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Optimisation of Cadmium Chloride solution processing of Close Space Sublimated thin film CdTe solar cells

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Abstract: In this paper, we describe the optimisation process for the Cadmium Chloride (CdCl_2) wet chemical treatment of cadmium telluride (CdTe) photovoltaics (PV). Various experiments were performed on Close Spaced Sublimated (CSS) CdTe cells, including optimisation of the cadmium chloride deposition process and optimisation of the annealing process. The treatment consisted of dipping the sample for various time periods in a methanol solution containing CdCl_2 using different concentrations and different temperatures. The samples were subsequently annealed in an oven at different temperatures and times. The optimum conditions were found to be: dipping for 15 minutes in a solution of 1%wt CdCl_2 in methanol heated to 50°C and annealing for 15 min at 370°C in a pre-heated furnace.

Keywords: Thin-film, CdTe, CdCl_2 , wet treatment, photovoltaics

1. INTRODUCTION

Thin film CdTe is currently the most commercially viable alternative to crystalline silicon for solar modules. The record efficiency has recently been improved for both for modules [1] and research cells [2]. Optimisation of each of the process steps in production is critical to obtain high performance devices.

A crucial process to obtain high efficiency CdTe solar cells is the post-deposition or activation treatment using cadmium chloride (CdCl_2). It promotes recrystallization and eliminates material defects such as stacking faults to produce highest quality thin films. There are various methods used to perform the treatment. They can be divided in two categories: one-step such as vapour transport [3] and Closed Space Sublimation (CSS) [4] and two-steps processes using evaporation [5] or wet treatment [6] followed by annealing. A wet chemical treatment has the advantage that it is a non-vacuum technique which can be performed easily and at low cost.

Various methods for the wet treatment have been reported in the literature, including dipping the substrate in the solution or dropping the solution on the substrate surface, using either $\text{CdCl}_2\cdot\text{CH}_3\text{OH}$ or $\text{CdCl}_2\cdot\text{H}_2\text{O}$ at different concentrations. The annealing phase can be performed at different

temperatures for different times and in different atmospheres (Air, N_2/O_2 mixture, pure O_2 , etc.).

2. THE EFFECT OF CdCl_2 TREATMENT

The treatment results in a consistent change to the thin film layer morphology producing better film quality. The process allows intermixing between the CdS and the CdTe layer, activating the junction [7]. Changes in morphology and texture causes enhanced electronic properties, affecting Open Circuit Voltage (V_{OC}), Short Circuit Current Density (J_{SC}), Fill Factor (FF) and efficiency (η). The recrystallization and creation of acceptor states decreases resistivity. Chlorine incorporation leads to the formation of an acceptor complex with cadmium vacancies. A single and shallow acceptor state is created as both the single-donor and the double-acceptor states are pushed closer to the band edges. The chlorine must not be in excess; otherwise it will compensate Cl_{Te} donors [7].

3. EXPERIMENTAL

3.1 Wet chemical treatment

A multi-stack sample of CdS/CdTe deposited using CSS on NSG-Pilkington TEC10 glass was used for this work. The solution was prepared by mixing CdCl_2 powder (99.99%) in 50ml of methanol. At room temperature (RT) the solubility of CdCl_2 in methanol is 2.15g/100g [8], so that 2g in 100ml results in a saturated solution. Heating improves the solubility, allowing a concentrated solution to be produced with reduced formation of precipitates [9]. Various concentrations were studied as the precise amount of CdCl_2 is crucial for the process optimisation. Too little and the junction is not activated, while an excess leads to defects in the absorber layer.

After the treatment process the sample was taken out of the solution and put directly in the oven for the annealing process. Annealing temperatures were varied between 360°C and 415°C . The process time was also varied. In the oven, the methanol evaporates, leaving a layer of CdCl_2 to interact with the CdTe/CdS stack. After the annealing process the residues of this layer are still visible on the sample surface and they are removed by rinsing the sample in de-ionised water and isopropanol (IPA). The activated samples were then back contacted using a ~50nm thick sputtered layer of gold with an area of about 0.25cm^2 on the CdTe layer. No

surface etching or copper treatments were included and this resulted in higher contacting resistances.

3.2 Characterisation

X-Ray Diffraction (XRD) was used to analyse the orientation of the material prior to and post the CdCl_2 treatment.

Scanning Electron Microscopy (SEM) was used to study the grain-morphology of CdTe layer as-deposited and after the different treatments.

The device performance was tested using a solar simulator (1000W Xenon short arc lamp from OSRAM). From the current density against voltage measurements, electrical measurements were obtained including V_{oc} , J_{sc} , FF and cell Efficiency.

4. RESULTS

4.1 Optimisation of the annealing process

The samples were tempered in a pre-heated oven. Device efficiencies varied in the range 3% to 7%, depending on the times and temperatures used in the process. The best results were achieved for annealing temperatures between 370°C for 15 min and 385°C for 10min.

For the same treatment conditions (15 min in 1%wt $\text{CdCl}_2/\text{CH}_3\text{OH}$ solution at room temperature) a comparison of the annealing processes at $T=385^\circ\text{C}$ for different times varying from 3 to 15 minutes is shown in Figure 1. Current density (J) in mA/cm^2 is plotted against voltage (V) in Volts. A similar set of results is presented for 370°C in figure 2.

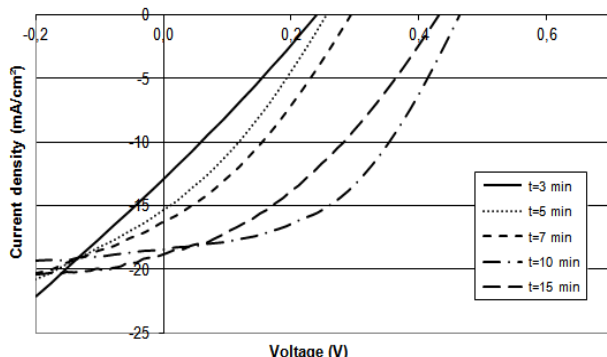


Figure 1: J-V curves referred to 385°C annealing temperature for different annealing times

The maximum efficiency of the sample annealed at 385°C was 4%, while for the sample annealed at 370°C it was 6.5%. The series resistance of the devices was high due to the back contact used on the devices. This can be improved by bromine etching and further treatment with copper before depositing the back contact. The shunt resistance increased with higher temperatures probably due to a higher level of diffusion of chlorine into the CdTe layer.

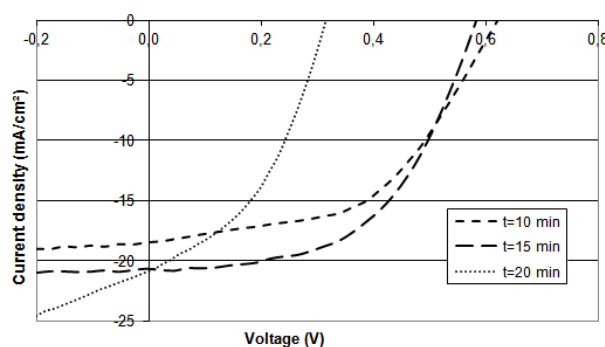


Figure 2: J-V curves obtained at a 370°C annealing temperature for different times.

4.2 Optimisation of the treatment process

Fixing the annealing process at $T=370^\circ\text{C}$ and $t=15$ min, the treatment parameters were then varied, including the treatment temperature and the concentration of the solution. Treatment temperature affected both the current and voltage. Heating the solution resulted in better efficiencies. The optimum temperature was found to be 50°C .

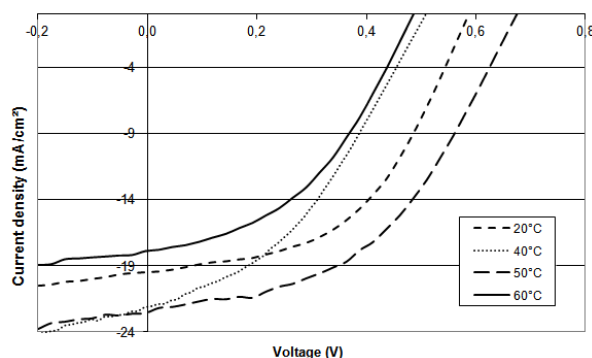


Figure 3: J-V curves for different treatment temperatures

The concentration of the solution also affected performance. Concentrations in the range 0.5-1%wt CdCl_2 resulted in the best efficiencies. When the concentration was further increased an excess of CdCl_2 was visible on the surface after annealing, resulting in lower performance. Figure 4 shows the J-V curves for different solution concentrations.

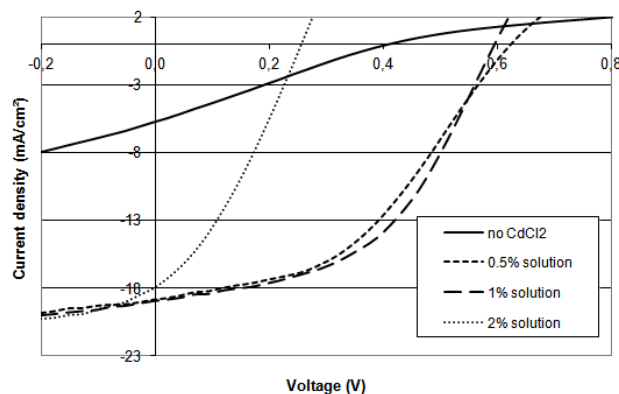


Figure 4: J-V curves for different solution concentrations

4.3 XRD results

Generally, as-deposited CdTe is highly orientated in the $\langle 111 \rangle$ direction. When treated it shows a random orientation with increased intensities of $\langle 220 \rangle$ and $\langle 311 \rangle$ and decreased intensities of the $\langle 111 \rangle$ directions as shown in figure 5. The treated samples examined with XRD had also gold (Au) back contacts deposited on the surface, resulting in an extra peak corresponding to the gold.

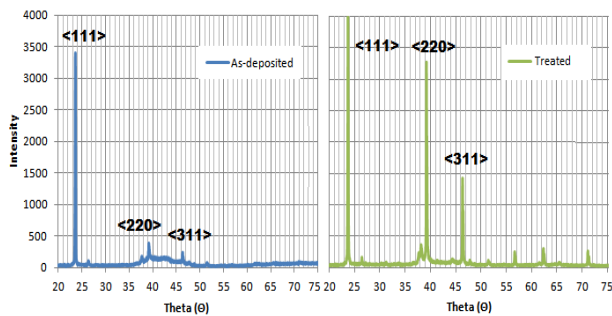


Figure 5: XRD results of as-deposited CdTe (left) and cadmium chloride treated (right) CdTe

4.4 SEM results

SEM images revealed a dramatic change in morphology between the as-deposited and the treated CdTe. Due to the high deposition temperature used for CSS, the as-deposited samples displayed grains size typically up to $1\mu\text{m}$ with clear boundaries (Figure 6). The CdCl_2 treated samples revealed grains that had coalesced with diffuse boundaries. This morphology provides a lower possibility for recombination. The treatment does not induce grain growth. The activated devices differed from the as-deposited device in both grain morphology and orientation.

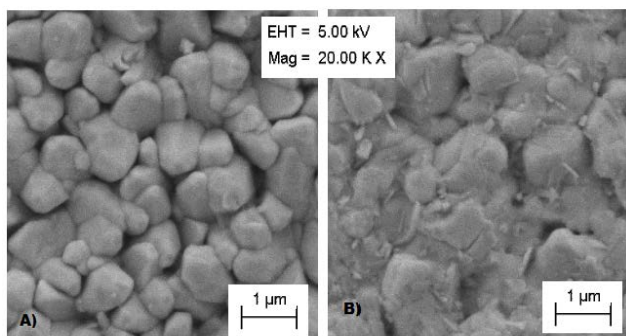


Figure 6: SEM images of as-deposited and CdCl_2 treated CdTe

5. SURFACE ETCHING

The CdCl_2 treated samples showed a high series resistance from J-V curves. This effect is due to the difficulty in creating an ohmic contact with CdTe. CdTe has a high ionisation energy, therefore the work function of the back contact material has to be higher than 5.8eV [10]. In order to minimize losses due to the high series resistance, the sample

surfaces can be etched prior to depositing the back contact to create a Te-rich surface.

The surface was etched using a nitric phosphoric acid (NP) solution. The concentration of the solution was chosen to be 1 HNO_3 , 76 H_3PO_4 , 29 H_2O [11]. This treatment has a double action on the surface. It removes the oxide-layer on the CdTe surface formed due to exposure to air and it also creates the p^+ -doped Te rich-layer for improved contacting.

The length of the treatment time and the concentration of the solution are the important parameters for this process. The activated samples were dipped for 20s, 30s, 40s, 50s and 60s in the solution, followed by a dip in DI water to rinse. From ~20s onwards the formation of bubbles on the surface was visible.

After the etching treatment, the surface changed in colour and corresponded to a change in resistance in the layer. It is advisable to deposit the back contact as soon as possible to prevent re-oxidation of the surface. The etching process helps to prevent the roll-over-effect at higher voltages. Figure 7 shows J-V curves for different etching times.

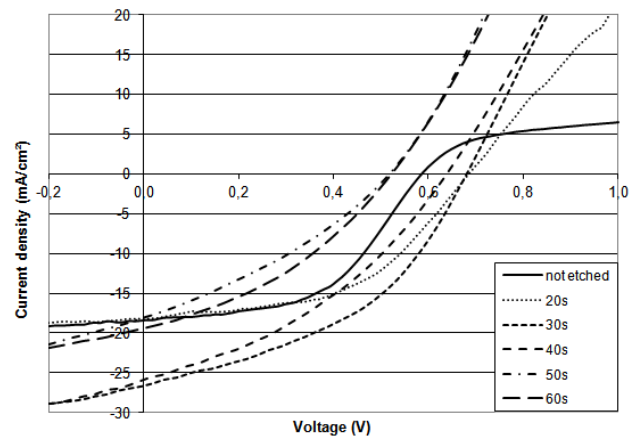


Figure 7: J-V curves for different etching times The devices were treated in a 1%wt CdCl_2 in CH_3OH solution at 50°C and annealed for 15 min at 370°C .

The etching process improves both the V_{oc} and the J_{sc} but the fill factor is diminished due to the reduced shunt resistance. The longer the etching process takes, the thinner the CdTe layer becomes, resulting in a lower shunt resistance and hence a lower FF. The best efficiency was obtained by etching for 30s and was $\eta=7.81\%$; however the FF was 0.43.

CONCLUSIONS

A process of optimisation was carried out for the wet chemical CdCl_2 treatment of CSS-deposited CdTe solar cells. Various parameters were studied and optimised. The treatment can be divided in two phases: the cadmium chloride treatment phase and the annealing phase. For the treatment phase, the optimum conditions were found by changing solution

concentration and solution temperature. Best results were obtained using 1%wt CdCl₂ in CH₃OH solution at 50°C. For the annealing phase, the temperature and time were varied, and it was found that 370°C for 15 min produced the best results. Efficiencies of about 7% were obtained for 0.25 cm² working cells and the results were reproducible.

SEM characterisation of treated samples showed eroded grains, merged together, with fewer crystal defects. XRD results showed that recrystallization had occurred for the treated CdTe surfaces. The treated material had randomised grain orientation.

The surface of the treated samples was also etched to create better contacts between the CdTe and Au back contacts. The etching process was carried out using NP etching for different exposure times. Although, the effect of this treatment reduced series resistance, it resulted in a lower shunt resistance. This etch treatment requires further optimisation to obtain higher FF and hence better efficiencies.

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