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INTERPRETATION OF BENEFICIAL ANNEALING OF CIGSE CELL BUFFURED WITH CO-EVAPORATED In_2S_3

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ABSTRACT

The present contribution aims at better understanding the origin of the beneficial effect of the annealing of CIGSe-based solar cell buffered with co-evaporated (PVD)In_2S_3. For long, most of the works dealing with such alternatives to chemical bath deposited (CBD)CdS buffer layer have been focused on the CIGSe/buffer interface, where the pn junction is formed. Herein, we show that as already suggested by Nguyen *et al.* [1] in the case of (CBD)In_2S_3 buffer, the annealing post-treatment most probably improves the Voc and FF of the devices because it changes the nature and/or the density of defects at the In_2S_3/r-ZnO interface. Such a conclusion is motivated by our observation that rinsing the CIGSe/(PVD)In_2S_3 structures with water before the window deposition induces the same effect as the annealing, then such treated samples are less improved by annealing. In addition, the X-ray photoelectron spectroscopy analyses performed on the CIGSe/(PVD)In_2S_3 structure before and after the water treatment show that Na carbonates are removed from the surface by the water. This latter observation suggests that the main impact of the annealing of the cells buffered with co-evaporated In_2S_3 would be the destruction or the out migration of the Na-based compounds at the buffer/r-ZnO interface.

INTRODUCTION

For environmental and industrial reasons, there is an active research aiming at replacing the CdS buffer layer deposited by chemical bath deposition (CBD) commonly used in $Cu(In,Ga)Se_2$ (CIGSe) thin film solar cell. Indium sesquisulfide (In_2S_3) based compounds are among the Cd-free alternative materials allowing the achievement of high efficiency [2].

However, independently of this alternative buffer growth process, it has been observed necessary to anneal in air the completed cell in order to achieve efficiency as high as that reached by the reference device buffered with the standard (CBD)CdS; such a heat treatment improves both the Voc and FF of the cell. Many models have been proposed to explain these parameters evolution, most of them being based on the change of the complex CIGSe/In_2S_3 interface [3].

At the end of the 90^{ies}, Nguyen *et al.* [1] have nevertheless proposed a model claming the annealing dependence of the defects nature and density at the In_2S_3/ZnO interface at the origin of the parameters improvement. The actual effect of the annealing is most likely a combination of both. In the present contribution, attention is focused on the impact of the annealing on the In_2S_3/ZnO interface.

EXPERIMENTAL

The samples investigated in this work were grown on 3 mm-thick soda-lime glass (SLG) substrates coated with molybdenum. The CIGSe layers have been co-evaporated following the 3-stage process. The Ga and Cu to group III ratio have been measured by energy dispersive X-ray spectroscopy (EDX) as being [Ga]/([In]+[Ga]) ~ 0.3 and [Cu]/([In]+[Ga]) ~ 0.9. The performance of the relative cells with standard (CBD)CdS is about 15 % (Voc = 660 mV; FF = 73 %).

The In_2S_3 buffer layer has been deposited by the co-evaporation of elemental In and S on the absorber at substrate temperature of 250 °C (temperature measured by a thermocouple in contact with the back side of the substrate). These CIGSe/(PVD)In_2S_3 structures have then been covered with our laboratory standard window bilayer consisting of r-ZnO (50 nm) and conductive ZnO:Al (200 nm). These two oxide layers have been deposited consecutively in the same chamber by RF sputtering (no air exposure after the r-ZnO deposition). However, for all series of prepared samples, half of the CIGSe/(PVD)In_2S_3 structures has been rinsed with de-ionized water (referenced to as 'water treated') and half has not (referenced to as 'reference'). The so-called 'annealing' in the following consists of heating the completed cells in air at 200 °C for 20 minutes. The cells have been characterized through J(V) measurements performed at 25 °C under AM1.5 (100 mW/cm²).

The surface analyses were performed by X-ray photoemission spectroscopy (XPS) using a Kratos Axis Ultra spectrometer and monochromatic Al Kα radiation (1486.6 eV).The base pressure in the analysis chamber was 10^{-8} Pa and the analyzed area was 700 x 300 µm². All spectra were charge referenced to the C1s XPS peak (284.7 eV).

The Raman spectra have been acquired with a Jobin-Yvon T64000, using an argon laser (514.5 nm) at 400 mW/µm² with 70 nm fences. All spectra were obtained after 5 minutes of acquisition.

RESULTS AND DISCUSSION

Fig.1 and Fig.2 respectively plot the means value (8 cells) of the Voc and FF and Fig.3 the QE of the investigated cells, (*i.e.* with and without water treatment) before and after annealing.

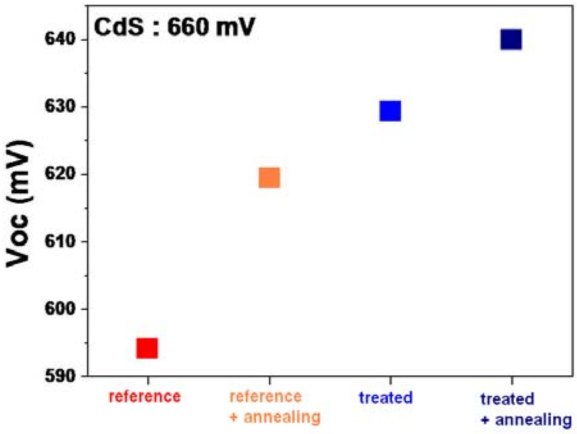

Figure 1: mean Voc of the reference (red and orange) and the water treated (blue and dark blue) cells before and after annealing respectivly.

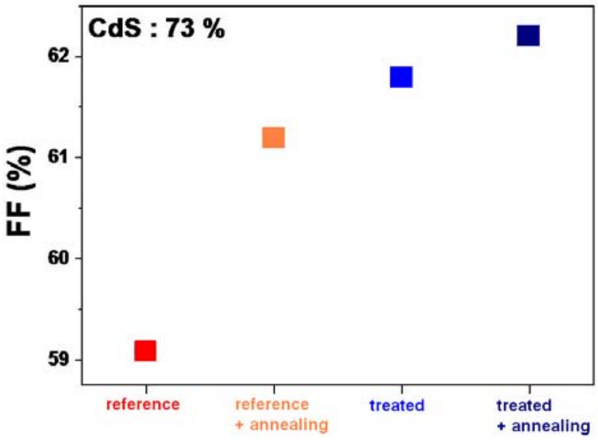

Figure 2: mean FF of the reference (red and orange) and the water treated (blue and dark blue) cells before and after annealing.

These figures show that, as already reported, the annealing of the reference sample (without water rinsing) improves both the Voc and the FF of the device while slightly decreases the Jsc, although the CIGSe/(PVD)In_2S_3 structure was formed at 250 °C and the annealing temperature is 200 °C. Much less expected is the effect of the water treatment; indeed, the rinsing of the CIGSe/(PVD)In_2S_3 structure yields Voc and FF slightly higher, and lower Jsc than those reached by the annealed reference cell. Then, the annealing of such treated devices only induces small increase of the Voc and FF and also a small decrease of the Jsc. It can be observed on the QE that, compared to reference cells, the losses are throughout all the spectra, meaning that this decrease is due to collection issues, whatever treatment has been applied.

In order to evaluate the modifications induced in the material nature of the highly diffuse CIGSe/(PVD)In_2S_3 interface, Raman spectra have been acquired on the so-called reference, water treated and annealed cells (see Fig.4). The comparison of these four spectra does not reveal obvious changes in the atomic structure (*i.e.* cristallinity, copper diffusion). The effects of the treatments seem to be mainly electrical.

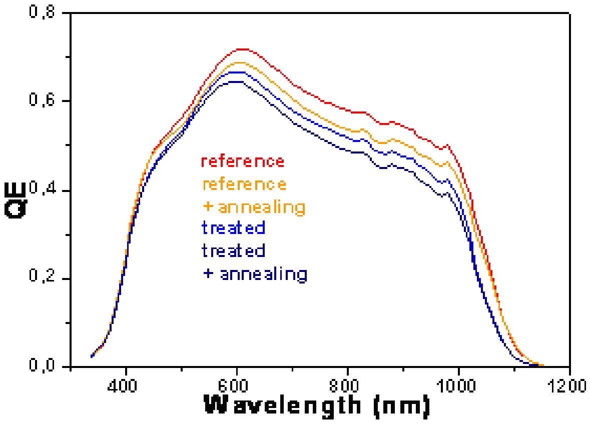

Figure 3: QE measurments of the reference (red and orange) and the water treated (blue and dark blue) cells before and after annealing.

Two interfaces have to be considered in order to better understand these effects; in the following, CIGSe/(PVD)In_2S_3 will be referenced to as “bottom interface”, and (PVD)In_2S_3/r-ZnO to as “top interface”. In a first approach, the water treatment is expected to only have an effect on top interface whereas the annealing may impact all of the device interfaces. Here it will nevertheless be assumed that the effect of annealing is mainly on bottom and top interface properties since it appears unlikely the Mo/CIGSe interface is changed by such low annealing temperature. Fig.1, Fig.2 and Fig.3 show that the changes relative to reference characteristics are observed either when the complete device is annealed or when the buffer surface is water treated. Moreover, as annealing of the water treated sample only yields slightly better Voc and FF, one can conclude that most of the improvement can be attributed to changes in the top interface.

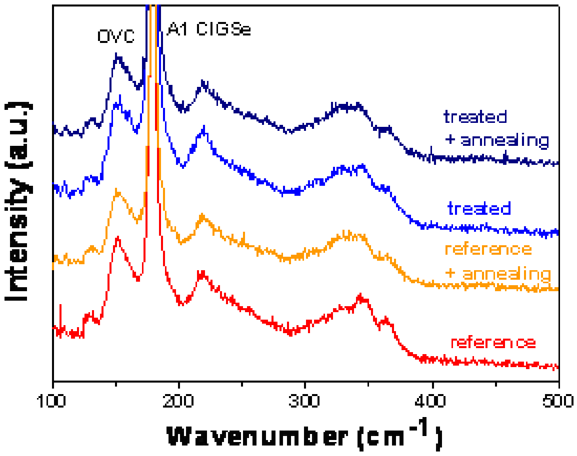

Figure 4: Raman spectra of reference (red and orange) and water treated (blue and dark blue) samples before and after annealing.

The investigations of Nguyen et al. [1] drove them to the conclusion that the performance of cells buffered with (CBD)In_2S_3 are strongly dependent on the defect density at the (CBD)In_2S_3/r-ZnO interface. The present experiments corroborate this model. Indeed, rinsing with water the In_2S_3 surface most likely changes the nature and/or the density of the defects at the top interface. Due to the properties of the CIGSe/(PVD)In_2S_3 interface, it is probable that the Fermi level is not pinned at the absorber/buffer interface and that the voltage distribution in such p-i-n structure is then controlled by the defect nature and density at the top interface. From the present results, it seems that rinsing the buffer surface may induce Fermi level position reducing the tunnel recombination and the electron collection, in a similar way the annealing may act.

In order to further explore what could be the material origin of such effect of water rinsing, the surface of CIGSe/In_2S_3 structure has been investigated by XPS before and after water rinsing. The main effect is observed on the peak relative to Na1s (see Fig.4); this latter peak can be considered as the sum of two contributions visible through the peak shouldering at the lower binding energy ($E_{B.high}$ = 1072.2 eV, $E_{B.low}$ = 1071.5). After the water treatment, the higher energy contribution of the Na1s almost completely vanishes, whereas the lower energy contribution is still clearly visible. Combining this information with the slight decrease of the carbon and oxygen contributions suggests that the rinsing with water cleans the CIGSe/In_2S_3 surface of Na carbonates. The remaining peak at the lower energy may be attributed to sodium linked to indium in the CIGSe structure. The hypothesis of some sulfur compounds will not be kept in this contribution since any noticeable change is visible in the sulfur contributions of the spectra. The present observation tends to suggest that the interface defects that hinder the as grown cells buffered with (PVD)In_2S_3 could be Na carbonates.

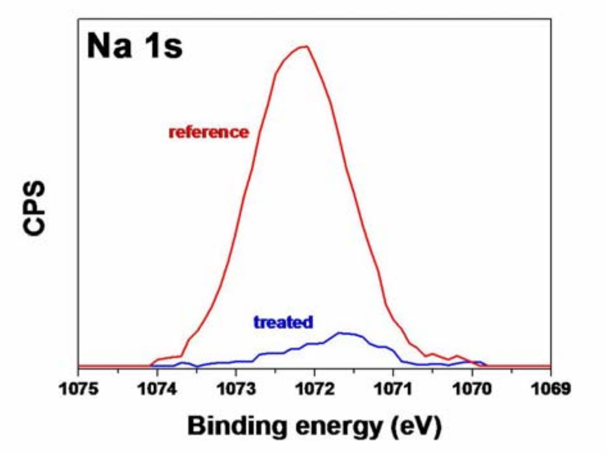

Figure 4: Na 1s XPS spectra acquired on CIGSe/(PVD)In_2S_3 surface before (red) and after (blue) water rinsing.

CONCLUSIONS

This work shows that the performance of CIGSe-based solar cell buffered with co-evaporated In_2S_3 can be increased by rinsing with water the CIGSe/buffer structure surface before the r-ZnO/ZnO:Al window deposition. The impact of such a treatment on the Voc, FF and Jsc of the cell is similar to that of the annealing generally performed on such In_2S_3 buffered devices. Furthermore, the annealing of the water treated devices as a smaller impact on their performance. These results suggest that the beneficial effect of the cell annealing observed on co-evaporated In_2S_3 buffered cells is mostly related to the modification of the In_2S_3/r-ZnO interface; particularly the destruction of Na carbonates at this interface appears realistic.

Most of the studies performed in the field of alternative buffer layers for CIGSe devices have been focused on the improvement of the pn junction through the CIGSe/buffer interface improvement. The present work emphasizes that the buffer/window interfaces should also be taken into account.

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