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Influence of CdTe thickness on structural and electrical properties of CdTe/CdS solar cells

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ABSTRACT

Due to its high scalability and low production cost, CdTe solar cells have shown a very strong potential for large scale energy production. Although the number of modules produced could be limited by tellurium scarcity, it has been reported that reducing CdTe thickness down to 1.5 μm would solve this issue. There are, however, issues to be considered when reducing thickness, such as formation of pinholes, lower crystallization, and different possible effects on material diffusion within the interfaces. In this work, we present the study of CdTe solar cells fabricated by vacuum evaporation with different CdTe thicknesses. Several cells with a CdTe thickness ranging from 0.7 to 6 μm have been fabricated. The deposition process has been optimized accordingly and their physical and electrical properties have been studied. Thin cells show a different electrical behavior in terms of open circuit voltage and fill factor. Efficiencies range from 7% for thin CdTe cells to 13.5% for the standard thickness.

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1. Introduction

CdTe solar cells have been demonstrated as one of the most promising technologies for large scale fabrication and production of energy due to their high scalability, low energy consumption in fabrication, low pay back time, and high efficiency [1]. However, it has been reported that a large scale production in the order of terawatts could be limited by tellurium scarcity as this is a rare element and generally mined as a by-product [2]. Moreover, reducing the absorber thickness would result in a relevant reduction of the production costs.

CdTe solar cells are typically produced with thicknesses between 4 and 6 μm [3]. This assures good coverage avoiding pin-holes and delivering high open circuit voltage devices. On the other hand, because of the high absorption coefficient, 2 μm is enough for absorbing all the light and converting sunlight into electricity [4], but in this case device performance is lower and the structural and electrical properties of thin absorbers are different [5].

In this work we analyze the physical properties of CdTe absorbers with different thicknesses and study the performance of the devices made without changing the other layers.

2. Experimental details

CdTe solar cells are prepared using vacuum evaporation. CdS and CdTe are deposited in the same vacuum chamber at 100 °C and 340 °C substrate temperatures, respectively, with a vacuum of 10⁻⁴ Pa on a

400 nm thick indium tin oxide (ITO) and 100 nm thick ZnO stack deposited by RF-sputtering at 300 °C.

The standard device is made with 400 nm CdS and 6000 nm CdTe. In order to deliver high efficiency, it is known that a CdTe solar cell needs an activation treatment which is typically made by depositing a layer of CdCl₂ on top of CdTe and then by annealing the stacks in air or argon at temperatures around 400 °C [3]. In our process the CdCl₂ treatment is made by depositing drops of CdCl₂ saturated in methanol solution followed by heating in air at 410 °C. The amount of CdCl₂ is modulated by measuring the amount of solution. The cells are then finished with a standard copper/gold back contact with 4 nm Cu and 50 nm Au, deposited by vacuum evaporation. The back contact is annealed at 190 °C in air for 20 min. Typical efficiencies range from 11 to 13% according to the preparation procedure.

For this specific work, cells with different absorber thicknesses were prepared. Single CdTe layers were analyzed, including their physical properties and the growth on CdS. Thicknesses of 0.7, 1, 1.8, 4, and 6 μm were evaluated. CdCl₂ treatment was modulated to the amount of CdTe thickness, reducing it for thinner CdTe. A comparison of the thin absorbers transformed with the same activation treatment has also been provided.

As-deposited and treated CdTe layers were observed by atomic force microscopy (AFM) with a NT-MDT Solver Pro in semi-contact mode. Image Analysis 3.5 (software from NT-MDT) was used for analyzing the AFM pictures and extracting the average size. X-ray diffraction analysis (XRD) on the different absorber layers was performed by a Thermo ARL X'TRA powder diffractometer, operating in Bragg–Brentano geometry equipped with a Cu-anode X-ray source (Kα, λ = 1.5418 Å) and using a Peltier Si(Li) cooled solid state detector.

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3. Results and discussion

3.1. Morphology of CdTe

A different CdTe grain size on the CdS/ZnO/ITO stack was observed for different CdTe thicknesses. As expected, by increasing the thickness, grains increase and the difference becomes very large, especially for the as-deposited case where the morphology depends only on growth conditions.

In Fig. 1 grain sizes of 1.8 and 6 μm thick CdTe on the CdS/ZnO/ITO stacks are compared. For thin absorbers a homogeneous morphology with similar grains in the whole layer was observed. This changed drastically for 6 μm , where sizes had higher order of magnitudes but at the same time showed a wide range of small and big grains. However, while in the thin CdTe the recrystallization brought an overall increase in the grain size of up to one order of magnitude, in the thick CdTe this enlargement is only from two to three times the initial size. An evident change in morphology with more compact grains was also registered for both cases.

Morphology and grain size have been addressed for all the different thicknesses by analyzing the AFM pictures and extracting the average size and mean quadratic deviation of as-deposited CdTe layers by Image Analysis 3.5, as shown in Fig. 2. It is clearly evident that there is a linear dependence of grain size with thickness (as also observed by Durose et al. [6]). The most interesting thing is that there is a constant increase in grain size-spreading so that for thick CdTe layers, grains range from 0.5 to 5 μm (see Fig. 1).

The difference in grain size with thickness is still maintained after CdCl₂ treatment, despite a general increase from the as-deposited case, but the morphology is more compact and grains are more similar to each other.

3.2. X-ray diffraction of CdTe layers

CdTe layers with 0.7, 1, 1.8 and 6 μm thickness deposited on CdS/ZnO/ITO stacks were analyzed in both as-deposited and treated cases. In the as-deposited case the layers show a very similar crystallization. The crystallites are highly oriented along the (111) direction with no other peaks observed, irrespective of the absorber thickness. This

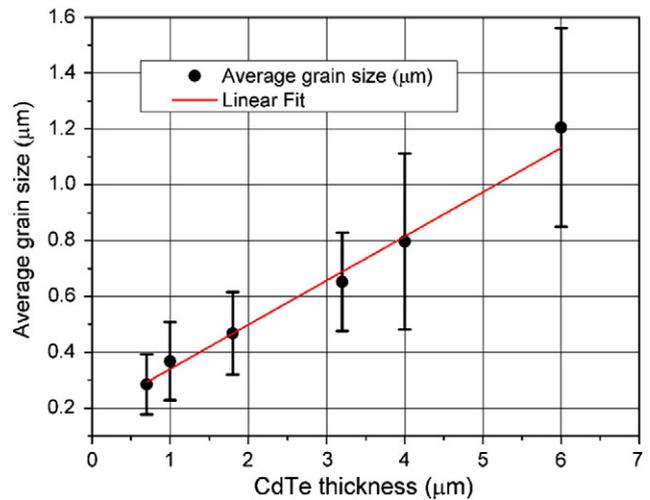


Fig. 2. Average grain size versus thickness, measured from AFM pictures with relative mean quadratic deviation.

indicates that the grains grow with the same orientation, which is also suggested by the AFM pictures wherein similar morphologies with different grain sizes can be seen.

On the other hand, the structure becomes very much different after the application of CdCl₂ treatment (see Fig. 3). The grain orientation is clearly depending on the different CdTe thicknesses, where the thinner CdTe still keeps a relative (111) preferred orientation which tends to be reduced by the increase of the thickness, so that the 6 μm thick CdTe has changed its preferred orientation to (311). So it is observed that a highly randomized CdTe, generally reported in literature [3], is actually seen for thicker CdTe.

Moreover for 0.7 and 1 μm CdTe, some clear CdS peaks are observed. Considering that X-rays are able to penetrate the layer down to 1 μm from the surface, this states that in this case the CdS–CdTe intermixed layer is a consistent part of the device. This is even more outlined in the thinner absorber where a peak attributed to an intermixed layer [(Cd₅S₄Te)_{0.8}] is observed (see Fig. 3), suggesting that in the very thin

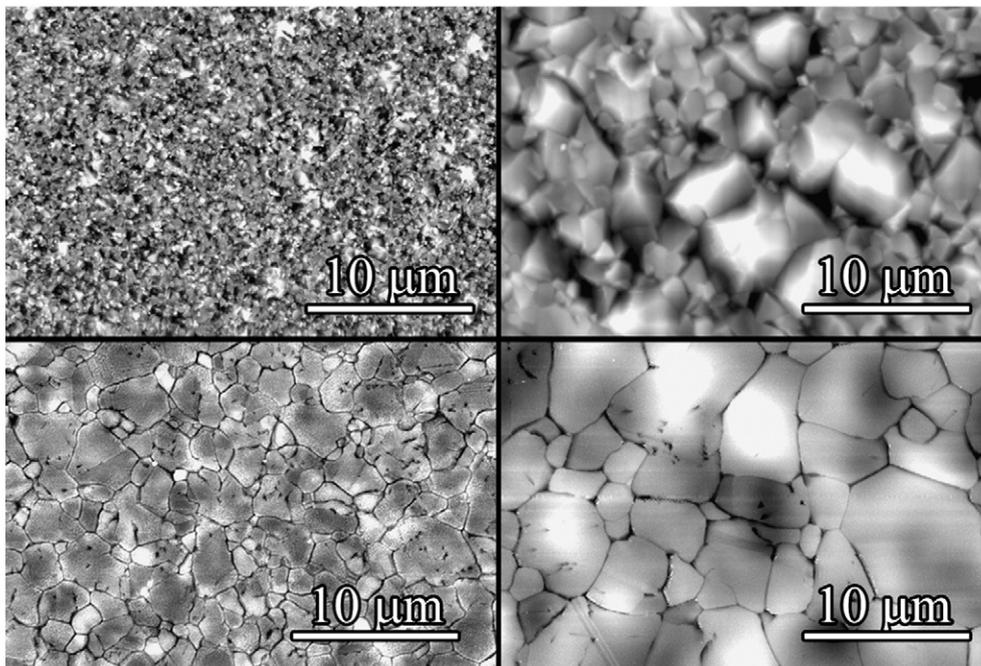


Fig. 1. AFM pictures of 1.8 and 6 μm as-deposited CdTe (top) and of 1.8 and 6 μm treated CdTe (bottom).

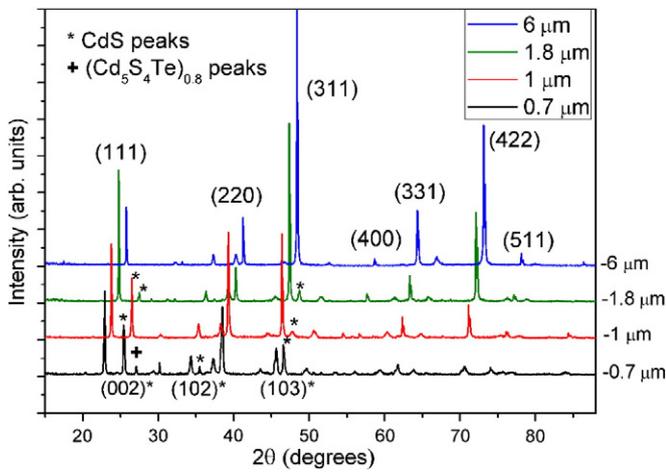


Fig. 3. XRD patterns of the treated CdTe absorbers with different thicknesses.

case the intermixed $\text{CdS}_{1-x}\text{Te}_x$ layer is not far from the back contact and it occupies a relevant part of the absorber.

In order to further investigate this aspect we analyzed the XRD peaks by applying a calculation which was firstly introduced by Nelson [7] and Taylor [8] and subsequently applied by Moutinho et al. [9]. For cubic structure it is possible to calculate the lattice parameters just by analyzing the positions of the XRD peaks with a very high precision.

Lattice parameters of treated CdTe with different thicknesses have been calculated by fitting the position of the different peaks as shown in Fig. 4, where the upper and lower limits of the thickness range are reported. The 0.7 μm treated CdTe shows a very small lattice parameter (6.451 Å) with respect to the standard 6 μm one (6.487 Å) and much smaller than the standard lattice parameter referred to the powder (6.481 Å) [9]. As generally known, intermixing of CdTe with sulfur brings a reduction of the lattice parameter as well as of band gap. This is supporting the fact suggested by the XRD patterns that the very thin absorber is made of an intermixed layer of CdTe and CdS.

To have an additional indication of these phenomena, transmission spectra of the different absorbers were collected and the corresponding band gaps have been extracted following the well known Tauc relation for direct transitions [10]:

$$\alpha hv = C(hv - E_g^d)^{1/2}$$

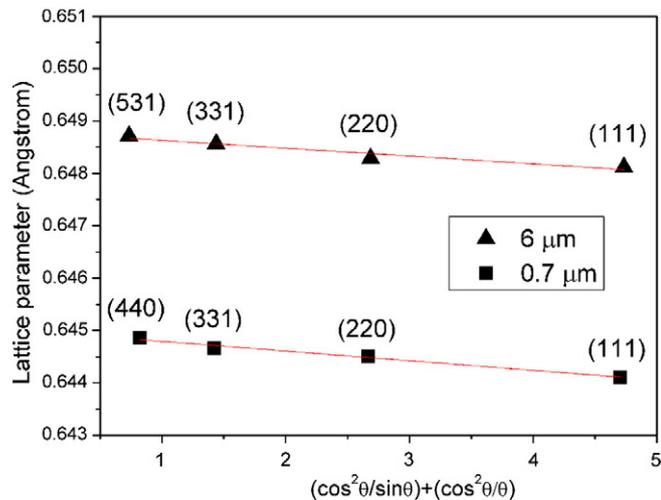


Fig. 4. Lattice parameters of 0.7 μm and 6 μm CdTe after CdCl_2 treatment.

where in the graph $(\alpha hv)^2$ vs hv the intercept is the band gap that we want to calculate. The calculations were processed with very precise fittings. This method is approximate for direct electronic band-to-band transitions because it assumes that the refractive index is constant in the energy range considered. Thus, the calculated band-gap may be only taken as a rough estimate.

In Table 1, band gaps and lattice parameters of the various samples are presented. The different absorbers have a similar band gap before treatment suggesting that there is not a strong difference in the growth conditions in relation to the CdTe thickness as also seen in the XRD patterns, however; when the activation treatment is applied, we have a general reduction of the band gap. This effect is particularly strong for the thinner absorber confirming a strong intermixing of the CdS and CdTe in the whole layer as also suggested by the lattice parameter calculation.

For thicker absorbers a significant difference between activated and not activated samples is not observed: the lattice parameters in the as-deposited case are similar to the ones of the recrystallized thinner samples and lower than the ones of as-deposited thinner samples.

In general, the high lattice parameter is attributed to compressive stress in the in-plane parallel to the substrate surface due to lattice mismatch and difference in thermal expansion coefficients between the CdTe and the CdS films [9]. This stress is clearly reduced when CdTe thickness is increasing and the bulk CdTe is far away from the junction. For this reason the polycrystals are in a more stable condition and the post-treatment structure change is minimized.

3.3. Solar cell devices

Several different devices have been prepared with the above mentioned CdTe thicknesses. A rough optimization procedure has been made, assuming that with less CdTe a reduced CdCl_2 amount was necessary to avoid over-treatment which results in excessive diffusion of CdS into CdTe.

Our CdTe deposition system, based on vacuum evaporation, allows to have a very fine control of the absorber growth and to reduce the formation of pin-holes. For this reason we have obtained very promising efficiencies even for ultra-thin absorbers, despite the performance being anyway limited compared to the 6 μm case, as shown in Fig. 5.

From the value of fill factor, it is interesting to observe that with just 1 μm CdTe we have almost no shunts and the stronger limitation comes particularly from the low current density, which is increasing with the thickness increase. In the ultra thin case a behavior with higher J_{sc} and lower V_{oc} , partly due to shunts but also surely attributable to the presence of the strongly intermixed bulk with the lower band gap reported above is clearly observed. This device is obtained with a reduced amount of CdCl_2 of 180 μl instead of the typical 720 μl , suggesting that the excessive intermixing is not due to a higher CdCl_2 vs CdTe ratio but to a reduced thickness where the junction is very near to the back contact. A confirmation of this condition is given by the behavior of the current–voltage characteristics of

Table 1

Lattice parameters and band gaps of as-deposited and treated CdTe with different thicknesses. Value uncertainties are on the last decimal digit.

Thickness (microns)	Activation treatment	Lattice parameter (Å)	Band gap (eV)
0.7	Treated	6.451	1.48
0.7	As-dep	6.494	1.50
1	Treated	6.488	1.49
1	As-dep	6.498	1.50
1.8	Treated	6.487	1.50
1.8	As-dep	6.484	1.50
6	Treated	6.487	1.50
6	As-dep	6.485	1.50

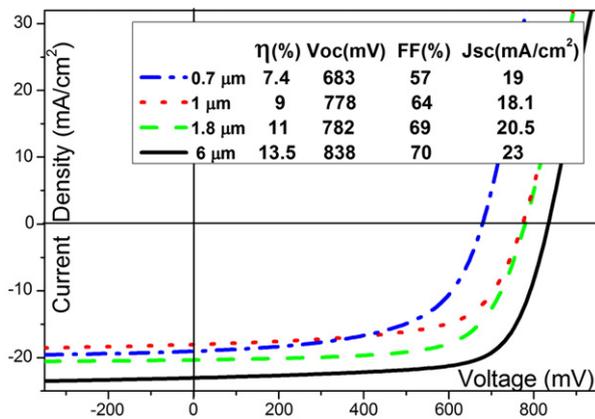


Fig. 5. Current–voltage characteristics of solar cells made with different CdTe thicknesses.

ultra-thin layers with the different amounts of copper and post-deposition annealing. It has been observed that for these samples no annealing after copper deposition was necessary to get rid of the roll-over in the first quadrant of the I–V curves, which demonstrates that even with lower mobility, the path for ultra thin layers is so reduced that there is no need to improve the carrier concentration as also observed by Hädrich et al. [11].

For comparison a set of devices with different CdTe thicknesses but with the same CdCl₂ amounts has been made. This shows that even with the same amount of solution prepared for the 6 μm case, cells with 0.7 μm thick CdTe have very similar performance (around 7%) to the ones made with only 180 μl. Again this indicates that the reduction in efficiency is mostly due to a different solar cell structure as described a few lines before.

The lower efficiency of the 0.7 μm CdTe devices can be attributed to the fact that a large part of the absorber is an intermixed compound of CdS_xTe_{1-x}, as attested by the energy band gap, lattice parameter extraction and especially by the detection of a (Cd₅S₄Te)_{0.8} XRD peak. As a matter of fact a band gap of intermixed absorber delivers lower open circuit voltage and higher current as effectively observed from the I–V measurements.

The slightly lower efficiencies of solar cells with 1 and 1.8 μm CdTe compared to the standard one is given particularly by low current density, preliminary admittance spectroscopy and drive level capacitance measurements (not shown here) reveal that the main reason is due to the extension of the depletion region to the back contact even at high temperatures as also suggested by Beach et al. [12].

4. Conclusions

Solar cells with different absorber layer thickness (0.7 μm, 1 μm and 1.8 μm) were prepared and compared with the standard 6 μm thick CdTe ones.

Despite the fact that the main scope of the work was exclusively to identify the different structural and electrical properties of devices with thin CdTe, solar cells with absorber layer of 0.7 μm have demonstrated a promising efficiency exceeding 7%. For cells with absorber

thickness of 1 μm and of 1.8 μm the efficiencies were 9% and 11% respectively, which are anyway lower than the ones of our standard devices (efficiencies around 13.5%). Higher efficiencies with thin absorbers have been reported by Gupta et al. [13] and Plotnikov et al. [14], but with RF-sputtering CdTe deposition.

A linear increase of CdTe grain size with the increasing of CdTe thickness was observed. On the other hand for as-deposited absorber layers with different thicknesses no significant difference was found in calculated lattice parameter and band gap energy. Moreover they all show a strong (111) preferential orientation in the XRD patterns.

After CdCl₂ treatment the CdTe grain size increases but still maintaining a similar difference between each other. The (111) preferred orientation is lost only for the thicker absorbers and lattice parameter is relaxed for thinner ones.

After the first comparison of devices made with the same fabrication parameters, CdCl₂ treatment, back contact deposition and annealing steps were adjusted for different absorber thicknesses in order to optimize their performance. However no significant change in performance between devices with standard (720 μl) and reduced amount (180 μl) of CdCl₂ has been registered. On the contrary, a small amount of copper (even without post deposition annealing) is enough for thin absorbers to collect the carriers.

Most importantly, we could observe that lower efficiencies for the thinnest absorber can be attributed to the intermixed compound of CdS_xTe_{1-x} as absorber, while for solar cells with 1 and 1.8 μm CdTe lower efficiencies are connected to the low current density due to the extension of the depletion region to the back contact.

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