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Process Development of Sublimated Cu-free CdTe Solar Cells

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Abstract

CdCl₂ treatment by evaporation has been optimised for CdTe solar devices without a copper annealing process. In this work, we show that the performance of CdTe devices follow a curvilinear trend by increasing the amount of chlorine used for the passivation treatment. It has been observed that the maximum of the curve represented the best performing devices. However, excessive CdCl₂ caused deleterious effect on electrical performances of the cells. The PL imaging analysis has been found to be a useful technique to assess the effectiveness of the activation treatment due to the presence of chlorine in CdS thin films. Electrical characterisation has been performed on each device and PL imaging analysis has been used to validate the performances of the CdTe solar cells. Results showed that the optimum performance corresponded to the highest PL image emission signal.

Introduction

Among II-VI compounds, CdTe is an excellent material for photovoltaic applications because it has a nearly ideal optical band gap (1.45 eV) and a high absorption coefficient ($>10^4\text{cm}^{-1}$). The cadmium chloride (CdCl₂) treatment is an essential step for high efficiency CdTe/CdS solar cells, which significantly changes the structural and electrical properties of the film. After CdCl₂ activation, CdTe films undergo a change in surface morphology, with coalescence of grain boundaries, recrystallization and grain reorientation. Furthermore, the annealing treatment reduces optical losses due to the interdiffusion mechanism, where S diffuses into the CdTe, forming CdTe_{1-x}S_x; while Te diffuses in CdS as CdS_{1-y}Te_y. CdTe band gap is reduced, which results in higher absorption at long wavelengths; however built-in voltage can reduce and shunt issues can result as the CdS is consumed. Treated devices show higher p-type conductivity, passivation of

interface defects, reduction of planar defect density and change in concentration and distribution of trapping states. Additionally, CdCl₂ post-annealing enhances the charge separation, increasing hole depletion near the grain boundaries and improves carrier collection [1].

However, the process window that allows beneficial impact for the device output is small. Under-treatment can result in limited device current, while an over-treatment can result in excessive consumption of the CdS layer limiting the device voltage [2] and possibly causing blistering and delamination [3].

Electrical performances and material characterisation are generally carried out to assess the effect of CdCl₂ treatment. PL imaging is an advanced characterisation technique that can assist device optimisation, allowing each processing stage to be analysed.

In this paper, we report the optimisation of the CdCl₂ treatment for CdTe solar devices, assisted by PL imaging characterisation. The amount of CdCl₂ evaporated on CdTe surfaces was the investigated parameter in this study. CdCl₂ was varied in the range of 0 - 0.8 grams to evaluate the effect and the homogeneity of the treatment. Electrical output of the CdTe devices were measured and related to the amount of CdCl₂ used. Pixel counts of the PL images were also related to the electrical performances.

Here, the emission present in the PL imaging, is likely from chlorine containing defects as both sulphur ($V_S\text{-Cl}_S$) and cadmium vacancies ($V_{Cd}\text{-Cl}_S$) in the CdS layer [4]. A low PL image signal indicates no chlorine presence in the films. In this case the image appears dark with low pixel counts (roughly estimated ~1,000). When a sample is CdCl₂ treated, the image appears brighter with higher pixel counts (estimated ~48,000) due to the presence of chlorine.

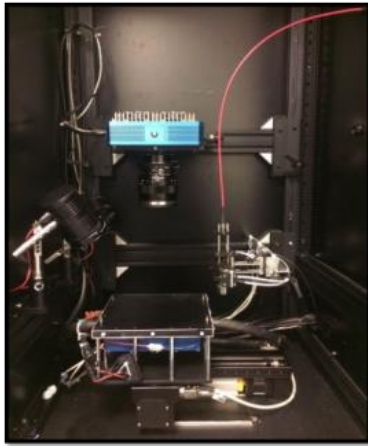


Figure 1: Bespoke PL imaging system used for this work with excitation wavelength of 405 nm and a 720 nm long-pass filter.

Experimental Procedures

Prior to CdS deposition, 50x50mm² substrates (Pilkington TEC 10, FTO) were ultrasonically cleaned in a de-ionised (DI) water solution containing 10% acetone and 10% IPA, for 1 hour at 80°C, and subsequently received a 5-minute plasma clean in an argon/oxygen environment. CdS thin films were deposited by ultrasonically assisted chemical bath deposition (sono-CBD) [5], where an ultrasonic probe has been used instead of a conventional magnetic stirrer to agitate the bath. 0.01M Cd(CH₃COO)₂, 0.1M CH₄N₂S, 25% NH₄OH were used as precursors in 200 mL DI water in a preheated vessel at 70° C, resulting in films of ~200 nm thickness [4]. After deposition, the substrates are rinsed with DI water and dried with dry compressed air.

The CdTe deposition was carried out in a homemade close-space sublimation system (CSS) [6]. The CdS substrate and source plate were loaded in the chamber and the sublimation procedure was initiated. Argon and oxygen were introduced in the chamber (6% O₂ in Ar); the deposition pressure during sublimation was 1 Torr. Sublimation is initiated when the substrate temperature and source temperature are 515° C and 630° C respectively. A 3 minute CdTe deposition results in 4-6 μm thick films.

The CdCl₂ treatment was carried out using thermal evaporation at various CdCl₂ concentrations. A quartz crucible was filled with 0.2, 0.4, 0.5, 0.6 and 0.8g of CdCl₂, which was evaporated at ~3x10⁻⁷ Torr,

until the crucible was empty. The samples were subsequently annealed on a hot plate using two-step ramping conditions 50°C / min up to 370°C and 5°C / min to the dwell temperature of 425°C, which was held for 1 minute. Devices were completed by depositing ~80 nm of gold using thermal evaporation, as the back contact.

PL imaging was carried out using a home-made system (Figure 1). An LED of 405 nm was used as the excitation source, with a Si CCD camera fitted with a 720 nm long-pass filter. Exposure time for all of the measured samples was kept to 10 seconds. All measurements were taken at room temperature, with the sample positioned with the glass side of the substrate facing the camera. Figure 2 shows a comparison of the PL emission detected for an untreated CdS film and a CdCl₂ treated CdS film, both on FTO. 0.2 g were evaporated on CdS film and annealed as for CdS/CdTe stacks. The intensity of the PL emission (pixel counts) is used as an indication of the effectiveness of the CdCl₂ treatment. The untreated CdS film has an average of 1,000 counts while the treated CdS film has an average of 58,000 counts. This is the range that the system can operate before the saturation limit of the detector is reached (~64,206 counts).

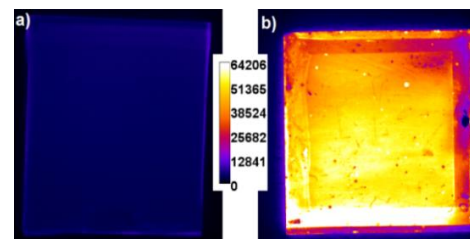


Figure 2: PL image of a) an as-deposited CdS layer and b) CdCl₂ treated CdS layer.

The electrical performance was studied using current density–voltage (J–V) curves, measured with the solar cell exposed under 1000 W/m² illumination and using an AM 1.5G filter.

Results

Figure 3 shows the J–V curve and the associated PL image of an as deposited device where no CdCl₂ treatment has been performed. The performance of this device is extremely poor, with an average V_{oc} of 370mV and an average J_{sc} of 0.3 mA/cm² and FF of 0.4. The average measurements were calculated using 10 cells across each CdS/CdTe device. PL

image analysis also confirmed that the post deposition annealing step performed without the presence of chlorine, had no effect on the device. In fact, low signal intensity was detected with an estimated average of ~1,000 counts.

The following experiments were carried out by varying the amount of CdCl₂. 0.2 g (Figure 2) of evaporated CdCl₂ has been deposited on CdS/CdTe thin films and the electrical properties have been studied. The average efficiency increased from ~0.03% (when no CdCl₂ was added) to 7.2%, with a V_{oc}, J_{sc} and FF of 727mV, 18.7mA/cm² and 0.5, respectively. These results were confirmed using PL imaging, which showed an average of ~13,700 counts contrary to the ~1,000 counts detected previously on the samples annealed with no CdCl₂.

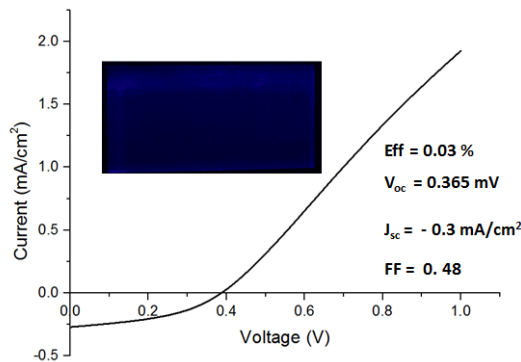


Figure 3: J-V Curve and PL image of an as-deposited CdTe device.

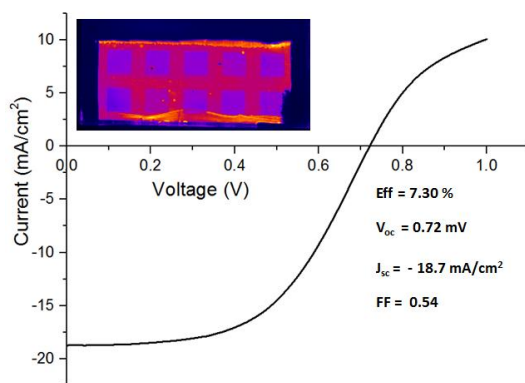


Figure 4: J-V Curve and PL image of a CdTe device with 0.2 g of evaporated CdCl₂.

Increasing the amount of CdCl₂ further during evaporation to 0.4g results in higher performance devices. The average efficiency of the CdTe device was 7.9 %

and the counts detected by PL image were ~ 22,240. The average of PL counts was taken over the area (0.25 cm²) of 10 individual cells for each sample.

The optimum device performance was achieved when CdS/CdTe thin films were treated with 0.5 g of evaporated CdCl₂ with the device showing the highest average efficiency (8.40%) with 0.762 mV voltage 18.77 mA/cm² current density and 0.59 FF. Figure 3 shows the J-V curve with the associated PL image, with an average emission of 23,300 counts

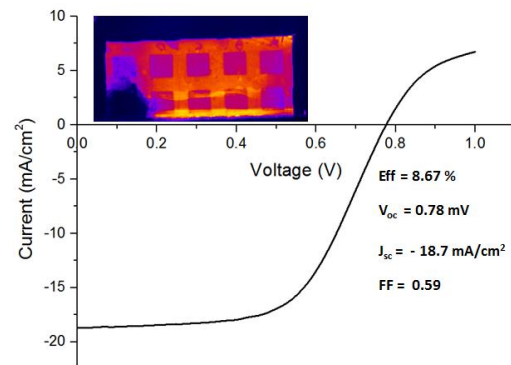


Figure 5: J-V Curve and PL image of a CdTe device with 0.5 g of evaporated CdCl₂.

Further increase in the amount of CdCl₂ used in the deposition proved to have a deleterious effect on the performance of the devices. A dramatic drop in electrical performance has resulted when using 0.6 g CdCl₂ on the CdTe device. The average V_{oc} dramatically decreased to 662 mV while the J_{sc} remained at approximately the same value (18.74 mA/cm²) and the FF decreased to 0.54. To conclude the study, 0.8 g of CdCl₂ was deposited on the CdTe, to identify an over-treated CdCl₂ treatment, performance of this sample was very similar with 0.6 g with average V_{oc}, J_{sc}, and FF to be 661 mV, -18.5 mA/cm², and 0.51 respectively. The drop in voltage can be an indication of excessive consumption of sulphur from CdS due to the intermixing between the CdS and CdTe layers during the activation process.

Figure 6 shows the clear trend of efficiency against the increasing amount of evaporated CdCl₂. The figure shows a curvilinear trend where the ascending part represents the progressive increase amount of the CdCl₂ used (starting from 0g), reaching the highest efficiency at 0.5 g. The descending part of the curve corresponds to the further increase of CdCl₂ used, where a deleterious effect has

been observed on the performances of the CdTe devices. A similar trend was observed in the PL imaging analysis (Figure 7) where the optimum performance corresponded to the highest intensity detected. This confirms the agreement between PL imaging analysis and electrical characterisation.

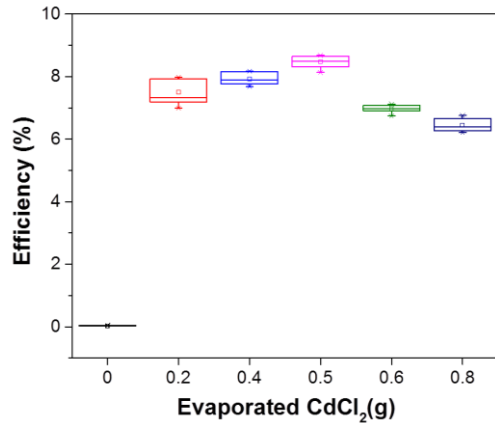


Figure 6: The efficiency trend versus the amount of evaporated CdCl₂.

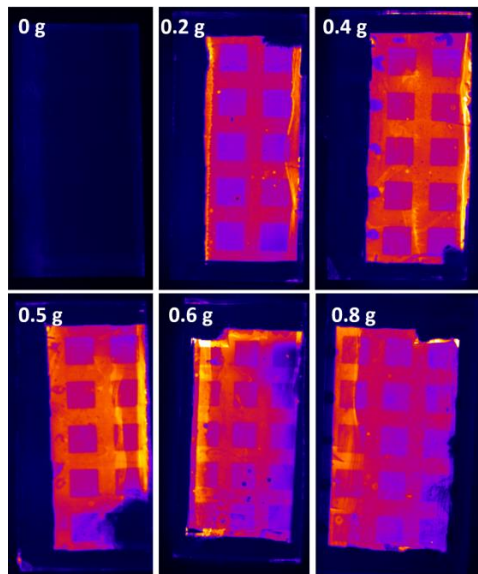


Figure 7: PL Images of CdTe devices treated with different amount of evaporated CdCl₂.

Conclusions

PL imaging and electrical characterisation were performed to investigate the effectiveness of CdCl₂ post-annealing treatment. Identical CdS/CdTe devices were fabricated and undergone different treatments by varying the amount of evaporated CdCl₂. Results showed that the electrical performance is interlinked with the amounts of CdCl₂ used to treat CdTe thin films. As deposited CdS/CdTe

films resulted in poor device performance with no efficiency, while treated devices showed a progressive increase in performance. A clear trend was identified in the CdCl₂ treated devices where the electrical output improved with increasing quantity of evaporated CdCl₂, up to an optimal amount (0.5 g) where the average efficiency was measured to be 8.40%. However, further increase of evaporated CdCl₂ caused a reduced performance of the CdTe devices, in particular for the V_{oc}. This is believed to be caused from excessive consumption of the CdS layer during the CdCl₂ annealing process, leading to a weaker p-n junction. Additionally, PL imaging analysis of the devices confirmed the trend identified from the electrical characterisation, where optimum performance corresponded to the highest PL image emission signal. This indicates that advanced characterisation techniques such as PL imaging can provide useful information about the effectiveness and uniformity of the CdCl₂ post-annealing treatment.

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