region. Although the films displayed a shift in the optical band edge to the IR region, the E_g of the film sintered with 25.9 J cm⁻² pulses only decreased slightly to 1.46 eV. These values, however, are close to literature reported E_g for CdTe.¹⁴

Figure 4(a-c, g-i) shows the SEM topographical images of as-deposited and IPL-treated CdTe. As expected, the low

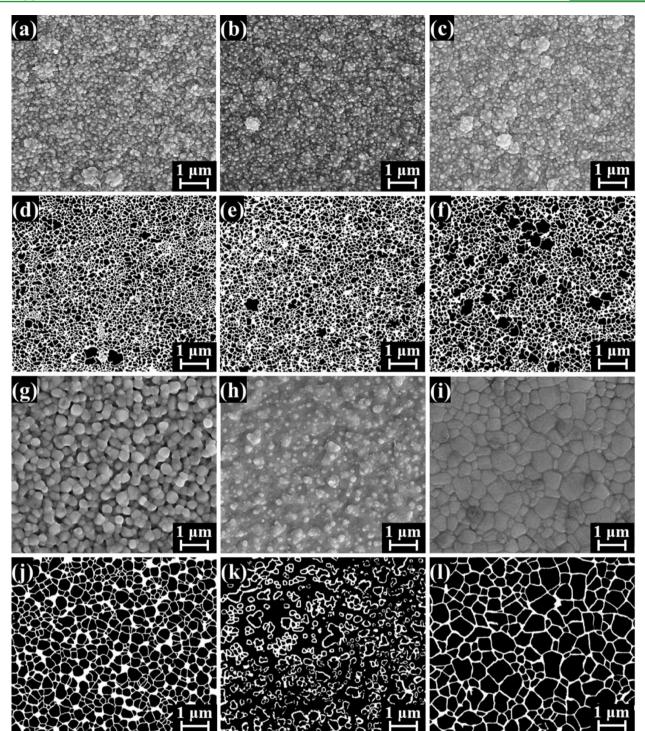


Figure 4. SEM and black and white topographical images of IPL-treated CdTe. The films were treated using 100 pulses of light with an energy density of (a, d) 0 (i.e., as-deposited), (b, e) 8.6, (c, f) 12.9, (g, j) 17.3, (h, k) 21.6, and (i, l) 25.9 J cm⁻².

temperature nature of the electrochemical deposition results in nanoparticles, growing up from the substrate to the surface of the film. Upon IPL treatment, the surface of the particles appears to become smoother and as the ED of the pulses was increased to 12.9 J cm⁻² particle growth and melting became more observable (Figure 4c). Increasing the pulse output further to 17.3 J cm⁻², results in significant particle growth, as the smaller particles have coalesced in to particles with cross sections as large as 400 nm (Figure 4g). Interestingly, when an ED of 21.6 J cm⁻² was used, the surface appears to have melted

in to an almost continuous surface (Figure 4h). Using pulses with an ED of 25.9 J cm⁻², the formation of particles as large as 1 μ m was observed (Figure 4i). These particles formed larger highly compact grains with an increased surface roughness. When CdTe was thermally processed using a laser light source, the high irradiation power of the laser created similar surface roughening. This phenomenon was found to be due to the loss of Cd during the heating process; resulting in a highly enriched Te surface.¹⁵ Therefore, the increased surface roughness in the

IPL-treated films with a decrease in the (111) reflection indicates the loss of material from the surface.

The unique features observed in Figure 4h 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 feature appears to alleviate the formation of pin-holes in the structure. The presence of a continuous surface layer could also help in the development of PV devices by reducing short circuiting. To observe the reproducibility of this feature, we repeated experiments using pulses with a pulse ED of 21.6 J cm⁻², but in this case, the number of pulses was varied from 80 to 90 and 110 pulses. The results from the films' SEM images are shown in Figure 5. The

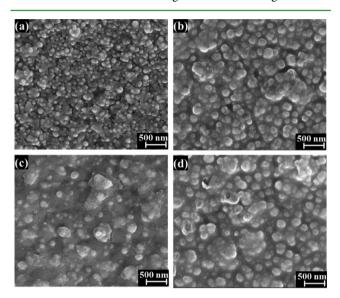


Figure 5. SEM topographical images of CdTe IPL treated using pulses of energy densities with 21.6 J cm⁻². The number of pulses applied was (a) 80, (b) 90, (c) 100 and (d) 110.

images confirm the reproducibility of this feature and its repeatability over a wide process window. Along with IPL's ability to process large-area films (in this case the processing area was approximately 58 cm^2), this outcome demonstrates the potential for IPL to be used in the manufacturing of thin film semiconductors.

The densification of the films may result in a delamination from the substrate. Tape pull experiments did not show any increase in adhesion of the films to the substrate; none of the films could be removed from the substrate using the tape pull test. Figure 6 shows the cross-sectional image of the CdTesubstrate interface after IPL treatment using 100 pulses with an ED of 21.6 J cm^{-2} . The image clearly shows that no delamination of the film occurs because of stresses induced by the IPL treatment. A close look at the cross section of the films shows a densification of the film at the air interface due to melting. This densification proceeds vertically down the film, to the glass substrate. Closer to the substrate the CdTe particles are significantly more defined. These results clearly demonstrate that the pulses of light induce a temperature gradient, in the vertical direction corresponding to film depth, and not in the lateral direction; with higher temperatures occurring closer to the surface and inducing melting.

During thermal processing, recrystallization initially proceeds, followed by particle growth. However, recrystallization is inextricably linked to both the particle size and stress in the Research Article

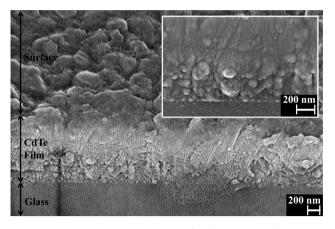


Figure 6. Cross-sectional SEM image of CdTe IPL treated using 100 pulses with an energy density of 21.6 J cm^{-2} at a tilt of 45° . The inset shows a close up of the glass–CdTe interface.

film. This is why CdTe films grown at high temperatures (e.g. CSS) do not always demonstrate changes to their large grains after treatment.⁷ The low-temperature growth of electrochemical deposition, on the other hand, produces small particles under stress that are susceptible to thermal treatment. Figure 7 shows the average maximum and minimum Feret

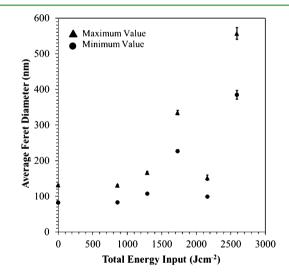


Figure 7. Average maximum and minimum Feret diameters vs. the total energy input during IPL treatment. Feret diameters were measured using the black and white images shown in Figure 3. The error bars were calculated using the standard error. N.B. The deviation in trend at 2157 J cm^{-2} is due to the formation of the continuous surface layer embedding smaller particles in the film.

diameter calculated from the monochromatic SEM images, with respect to the energy input during the IPL process. During IPL treatment, pulses with low ED's less than or equal to 12.9 J cm⁻² generates sufficient energy for the recrystallization process to begin (Figure 4c). 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 energy input exceeds 1290 J cm⁻², a sharp increase in the particle size was observed. At this point melting of the particles was also observed (Figure 4g). CdTe in its bulk form is known to have a melting point of approximately 1100 °C.¹⁶ Therefore, the very high temperature rise induced by the pulses of light in conjunction to the very small particle size of the as-

deposited films accounts for the significant melting and particle growth observed during IPL treatment.

Figure 8 shows the room-temperature photoluminescence (PL) spectra for the as-deposited and IPL treated electro-

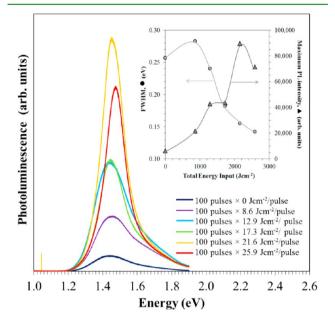
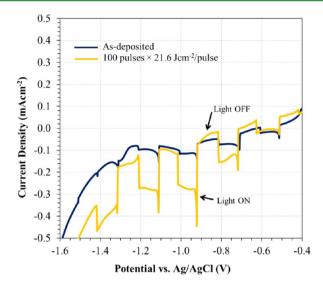


Figure 8. Room-temperature photoluminescence (PL) of the asdeposited and IPL treated films excited with a 632 nm laser. The inset shows the effect of the total energy input during the IPL treatment on the full width at half maximum (FWHM) of the PL peaks and the maximum intensity of the peaks.

chemically deposited CdTe layers in the energy range of 1.0 to 1.9 eV. The wavelength of the laser beam used for excitation was 632 nm (1.96 eV). The signal observed for the as-deposited layer has a broad peak with a low intensity. This indicates the presence of a large number of shallow donor and acceptor type defects in the material. Therefore donor to acceptor like transitions occur producing photons less than the $E_{\rm g}$. Also, emissions greater than the $E_{\rm g}$ are present because of the existence of nanosized particles showing quantum confinement effects. As a result, the band to band emissions showing the $E_{\rm g}$ are low, and both high and low energy photons are emitted producing a weak and broad signal.

As the layers are treated with pulse ED's increasing from 8.6 to 21.6 J cm⁻², the band-to-band emissions were also observed to increase. The width of the peak (i.e., FWHM) is also reduced, showing the best results at treatments with 21.6 J cm⁻² (Figure 8 inset). Photon emissions below the E_g are reduced because of 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. Therefore, optimum IPL pulse ED for CdTe appears to be close to 21.6 J cm⁻². Treatment with higher energy pulses (25.9 J cm⁻²) displayed a reduction in band to band emissions reducing the peak intensity and a slight shift to higher energies. This indicates deterioration of the optical/electrical properties.

Photoelectrochemical (PEC) measurements were conducted in order to elucidate the effect of the IPL treatment on the CdTe films. Figure 9 shows the current density vs. potential (J-V) characteristics of an as-deposited and IPL treated film using 100 pulses with an ED of 21.6 J cm⁻². The J–V curves



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Figure 9. Chopped J-V measurements of the as-deposited and IPL treated CdTe films using 100 pulses with an energy density of 21.6 J cm⁻². The films were illuminated from the front side using AM 1.5 simulated light in an aqueous 0.1 M Na₂S solution using platinum as the counter electrode.

were measured under chopped illumination conditions to show the film under dark and light conditions. Both the as-deposited and IPL treated samples display cathodic photocurrent confirming the p-type behavior of the films. As expected the increased grain size, improved crystallinity and reduced defect density of the IPL treated film has resulted in a significant increase in photocurrent. The shape of the photocurrent transient is similar for both films, with an initial spike in photocurrent which rapidly decays to steady state values. In many materials these spikes have been attributed to surface recombination as a result of the charging and discharging of surface states.^{17,18}

Both XRD and SEM results have shown a phase transition in the CdTe films when treated with IPL. The as-deposited material demonstrated a preferential orientation along the (111) planes, with the intensity increasing until the total energy input during IPL treatment reached 2167 J cm⁻². However, when the energy input exceeded this value, a reduction in the (111) intensity of the XRD pattern was observed. The room temperature PL study also indicated that the largest band-toband transition occurred after 2167 J cm⁻² of energy was applied. At higher energy inputs, the reduction of the PL intensity, and hence the deterioration in the optical and electrical properties of the material was observed, although the grain size continued to increase. Therefore, after this point, device efficiency may suffer, although the particle sizes continued to increase. This observation has been reported by Abaas et al.¹⁹ who showed the measured device efficiencies as a function of temperature during thermal processing. The efficiency was observed to increase until 390 °C, but raising the temperature further led to a drop in efficiency.

4. CONCLUSION

We have reported for the first time the intense pulsed light treatment of CdTe thin films. The low growth temperature resulted in films consisting of nanoparticles, promoting a reduction in the melting point temperature. In combination with the high temperature rise produced by pulses of light, the

lower melting temperature resulted in pores/voids being filled as well as significant grain growth. As a result, pin holes and grain boundary recombination may be diminished. Subsequently the fill factors of PV devices are likely to be significantly increased. Unlike many conventional heating techniques, IPL irradiates the entire surface of the film and a temperature gradient is only expected in the vertical direction corresponding to the film depth, and not in the lateral direction. This phenomenon was demonstrated by film densification closer to surface. This also results in the particles showing significant lateral growth producing grains as large as 1 μ m in less than 2 minutes, in addition to the gaps between particles being reduced. The fast processing times under atmospheric conditions without evidence of oxidation, demonstrate the suitability of IPL to be used to thermally process semiconductors for PV devices. Now that the individual parameters have been tuned for the individual layers, work is in progress to apply this knowledge to the combined CdS/CdTe structures.²⁰

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Notes

The authors declare no competing financial interest.

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