

Cl Diffusion in CdTe Solar Cells Activated by Gaseous CHClF_2 Atmosphere

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Abstract — The activation treatment is considered of dramatic importance for CdTe solar cells. The most effective activation processes are based on chlorine compounds. However it is still not clear how Cl diffusion depends on the chlorination method. In this paper we activated CdTe solar cells by gaseous CHClF_2 and investigated the Cl presence by TEM and XPS. Preliminary results show clear presence of Cl trapped at the CdS/CdTe interface. Thanks to the flexibility of the gaseous activation treatment, further samples will be prepared in order to force larger quantity of Cl into the absorber and they will be similarly analyzed. TEM will be used to investigate Cl presence at grain boundaries and XPS to determine the compounds formed by Cl.

I. INTRODUCTION

The photovoltaic (PV) technologies are constantly improving and in the last years new materials and solutions have been presented by the community. In this scenario CdTe thin film solar cells represent one of the most important players of the market. It is well known that best performance is achievable only when the so called *activation treatment* is applied to the CdTe [1], this is usually performed by means of CdCl_2 being applied to the absorber surface in different ways (e.g. vacuum evaporation, dipping, vapor transport, etc..) [1], [2]. Many physical and electrical changes are attributed to the activation of the device: recrystallization (grain growth and orientation change), grain boundaries passivation [3], doping of the CdTe [4], etc. In the 2010, Romeo et al. [1] demonstrated that the transformation of the absorber is connected to the action of chlorine activating the CdTe by using a Cl containing gas atmosphere, more recently Major et al. [5] presented an effective non toxic activation treatment replacing the CdCl_2 with MgCl_2 and obtaining similar results. However, there are many open points on the Cl diffusion and interaction with the lattice atoms during the activation and their dependency on the way how the chlorination is performed.

In this paper we address the effects of chlorination performed in a gaseous atmosphere containing CHClF_2 . JV brings out the differences in the finished devices performance due to the chlorination. TEM will be used to reveal the grains transformation and Cl diffusion, XPS depth composition analysis will confirm the presence of chlorine after the treatment within the grains and or at the grain boundaries.

II. EXPERIMENTAL

In order to avoid unwanted effects on the absorber, the preliminary results presented in this study were obtained using a very simple device structure. The substrate is commercially available Delta Technologies boro-aluminosilicate glass coated with 200 nm of ITO. To avoid In diffusion a 200 nm buffer layer of ZnO was deposited by reactive RF sputtering at 400 °C in Ar/O₂ atmosphere. CdS was also sputtered at 300 °C with a thickness of 120 nm in Ar. The absorber layer was deposited by closed space sublimation (CSS) at 515°C and 0.530 mbar of Ar/O₂ dynamic vacuum. Some samples were analyzed after this step, in this paper we will refer to them as as-deposited. The activation was performed in a vacuum tube placed in a lamp heating furnace. The base vacuum pressure was $< 10^{-5}$ mbar, and CHClF_2 - Air mixture was introduced up to reach a static pressure of 300 mbar at RT. The temperature was slowly increased up to 400 °C and maintained constant for 15 min, then the sample degassing was performed at 400 °C, 10^{-5} mbar for 10 min. In this paper we will refer to the samples fabricated without the activation as *untreated*. Finally the back contact has been deposited by sequentially sputter 2 nm of Cu and 1.4 μm of Mo and then annealed in Ar at 200 °C for 20 min.

Scanning Transmission Electron Microscopy (STEM) images were obtained using a Tecnai F20 (S)TEM equipped with a silicon drift detector allowing high spatial resolution Energy Dispersive X-ray (EDX) measurements and chemical mapping. STEM images were collected using a High Angular Annular Dark Field (HAADF) detector at 200 kV. X-Ray Photoelectron Spectroscopy (XPS) measurements were performed in a Thermo Scientific K-Alpha equipment with an Al X-ray source, calibrated by the C1s photoemission emission at 284.6 eV. All spectra were recorded by using a step size of 0.025 eV. The efficiency of the solar cells was evaluated by using a Newport Oriel solar simulator Sol2A under AM 1.5 illumination. The current density vs. voltage (J-V) measurements were obtained using a Source/Meter 2420 from Keithley and home-made LabviewTM software.

III. RESULTS

A. Current-Voltage

The typical J-V characterization was performed to check the effectiveness of the CHClF_2 chlorination. In Fig.1 the comparison with an untreated sample is made.

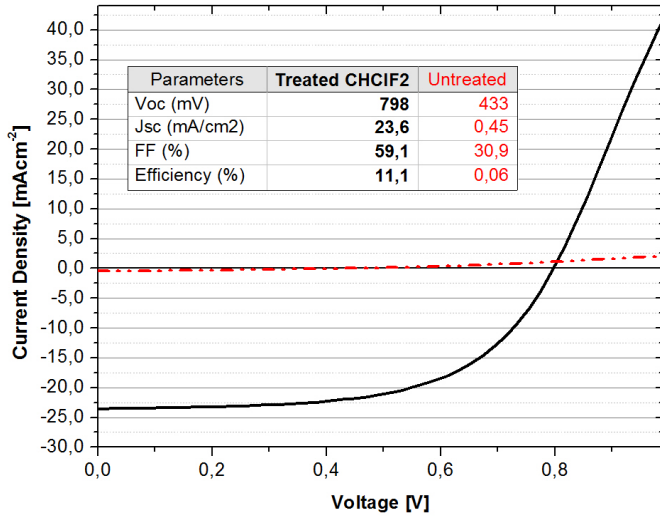


Fig. 1. J-V characteristic of the untreated (red) and CHClF_2 finished solar cells.

The dramatic changes in the electrical properties due to the activation treatment involve all the solar cell parameters. In particular the collected current is very small, indicating a too high resistance of the absorber material. The increase in Voc after the activation, indicates both an increment of the CdTe doping and a better p-n junction formation.

B. Transmission Electron Microscopy

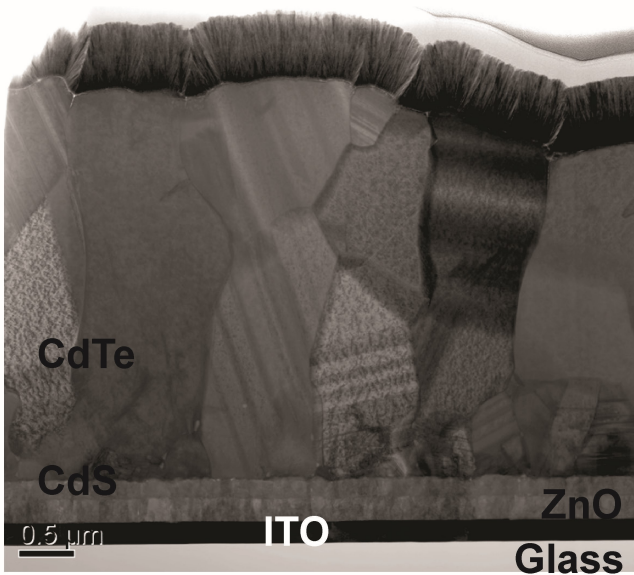


Fig.2. TEM cross section of the untreated sample.

From the TEM analysis (Fig. 2, 3) it is possible to see the physical effects of the CHClF_2 on the absorber.

In particular, after the activation (Fig. 3), the grain shape appears smoother and more homogeneous indicating some recrystallization has taken place. In the activated device the CdTe grains contain twin boundaries, whereas in the untreated device the CdTe defects appear less clear due to the high densities of stacking faults (Fig. 4). However in the treated samples the CdS/CdTe interface show many interruption points not presents in the untreated sample (Fig. 3).

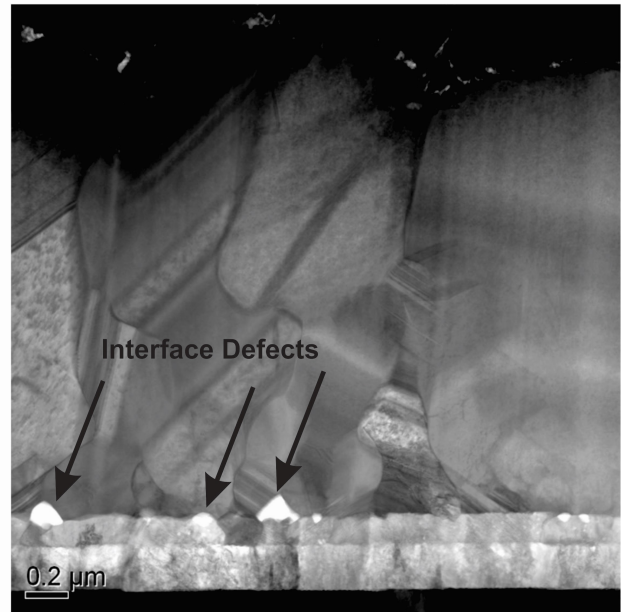


Fig.3. TEM cross section of the CHClF_2 treated sample.

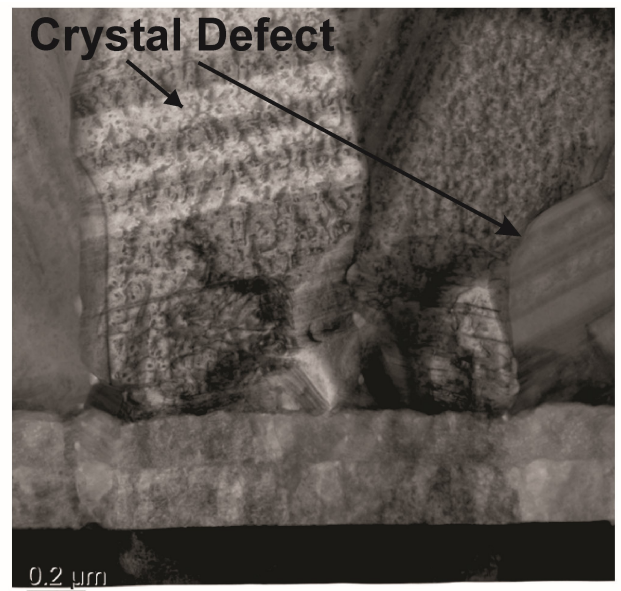


Fig.4. TEM image of crystal defect at the interface of the untreated sample.

The elemental analysis (Fig. 5) shows the symmetrical interdiffusion of S and Te and also a small amount (0.35%) of Cl placed exactly at the CdS/CdTe interface.

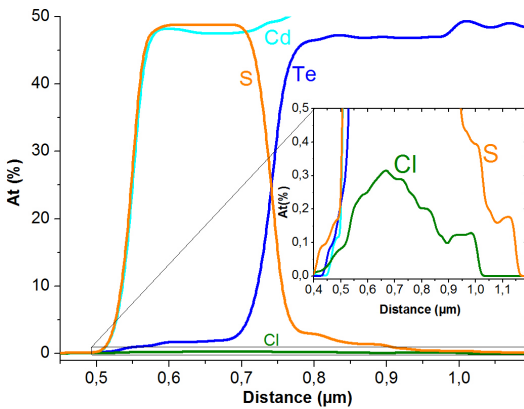


Fig. 5. Elemental analysis of the CdS/CdTe interface for a CHClF₂ treated sample.

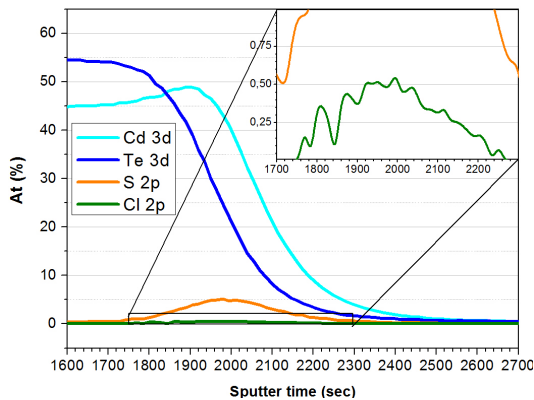


Fig. 6. XPS analysis at the interface of the CHClF₂ treated sample.

C. X-ray Photoelectron Spectroscopy

The XPS elemental analysis (Fig. 6) confirms the presence of Cl at the CdS/CdTe interface in the atomic percentage of 0.5 %. A further deconvolution of the Cl 2p, S 2p, Te 3d and Cd3d peaks respectively should indicate the possible compounds generated by the Cl at the interface.

IV. DISCUSSION

The chlorination (also known as activation) is essential to high quality CdTe solar cells production. Many different ways to perform the treatment have been presented in the past [1][2][4], but it is still not clear the reasons that make one more effective than others. To clarify the behavior of the chlorine will probably help to match the right chlorination method to the absorber deposition process and also reduce the optimization time.

The Cl diffusion through the absorber could be the key to understand the mechanism of the absorber transformation. It is in general believed that Cl diffuses mainly via the grain

boundaries [1][4] because there are not direct evidences of Cl presence within the grains. In other works, Cl presence after the CdCl₂ activation treatment has been registered only at the CdS/CdTe interface [6]. In this paper we replace the typical solid state CdCl₂ activation by a gaseous CHClF₂ atmosphere addressing the Cl diffusion dependency by the chlorination methods. Preliminary results confirm that CHClF₂ involves similar changes than usual CdCl₂ such as recrystallization and CdTe_{1-x}S_x formation. Electrical measurements support this conclusion: performance dramatically improves after the gaseous activation. No presence of Cl is registered within the grains whereas a small amount is revealed at the CdS/CdTe interface as reported in [1] for CdCl₂ solid state activation. This result suggests that independently by the methods in which Cl is introduced, it is subsequently expelled from the absorber, leaving traces trapped at the interface. To complete this job, we plan further experiments taking advantage on the flexibility of the CHClF₂ chlorination process, in particular avoiding the 10 min vacuum degas (see section Experimental) and reducing cooling time in order to reduce the Cl expulsion from the sample, then to reveal its presence in the absorber and measure how it affects the performance.

V. SUMMARY

The chlorine diffusion through the absorber layer due to the gaseous CHClF₂ activation of CdS/CdTe solar cell has been addressed. TEM and XPS were used to address the diffusion of Cl. The solar cell activation is confirmed by the improvement of the efficiency, and also the Cl presence at the interface and its absence within the grains. Further experiments will be performed to reduce the Cl expulsion from the absorber and register how it affects the device performance.

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