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Photoluminescence imaging analysis of doping in thin film CdS and CdS/CdTe devices

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Abstract — The use of photoluminescence (PL) imaging analysis to assess the effectiveness of the passivation treatment due to the presence of chlorine in CdS thin films has been investigated. In this work, we show that the chlorine doping effect in the CdS window layer can be detected by PL imaging analysis, due to the formation of a defect complex of sulfur vacancy and Cl_s (V_s-Cl_s) and complexes between halogen ions and cadmium vacancies (V_{Cd}-Cl_s). CdTe devices with differently doped CdS layers were investigated. PL imaging, TEM, IV performance indicators and EQE analysis were performed to understand the effect of the different dopants on the electrical performances of CdTe devices.

I. INTRODUCTION

Thin film CdTe solar cells are already a commercially successful technology, due to a combination of low processing costs, and high module efficiency. The current efficiency record is 22.1 % by First Solar [1], where an important step in the device fabrication is the CdCl₂ post annealing treatment. The CdCl₂ treatment is necessary to produce high performing devices due to the beneficial structural and electrical impact on CdS/CdTe heterojunction devices. However, a weak CdCl₂ activation treatment results in poorly passivated grains, limiting the performance of the device, whilst an aggressive CdCl₂ activation process can cause excessive consumption of the CdS layer and may damage the junction with excessive chlorine build up at the interface [2], leading to delamination [3]. Usually optimization of this process consists of assessing the performance of completed devices which can be very time consuming and not cost effective.

Photoluminescence (PL) imaging is a powerful technique which allows fast, non-contact device analysis at each step of the fabrication process. This technique is suitable for large scale manufacturing use and assists the quest for further cost reduction of CdTe solar cells [4].

Commonly in CdS/CdTe solar cells, PL spectra peaks in the range of 1.3 – 1.5 eV originates from CdTe, while peaks in the range of 1.9 – 2.2 eV are related to CdS [7]. When the CdS is subjected to the CdCl₂ annealing treatment, a broad PL emission is generated at around 1.7 eV, which is associated with a defect complex of a sulfur vacancy and Cl_s (V_s-Cl_s) [5][6]. CdCl₂ activation introduces large amounts of Cl atoms which

may occupy sulfur vacancies and introduce the Cl_s states. Additionally, deep and shallow states are formed since complexes between halogen ions and cadmium vacancies are also likely to occur (V_{Cd}-Cl_s) [6]. The emission signal generated by the presence of chlorine in CdS films can be detected by PL imaging. This analysis can provide useful information about the effectiveness of the CdCl₂ treatment in CdS/CdTe devices even before the application of the back contact.

In this report, PL Imaging analysis was used to investigate the effect of different chlorine dopants in the CdS thin films used for CdTe solar cells. CdCl₂ treatment followed by annealing is known to improve the structural and electrical properties of CdS[6], as well as CdTe. Here we have used different chlorine dopants to understand whether the same improvements could be achieved on the as deposited CdS layer and on the electrical performance of the CdTe devices. The resulting electrical characteristics were studied against the presence of the various chlorine dopants.

II. METHODOLOGY AND EXPERIMENTAL PROCEDURES

A. PL imaging analysis

PL imaging was carried out using the system shown in Fig. 1. A 405nm LED was used as the excitation source, with a Si CCD camera fitted with a 720 nm long-pass filter used to detect the PL signal. The exposure time for all of the measured samples was kept at 10 seconds. All measurements were taken at room temperature and with the sample positioned with the glass facing the camera.

Fig. 2 shows the PL images of as-deposited CdS and CdS following a wet-CdCl₂ treatment. PL image acquisition shows the effect of the treatment on the film. The intensity of the signal (pixel counts) was used to compare untreated and treated material (Fig.2). When the Cl signal is not detectable the image appears completely dark as shown in the response from the untreated material. High intensity signals result in a brighter image, indicating the presence of chlorine complex emission from the CdCl₂ treated material. Using the scale bar as a reference, the intensity of ~1000 counts corresponds to

untreated material and $\sim 65,000$ counts (detector saturation limit) is typical for a heavily treated layer.

Figure 1: PL imaging system schematic diagram.

These values have been used to establish two extremes of the range and to investigate the performance and homogeneity of the passivation treatment.

During the CdCl_2 activation treatment, Te diffuses into the CdS to form a $\text{CdS}_{1-x}\text{Te}_x$ layer. This creates a broad PL emission in the range of 1.6-1.8 eV [5]. However, since the CdTe was not present, the contribution from Te diffusion into the CdS is removed and therefore the detected signal is due to the presence of chlorine in the CdS film. We believe that chlorine is responsible for the formation of sub band gap $V_s\text{-Cl}_s$ and $V_{\text{Cd}}\text{-Cl}_s$ complexes in the CdS [6].

Figure 2: PL images of as deposited CdS (a) and CdCl_2 treated CdS (b) thin films.

Fig. 3a) shows the same sample as in Fig. 2, however after the deposition of the CdTe layer. The average PL signal decreased to 1.42×10^4 , due to the formation of the p-n junction. This results in consumption of the CdS layer, therefore the detection of $V_s\text{-Cl}_s$ and $V_{\text{Cd}}\text{-Cl}_s$ complexes, by PL imaging, was limited and the PL emission showed a reduced signal. In Fig. 3b) The same sample after the CdCl_2 passivation treatment is illustrated. The average PL counts increased to 4.93×10^4 as a direct result of reintroduction of Cd and Cl in the CdTe device, which diffused into the CdS layer, due to the CdTe activation treatment by evaporation of CdCl_2 .

PL imaging analysis can be related to the electrical properties of the devices. This investigation was assisted by measuring current density–voltage (J-V) curves, with the solar cell exposed to AM1.5G, 1000 W/m^2 illumination. EQE measurements were taken using an USHIO UXL-150so Xe Lamp with Newport 67005 lamp housing and H10 Horiba Jobin Yvon monochromator.

Figure 3: PL images of CdS: a) after CdTe deposition and b) after the second CdCl_2 activation treatment.

For a comprehensive analysis of on the effect of the dopants in CdS on the CdS/CdTe stack, structural investigations were also performed, using a Leo 1530 VP high-resolution field emission gun scanning electron microscope (FEGSEM).

B. CdS thin film deposition by sono-CBD

The substrates ($50 \times 50 \text{ mm}^2$) (Pilkington TEC 10, FTO) were ultrasonically cleaned before CdS deposition, in a de-ionised (DI) water solution containing 10% acetone and 10% IPA, for 1 hour at 60°C . They then received a 5-minute surface activation pre-treatment in an argon and oxygen plasma. CdS thin films were deposited using a sono-chemical bath (sono-CBD) [7], where an ultrasonic probe was used to replace a conventional magnetic stirrer to agitate the bath. 0.01M $\text{Cd}(\text{CH}_3\text{COO})_2$, 0.1M $\text{CH}_4\text{N}_2\text{S}$, 25 wt % NH_4OH were used as precursors in 200 mL DI water in a preheated vessel at 70°C , resulting in films of $\sim 150 \text{ nm}$ thickness [4]. After CdS deposition, the substrates were rinsed with DI water and dried with dry compressed air. CdS doping was carried out using the same procedure, however in each case, alternative chlorine dopants were added to each bath (50% of the concentration of Cd source), with each deposition lasting for one hour. This resulted in different final thicknesses of the CdS films, according to the dopant added in the bath. In this work AlCl_3 , and CdCl_2 were the investigated dopants. In the case of CdCl_2 , this was used as a replacement cadmium source to the cadmium acetate used in the baseline process. The presence of AlCl_3 in the bath affected the deposition rate of the CdS layer significantly and resulted in an approximately 50 nm thick film.

C. CdTe film deposition by Close Space Sublimation and the CdCl₂ activation treatment

CdTe thin films were deposited in a home-made close-space sublimation system (CSS), using IR lamps, and graphite susceptors [8]. The prepared CdS film and source plate were placed in the vacuum chamber, and separated using quartz spacers. The deposition pressure during sublimation was 1 Torr, with a 6% O₂ in Ar gas mixture. The source and substrate temperatures were rapidly increased, to 630°C and 515°C, and the deposition time was fixed to 3 minutes, which results in 4 to 6 μm thick films. The CdCl₂ activation treatment was carried out by thermal evaporation. A quartz crucible was loaded with 0.5 g of CdCl₂, which was evaporated at $\sim 1 \times 10^{-6}$ Torr. Post-annealing treatment was carried out after thermal evaporation. The samples were annealed on a hot plate at a dwell temperature of 415°C for 1 minute with ramping rate of 4°C/min starting from 370°C. Devices were completed with 80nm gold contacts deposited using thermal evaporation, with no intentional copper doping added in this study.

III. RESULTS

A. PL imaging analysis on CdS/CdTe devices

CdS/CdTe devices have been fabricated by varying the dopants in the CdS layer, as described in the experimental section. All samples underwent the same CdCl₂ post annealing treatment. Fig. 4 shows the PL image of CdTe devices with un-doped CdS, CdCl₂ wet-treated CdS, CdS deposited with CdCl₂ as Cd source and CdS:AlCl₃.

Figure 4: PL images of CdS/CdTe devices with differently doped CdS layers: a) un-doped CdS, b) wet treated CdS c) CdS with CdCl₂ as Cd Source and d) CdS:AlCl₃.

The PL signal was averaged over the 8 individual cells on each sample (each cell has an area of 0.25 cm²). The baseline CdS/CdTe structure with no doping in the CdS layer, showed 2.36×10^4 average PL counts with a range of 8.7×10^3 to 4.08×10^4 counts. The CdS which has been CdCl₂ wet treated (Fig 4b) showed an average count intensity of 4.93×10^4 (as presented before in the methodology in Fig. 3b). Replacing Cd(CH₃COO)₂ with CdCl₂ as Cd source, for the deposition of the CdS layer, the average counts remain comparatively the same (2.32×10^4), whilst the maximum PL counts increased up to (4.36×10^4). This can be an indication of a favorable

incorporation of Cl inside the CdS layer. A low signal intensity was detected for CdS layers doped with AlCl₃ (2.2×10^3 average PL counts). This is an indication of either an under treated device, where the incorporation of CdCl₂ is almost undetectable or an over treated cell, which resulted in excessive consumption of CdS.

B. Electrical characterization of CdS/CdTe devices

Fig. 5 shows the J-V curves of CdS/CdTe devices with different CdS layers. The performance of the CdS/CdTe device where CdS layer has been deposited with no additional doping (considered as the baseline structure) gave 10.25 % efficiency with Voc, Jsc and FF of 811mV, 19.2 mA/cm² and 65% FF, respectively. Using CdCl₂ as the Cd source for the deposition of the CdS layer, the device parameters improved. Efficiency increased to 10.90 % due to an increase in the Jsc (19.9 mA/cm²) and FF (67%) while Voc remained constant (807 mV). This is in agreement with the PL imaging analysis, which showed an increase of the maximum PL counts.

Figure 5: J-V curve of CdS/CdTe devices with different CdS doped layers (un-doped CdS, CdS with CdCl₂ as Cd Source, CdS: ZnCl₂, wet treated CdS and CdS:AlCl₃).

The CdTe device where the CdS layer was CdCl₂ wet-treated, prior to CdTe deposition, showed a reduction in electrical performance. The efficiency, Voc and FF decreased to 9.46%, 784 mV and 58%, respectively. There is a slight increase in current density (20.6 mA/cm²). PL imaging analysis showed an average of 4.93×10^4 counts, which was significantly higher in comparison to the other investigated devices. However, this sample cannot be directly compared, since it has been undergone a double CdCl₂ treatment (before and after the deposition of CdTe). Additionally, since the wet activation treatment performed on CdS films was not totally uniform, this

could have affected the final performances of the device. In fact, in agreement with the PL imaging analysis, SEM results showed some areas completely depleted of CdS, as an effect of the over treatment. Doping CdS with AlCl_3 had a deleterious effect on the overall performance of the device. Efficiency, V_{oc} , and FF decreased to 6.20%, 504 mV and 0.55, respectively. The significant decrease in voltage (~ 300 mV reduction compared with the baseline device) indicated a poor p-n junction formation. This was also confirmed by the PL image analysis where the PL emission showed 2.2×10^3 counts.

C. External Quantum Efficiency (EQE)

Fig. 6 shows the normalised external quantum efficiency (EQE) analysis performed on the investigated devices. The baseline CdTe structure with the un-doped CdS layer and the CdS layer deposited using CdCl_2 as source of cadmium showed comparable EQE responses. Only, in the range of 360 to 580 nm a slight decrease in EQE was observed for the un-doped CdS layer compared to the CdS deposited with CdCl_2 in the bath.

Figure 6: EQE spectra of the investigated samples (un-doped CdS, CdS with CdCl_2 as Cd Source, wet treated CdS and $\text{CdS}:\text{AlCl}_3$).

The CdTe device with the wet treated CdS layer showed a slightly higher EQE in the range of 450-600 nm. Additionally, the EQE response showed less back surface recombination (700-850 nm) in comparison with the un-doped and CdCl_2 doped devices[9]. The CdTe device with $\text{CdS}:\text{AlCl}_3$ doped layer showed an atypical EQE curve. The dramatic decrease in absorption in the range of 300-540 nm suggests significant consumption of CdS layer during the CdCl_2 activation treatment. It must be mentioned that the as deposited CdS layer doped with AlCl_3 was only 50 nm thick, with a consequence that the CdCl_2 activation treatment results in the CdS layer becoming fully consumed. This is also in agreement with the PL imaging analysis, where the PL image gave a low signal of 2.2×10^3 counts.

D. SEM, EDX TEM and XRD analysis on CdS/CdTe Devices

To have a comprehensive understanding on how the dopants affect the CdS/CdTe interface after the CdCl_2 treatment, morphological and structural analyses were carried out. Fig. 7 shows the SEM cross section analysis of the investigated devices, focusing on the CdTe/CdS interface. The baseline structure with the un-doped CdS layer and the CdS deposited with CdCl_2 as the cadmium source exhibit uniform CdS layers with an average thickness of ~ 120 nm (Fig. 7a,b). Fig. 7c) shows the CdTe/CdS interface with the CdCl_2 wet treated CdS layer. This device showed a non-uniform CdS layer where some areas were completely depleted as an effect of the double treatment, causing shunt-paths in the device. SEM images of the CdTe device with the $\text{CdS}:\text{AlCl}_3$ doped window layer (Fig. 7e) showed that the CdS layer is barely visible, indicating total CdS consumption during the CdCl_2 activation treatment due to the insufficient initial thickness (~ 50 nm).

Figure 7: SEM cross section of CdS/CdTe interfaces with: a) un-doped CdS, b) CdS with CdCl_2 as Cd Source, c) wet treated CdS and d) $\text{CdS}:\text{AlCl}_3$.

These results agree with PL imaging analysis and electrical performance of the investigated devices.

TEM analysis was also performed on the device where CdCl_2 was used as Cd source for the deposition of the CdS layer. This showed the highest PL emission and electrical response. The TEM analysis confirmed the presence of chlorine at the CdTe/CdS interface (Fig. 8) after the CdCl_2 activation treatment. This is in agreement with the PL analysis where the chlorine can be detected due to the formation of $V_s\text{-Cl}_s$ and $V_{Cd}\text{-Cl}_s$ complexes which have energy levels in the band gap of the CdS layer.

Figure 8: CdS/CdTe device with CdCl₂ as source of Cd during CdS deposition a) TEM image and b) chlorine map of the device.

It is known from literature that CdS films exhibit both zincblende (cubic) and wurzite (hexagonal) crystal structure, where the latter is the most stable one [6]. The introduction of dopants in CdS films might influence the crystal growth. Therefore, XRD was performed on all the investigated CdS layers to access any structural change. All the CdS films showed a mixed cubic-hexagonal structure, except the CdCl₂ wet treated layer, which showed the hexagonal phase. Furthermore optical characterisation showed a wider bandgap (2.4 eV) compared to the other investigated samples which can explain the reduction of absorption in the range of 450 nm – 550 nm.

IV. CONCLUSION

CdS thin films were deposited by CBD with a variety of different dopants. A comparison was made between CdTe devices where CdS layers were un-doped and doped with AlCl₃ and CdCl₂. These devices were subjected to the same CdCl₂ activation treatment. The presence of chlorine causes the formation of V_S-Cl_s and V_{Cd}-Cl_s complexes in the sub band gap of the CdS material. PL imaging analysis was used to detect the emission originated from these complexes. It has been verified that the PL signal is related to the presence of chlorine when the CdS film was treated with CdCl₂ prior to the deposition of CdTe.

It has been shown that the presence of different chlorine dopants (CdCl₂, AlCl₃) in CdS films affected the PL emission signal, once the CdCl₂ treatment was performed on the final device.

Furthermore, PL emission was found to be useful to provide qualitative information about the effectiveness and the uniformity of the CdCl₂ treatment on the investigated CdTe devices.

Morphological and structural characterization has been also performed to have a comprehensive understanding on the role of the dopants on the final performance of the solar cells.

Further investigation using alternative dopants may lead to improvement of devices performances. Even though PL was proved to be a powerful tool in the assessment of different CdS dopants use, deeper characterization could enlarge the understanding on the process.

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