Laser Annealing of thin film CdTe solar cells using a 808 nm diode laser

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***Abstract* – We report on the effect of a new laser annealing treatment for thin film CdTe solar cells using a 808 nm diode laser. As-deposited, laser annealed and $MgCl_2$ treated/laser annealed CdTe thin films have been analysed. One part of the work has been focused on understanding the efficacy of the activation treatment by laser annealing. The results show partial chlorine diffusion and associated partial re-crystallisation of the absorber. The second part of this work has been focused on the effect of the treatment on the chemical composition of the CdTe surface. It has been found that the process also contributes to the formation of a Te-rich layer on the surface of the CdTe absorber, which may provide a useful process to produce a back contact. This paper reveals the effect of the laser treatment on the micro-structural properties of the CdTe absorber material. The microstructure has been analysed using STEM/EDX, HRTEM and XRD. Further work is required to optimise the process but it has the potential to provide much greater control than current activation methods and also to provide a Te back contact suitable for CdTe solar cells.**

***Index terms*: Laser annealing, diode laser, thin films, Cadmium telluride, Magnesium Chloride, Photovoltaic cell, microstructural, morphological analysis.**

I. Introduction

Group II-VI chalcogenides are important materials for low cost photovoltaic applications [1][2]. Cadmium Telluride (CdTe) with its high absorption coefficient ($5.1x10^5$/cm), ideal band gap (E_g) of 1.45-1.5eV [3][4][5] and its long term performance stability [6] is a proven and successful solar technology. CdTe solar cells can be fabricated using a wide range of deposition techniques, including physical vapour deposition (PVD) techniques such as Close Space Sublimation (CSS), vapour transport, thermal evaporation, and magnetron sputtering [7]. Thin film CdTe solar cells require a post deposition annealing activation process to achieve high efficiency. Although this is a crucial step, the mechanisms involved are still not fully understood. It is now recognised that the treatment removes high densities of microstructural defects such as stacking faults [8]. The activation of CdTe solar cells is usually achieved using $CdCl_2$ either as a vapour or in a solution at ~400^0C. The use of laser annealing holds the promise of controlling where the annealing takes place and avoiding undesired effects such as sulphur migration into the absorber.

In this study a laser annealing treatment using $MgCl_2$ has been performed as the post deposition activation treatment on CdTe thin films grown by Close Space Sublimation (CSS). The annealing process takes place in atmosphere and the use of $MgCl_2$ avoids the severe health and safety issues associated with $CdCl_2$ [9].

In this work, a comparison between as deposited, laser annealed and $MgCl_2$/laser annealed CdTe thin films has been carried out. The second part of this work has been focused on the use of the laser annealing treatment to produce a potential back contact for solar cells. One of the crucial steps in the fabrication of CdTe solar cells is the development of a stable and efficient back contact, which is essential for the long term stability of the device. It has known that CdTe has a high electron affinity and a high work function metal is required to form a good ohmic contact on p-type CdTe [10]. If a high work function material is not used, a Schottky barrier is formed at the back contact. This acts as a diode reverse biased to the CdTe/CdS junction diode and increases the contact resistance, thereby reducing the solar cell performance [11]. This problem may be overcome by lowering the barrier by increasing the conductivity of the CdTe top layer to create a tunnelling barrier. Usually CdTe surface etching is performed to produce a Te-rich surface (p+ type) [12].

Microstructural analysis was carried out using an FEI Tecnai F20 Transmission Electron Microscope (TEM) and Scanning Electron Microscopy (SEM). TEM samples were prepared by Focused Ion Beam (FIB) using an “in situ” lift out method in a FEI Nova 600 Nanolab. Structural and chemical analysis was performed using X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction Spectroscopy (XRD), and Energy Dispersive Spectroscopy (EDX). Thermo-gravimetric analysis (TGA) and Mass Spectrometry (MS) have been carried out to investigate the thermal decomposition of $MgCl_2$ used for the treatment.

II. Experimental

The laser annealing treatment of thin film CdTe was performed using a system with an 808 nm diode laser, rated at 35 W (Figure 1). Due to the sensitivity of diode lasers to temperature fluctuations, a Peltier diode cooling system was added to ensure a temperature stability of 0.01°C (Figure 1).

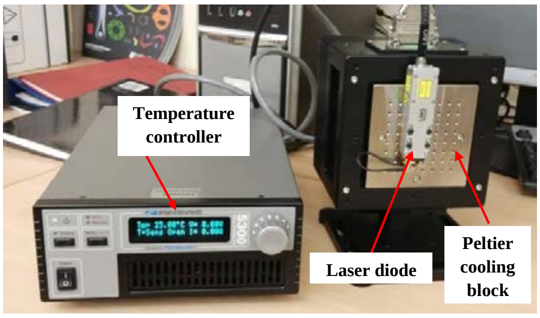

Figure 1: The laser diode and the laser cooling experimental setup.

A 1.5 m long, 100 µm diameter optical fibre was added for the beam transport between the laser and the processing head. The processing head was mounted on a manual z-axis stage inside an interlocked safety cabinet, as shown in Figure 2.

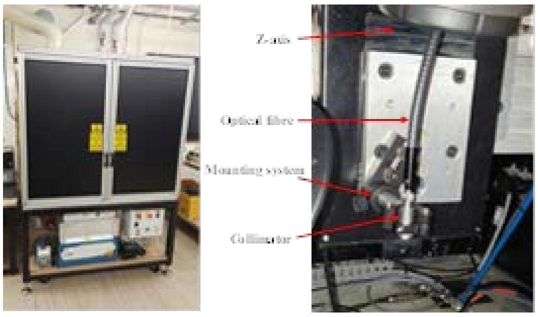

Figure 2: Laser closed cabinet and laser setup inside the cabinet.

The process was monitored using cameras mounted inside the cabinet which produced live recordings of the experiments. In addition, a FLIR Thermovision A40 high-temperature thermal camera was used to record the temperatures of the devices as they underwent the laser process. These recordings were then analysed using ThermaCAM software and temperature data were extracted.

Samples were mounted in an insulated jig, set in an open-topped chamber designed also to maintain an inert argon atmosphere. CdTe/CdS devices with ~2 µm absorbers were deposited by CSS and the $MgCl_2$ treatment was performed by using 1 M $MgCl_2$ aqueous solution prior to the annealing step in the laser cabinet. The samples were simply dipped into the $MgCl_2$ solution and positioned under the laser. For these experiments, the power was set at 11 and 5W, the scanning velocity at 4 and 11mm/s for the laser beam irradiance and linear scans were run on each of the samples.

III. Results

A. The activation treatment

HRTEM analysis has been performed on the as deposited CdTe films confirming the presence of a high density of planar defects, predominantly stacking faults, through all the CdTe grains, as shown in (Figure 3).

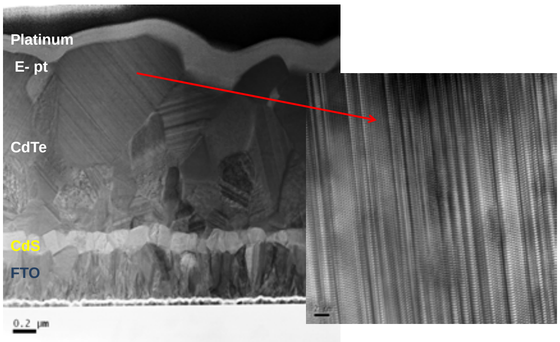

Figure 3: TEM and HRTEM images of CdTe as deposited with high density of planar defects.

The TEM and HRTEM images of the $MgCl_2$/laser annealed (with a power of 11 W and a scanning speed of 4 mm/s) devices show that the grains still contain defects. However near surface grains show the onset of re-crystallisation (Figure 4). The HRTEM analysis confirms the removal of stacking faults, with twin boundaries remaining.

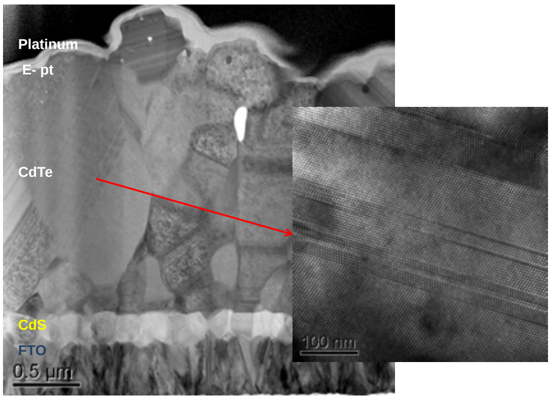

Figure 4: TEM and HRTEM images of CdTe after $MgCl_2$ and laser annealing treatment. Near surface grains have a visible reduction of planar defects.

The laser treatment induced diffusion of Cl into the CdTe layer. EDX analysis in Figure 5 shows the Cl diffusion is predominantly near surface and penetrates about 60% into the CdTe layer, but does not reach the CdS junction.

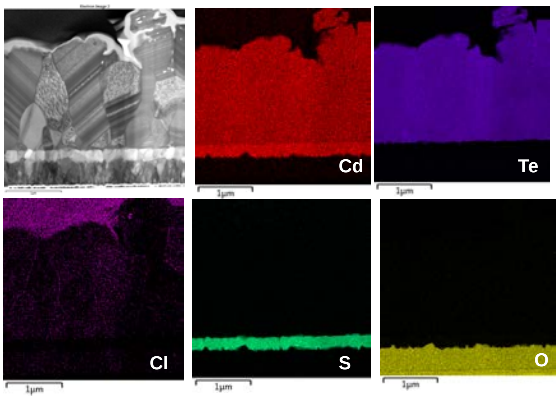

Figure 5: EDX mapping of the CdTe/CdS device after $MgCl_2$/laser annealing treatment with Cl, Cd, Te, O, S and elemental maps.

Chlorine does not penetrate down to the CdS/CdTe interface, possibly due to the rapid heating and quenching process induced by the laser. As a result, a high density of defects (mostly stacking faults), remain in the interface region as shown in

Figure 6.

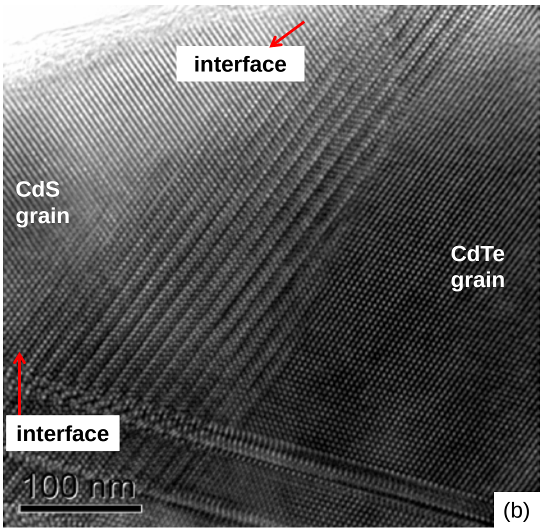

Figure 6: HRTEM image of CdS/CdTe interface with a high density of planar defects after laser annealing.

EDX analysis shows that there is no S diffusion at the interface between the CdS and CdTe. The XRD analysis shows that the $MgCl_2$/ laser annealing process performed at 11 W with a scanning speed of 4 mm/s orientated the CdTe grains into the <111> direction (Figure 7).

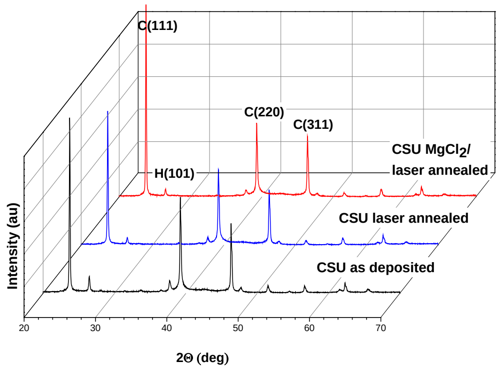

Figure 7: XRD analyses of as deposited, laser annealed and $MgCl_2$ /laser annealed CdTe thin films.

UV-Vis analysis and Hall measurements showed that the band gap of the CdTe decreased slightly after the activation process.

B. Te-rich layer as a back contact

We have discovered a way to process CdTe thin films to provide a Te-rich top layer, p+ type, with and without the use of the active Chlorine agent. This has a potentially useful application to create a back contact, without the introduction of an extra etching step in the fabrication process. After performing the laser annealing treatment (with and without the presence of the active agent Chlorine), a Te rich layer, ~100 nm thick was observed to form on the CdTe surface.

Figure 8 shows a cross-sectional TEM image of a CdTe thin film processed by laser annealing with a linear scan, for 10 min, using 5 W and a laser speed of 11min/s. The device was dipped into 1M $MgCl_2$ solution for 10 seconds prior to the annealing treatment. The surface contained Te at a concentration of 90At%. The bulk CdTe stoichiometry was maintained at a Cd:Te 1:1 ratio.

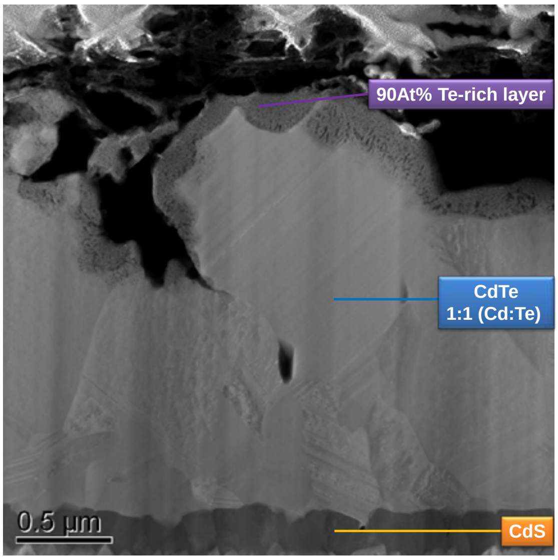

Figure 8: TEM image of CdTe after $MgCl_2$ and laser annealing treatment. EDX analysis shows the top layer is 90At% Te-rich. The bulk composition remains as CdTe.

A reduction of structural defects in the absorber layer was also observed, confirming the potential use of laser annealing for the activation treatment.

Figure **9** shows a SEM image of the surface. The surface does not appear to be damaged by the treatment. Similar features are visible on the as deposited (untreated) and treated surfaces (Figure 11).

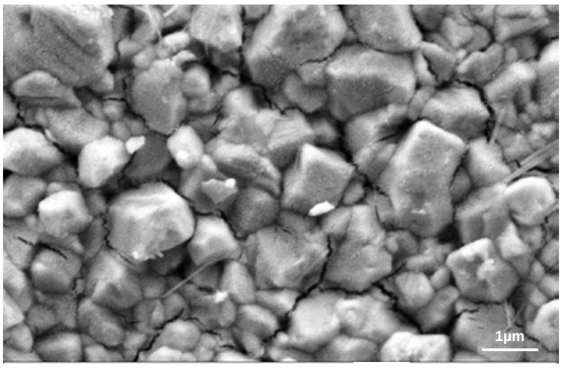

Figure 9: SEM planar view of CdTe films after $MgCl_2$/laser annealing treatment. The surface shows no damage.

Devices have also been laser annealed for 20 min without the presence of $MgCl_2$. It is interesting to note that the simple annealing treatment was sufficient to generate a Te-rich layer (~100 nm thick) on the top surface of the CdTe film. EDX analysis show that the top layer is slightly Te-rich (53At%) .

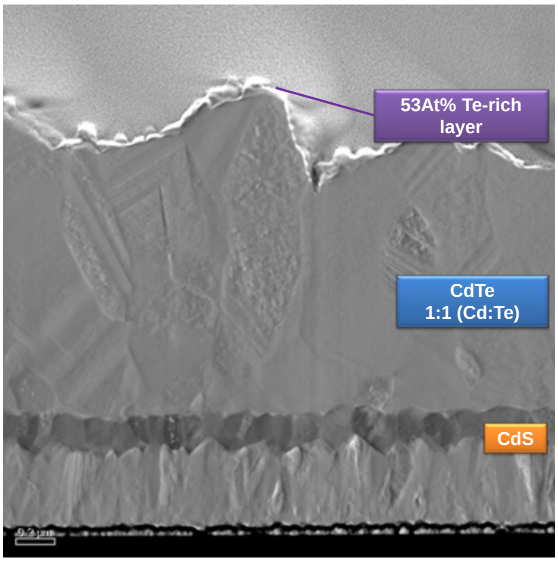

Figure 10: TEM image of CdTe after laser annealing treatment without the active chlorine agent. EDX analysis shows the top layer is Te rich (53At%).

The surface morphology of laser annealed CdTe layers (Figure 11 (a) is similar to the untreated CdTe (Figure 11 (b)).

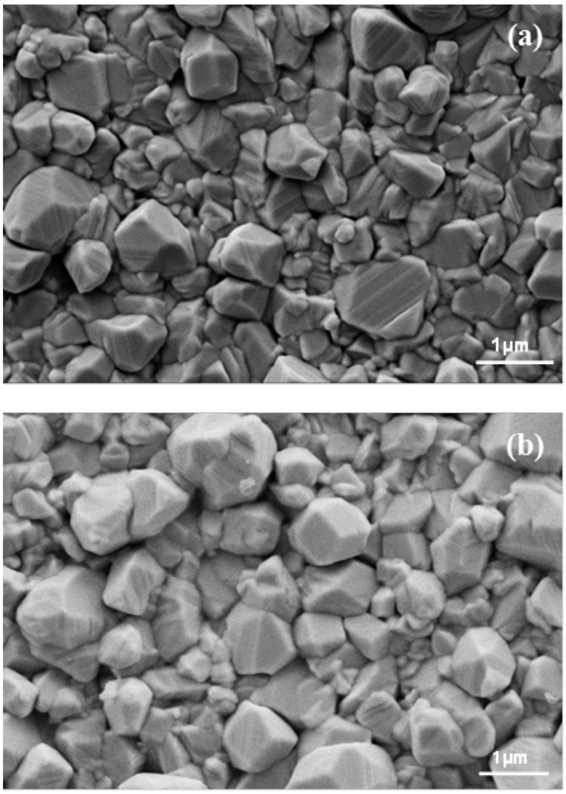

Figure 11: SEM surface image of a CdTe film after laser annealing treatment (a) and as deposited CdTe film (b). The surface shows no discernible alteration by the treatment.

While further work is required, it is possible that during the laser treatment Cd on the surface reacts with Oxygen from the atmosphere at high temperature (in the range of 300-400ºC) forming an oxide compound in the gas phase. Cd is the more volatile species in CdTe [13][14] .

When $MgCl_2$ is used as the active agent during the laser annealing process, residues of the salt are visible on the treated surfaces.

Figure 12 shows the particles visible after the treatment. These surfaces were not rinsed with deionised-water. EDX analysis shows that $MgO/MgCl_2$ and Mg(OH)Cl compounds are formed. TGA-MS analysis of $MgCl_2*6(H_2O)$, performed in the RT-600ºC range, showed that at ~200ºC and 400ºC a mass loss occurs corresponding to Cl_2 / HCl.

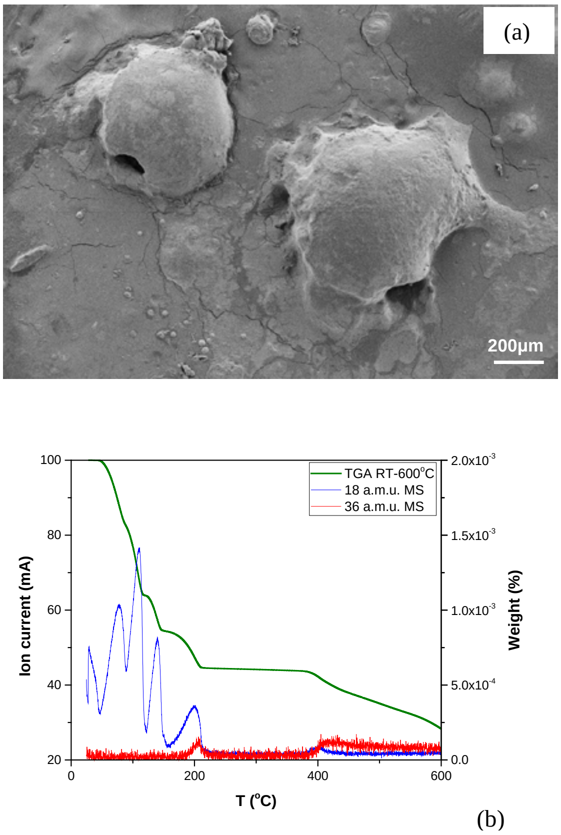

Figure 12: SEM surface image of residues of $MgCl_2$ remaining on the device after the laser annealing treatment (a), TGA-MS analysis of $MgCl_2$ salt analysed in the range RT-600ºC with a ramp temperature of 3ºC/m (b).

Sheet resistance measurements have been performed on three samples: an untreated sample, a laser annealed sample and a sample laser annealed with $MgCl_2$, to investigate if the Te-rich surfaces had higher electrical conductivity. The as deposited, untreated, CdTe films showed a high sheet resistance, (6 x 10^9 Ω / □). The laser annealed CdTe had a slightly lower sheet resistance (6 x 10^7 Ω / □). The CdTe laser annealed CdTe in the presence of $MgCl_2$ had a sheet resistance of 5 x 10^5 Ω / □ as shown in Table 1.

Table 1

	As deposited CdTe	Laser annealed CdTe	Laser Annealed + $MgCl_2$ Treated CdTe
Resistivity (Ω cm)	$1.2*10^6$	$1.2*10^4$	$1*10^2$

Table 2: Measurements of CdTe resistivity (Ω cm) of the as deposited sample, laser annealed sample and CdTe laser annealed in the presence of $MgCl_2$.

IV. Conclusions

A laser annealing treatment has been performed on CdTe thin films deposited by CSS, using a 808 nm diode laser. This treatment has the potential to replace conventional thermal annealing. Also, an activation process has been carried out using $MgCl_2$ as a replacement for $CdCl_2$; since these experiments have been performed in atmosphere. The effect of the treatment on the microstructure of the devices has been investigated, comparing microstructure of the as deposited, laser annealed and $MgCl_2$/laser annealed materials. Analysis of as-deposited CSS thin film CdTe confirms the presence of high densities of planar defects through the grains of the CdTe absorber layer. $MgCl_2$/annealed CdTe devices show that the treatment initiates re-crystallisation but that in these preliminary studies chlorine does not diffuse through the CdTe layer to the junction. This may be caused by the rapid heating and quenching induced by the laser. Further work is required to optimise the laser processing parameters. A study of the CdTe surface chemical composition after the laser annealing/$MgCl_2$ treatment revealed the formation of a Te-rich top layer, ~100 nm thick. This may provide a useful way to fabricate a Te rich back contact.

Laser annealing has several potential advantages over conventional thermal annealing. These include localised high thermal treatment, annealing selective layers in the device or substrate, high speed process and precise control of the heating time and zone [15].

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