



CdTe thin film solar cells: Interrelation of nucleation, structure, and performance

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ARTICLE INFO

Available online 6 November 2008

Keywords:

Cadmium telluride
Growth mechanism
Texture
Scanning electron microscopy
X-ray diffraction

ABSTRACT

The performance of CdTe solar cells as prototype of thin film solar cells strongly depends on film morphology. The needs for high solar cell performance using thin film materials will be addressed covering nucleation and growth control of thin film materials. In order to understand the basic growth mechanisms and their impact on cell performance, we have systematically investigated the growth of CdTe thin films by Close Spaced Sublimation (CSS) using the integrated ultra-high vacuum system DAISY-SOL. CdTe thin films were deposited on TCO/CdS substrates (transparent conductive oxide) held at 270 °C to 560 °C. The properties of the films were determined before and after CdCl₂ treatment using X-ray diffraction and electron microscopy. In addition, solar cells were prepared to find correlations between material properties and cell efficiency. At low sample temperature the films tend to form compact layers with preferred (111) orientation which is lost at elevated temperatures above 450 °C. For CdS layers without (0001) texture there is in addition a low temperature regime (350 °C) with (111) texture loss. After activation treatment the (111) texture is lost for all deposited layers leading to strong recrystallisation of the grains. But the texture still depends on the previous growth history. The loss of (111) texture is evidently needed for higher performance. A clear correlation between cell efficiency and the texture of the CdTe film is observed.

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1. Introduction

The performance of CdTe solar cells as prototype of thin film solar cells strongly depends on cell inhomogeneities as given by the structure and morphology of the polycrystalline film. Grain boundaries, pin-holes, as well as weak diodes may strongly affect the performance of the cell [1–3] and usually the performance of thin film solar cells are drastically below the theoretical limits. The possible effects of structural inhomogeneities on the electronic performance of solar cells have been discussed in a generalized theoretical approach by Werner and Rau considering mostly band edge fluctuations [4]. However, for a detailed understanding the specific properties of a technology must be addressed in a very detailed approach. For this reason we will address the needs for high solar cell performance of CdTe thin film solar cells in this contribution covering nucleation and growth of films deposited by close space sublimation (CSS).

Especially for CdTe solar cells, which are prepared in the superstrate configuration, the glass substrate or the small grains of the TCO layer will hardly lead to interfacial epitaxy relations but nucleation and growth will be controlled by kinetic growth factors governing absorption and surface, interface and bulk diffusion. It has been found that deposited CdTe films tend to grow in columnar layers with (111) orientation, when physical vapour deposition (PVD or CSS) is applied at low sample temperatures [5–7]. The given (111) texture relates to

the fast growth direction of zincblende compounds. If the sample temperature is strongly increased, which will only be practicable for Closed Space Sublimation (CSS) deposition, the (111) texture is lost and large 3D grains of nearly statistical orientation are formed [5,6,8]. This recrystallisation can also be observed during the well known activation process of CdTe solar cells using e.g. CdCl₂ treatment: (111) textured films of small grains form statistically oriented large grains, whereas the large grains remain mostly unaffected in their structural properties [8,9]. The crystallites formed at elevated temperatures are 3D grains of similar dimension in all directions and with different morphologies as they expose different orientations. As a consequence there is a strong tendency to form recombination pathways along grain boundaries and pinholes existing in the films which lead to rather low parallel resistances and thus to a strong loss in performance of most CdTe solar cells and modules (see e.g. a comparison of CdTe solar cells to related GaAs cells given by Sites [10]). Recombination losses across the absorber layer are of even stronger influence after chemical etching using etching in nitric-phosphoric acid (NP etch) [11] or if thinner films are approached to consider the physically defined needs for improved solar cells or tandem cells. For such improved cells absorber films are needed with maximized lateral dimensions and vertical dimensions close to the absorption length of about 1 μm.

In order to understand the basic growth mechanisms and their impact on cell performance, we have systematically investigated the growth of CdTe thin films by Close Spaced Sublimation (CSS) using the integrated ultra-high vacuum system DAISY-SOL. We systematically investigate the structural and morphological properties of CdTe films by varying the pre-treatment of the CdS layer, the substrate temperature

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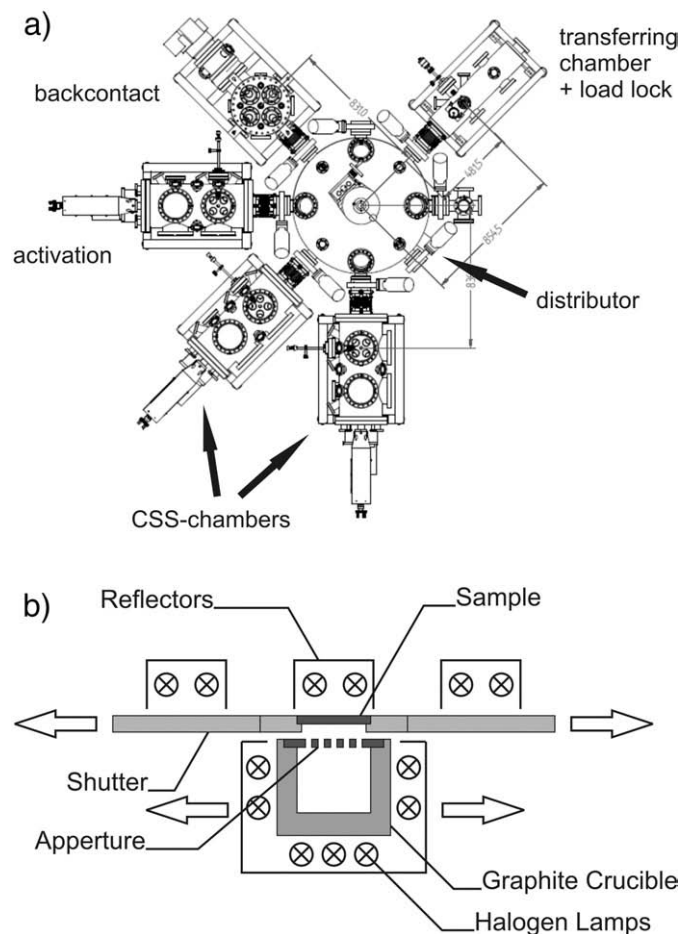


Fig. 1. Experimental set-up of the preparation unit of DARMstadt Integrated SYstem for SOLar energy research (DAISY-SOL): a) arrangement of deposition set-ups, b) home made CSS deposition set-ups as used in our experiments.

and the growth rate during film deposition. The structure of the films was studied using X-ray diffraction, electron microscopy and AFM. The structural data are compared to the performance of solar cells reached for the different CdTe layers. In order to keep comparable conditions a standard set of cell manufacturing conditions have been applied without optimizing these for maximized performance. In addition, we have also investigated the growth of CdTe on differently oriented CdS single crystal surfaces to obtain a better understanding of interface interactions.

2. Experimental

The experiments have been performed in the DAISY-SOL system at TUD (Technical University of Darmstadt). The system connects ultrahigh vacuum chambers for CSS (close-spaced sublimation) of CdTe and CdS and two other vacuum chambers for in-situ CdCl₂ treatment and back contact metallization, respectively, to a high-resolution photoelectron spectrometer (VG ESCALAB 250 XL) via an ultrahigh vacuum transfer mechanism. More details can be found in [12]. With the exception of the TCO deposition, complete CdTe thin film solar cells can be fabricated in this system. The schematic set-up of the deposition chambers is shown in Fig. 1. We have used movable home-made CSS deposition chambers (Fig. 1b) which can be controlled in the temperatures (sample and source temperatures) by halogen lamp heaters.

CdTe thin films were deposited using different deposition rates on TCO/CdS substrates held at 270 °C to 560 °C. CdS films were also prepared by CSS at different substrate temperatures. The properties of the films were determined before and after activation using CdCl₂. In

addition, solar cells were prepared to find correlations between material properties and cell efficiency. The structure of the films was studied using X-ray diffraction, electron microscopy and AFM. X-ray diffraction was used to determine phase composition, lattice parameters, texture coefficients, and concentration of planar defects.

For the single crystal studies either experiments at DAISY-FUN (DARMstadt Integrated SYstem for FUNdamental investigations) [13] or at the SoLiAS (Solid Liquid Analysis System) at BESSY [14] were performed.

3. Experimental results and discussions

The growth of CdTe films generally proceeds in three different growth regimes (see Fig. 2) depending on substrate temperature [5]. For this investigation the CdS buffer layer has been deposited at elevated substrate temperatures of 515 °C as often used for CdTe solar cell production, e. g. following the ANTEC technology [15,16], showing a mostly statistical orientation of the grains [5,17,18]. At low temperature, the CdTe films grow almost purely (111)-textured. At temperatures exceeding 450 °C the (111) texture is lost and a mostly statistical orientation of the grains is obtained as already known from previous investigations [5,17,18].

A close inspection of the diffraction patterns indicates that at lower substrate temperatures around 350 °C already an intermediate reduction of texture is observed. The change in surface texture can be better inferred from a plot of the texture coefficient as function of substrate temperature. The texture coefficient has been determined according to the formula

$$C_i = \frac{\frac{I_i}{I_{0i}}}{\left(\frac{1}{N}\right) \sum_{i=1}^N \frac{I_i}{I_{0i}}}$$

and is displayed in Fig. 3 in more detail. Independent on the mode of temperature control, a dip in (111) texture occurs at about 340 °C

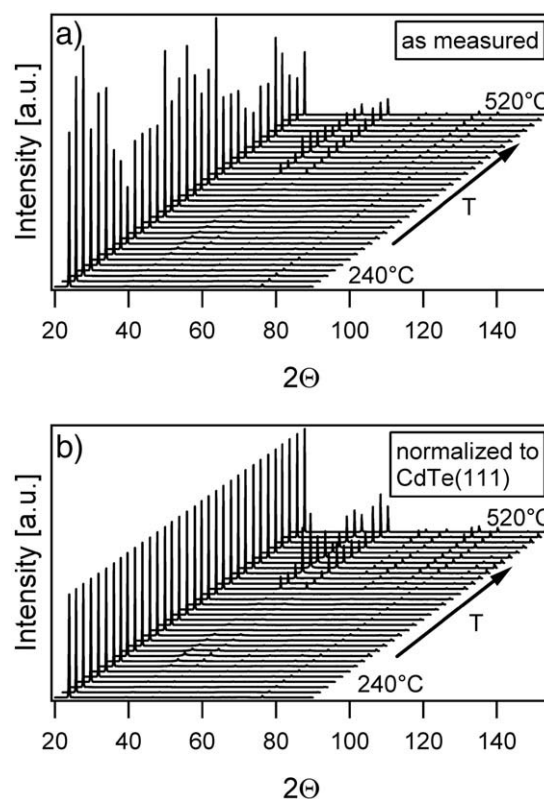


Fig. 2. XRD patterns of CdTe grown on CdS/SnO₂/ITO substrates with statistical pre-orientation of the CdS grains: a) as measured, b) normalized to the (111) peak intensity.

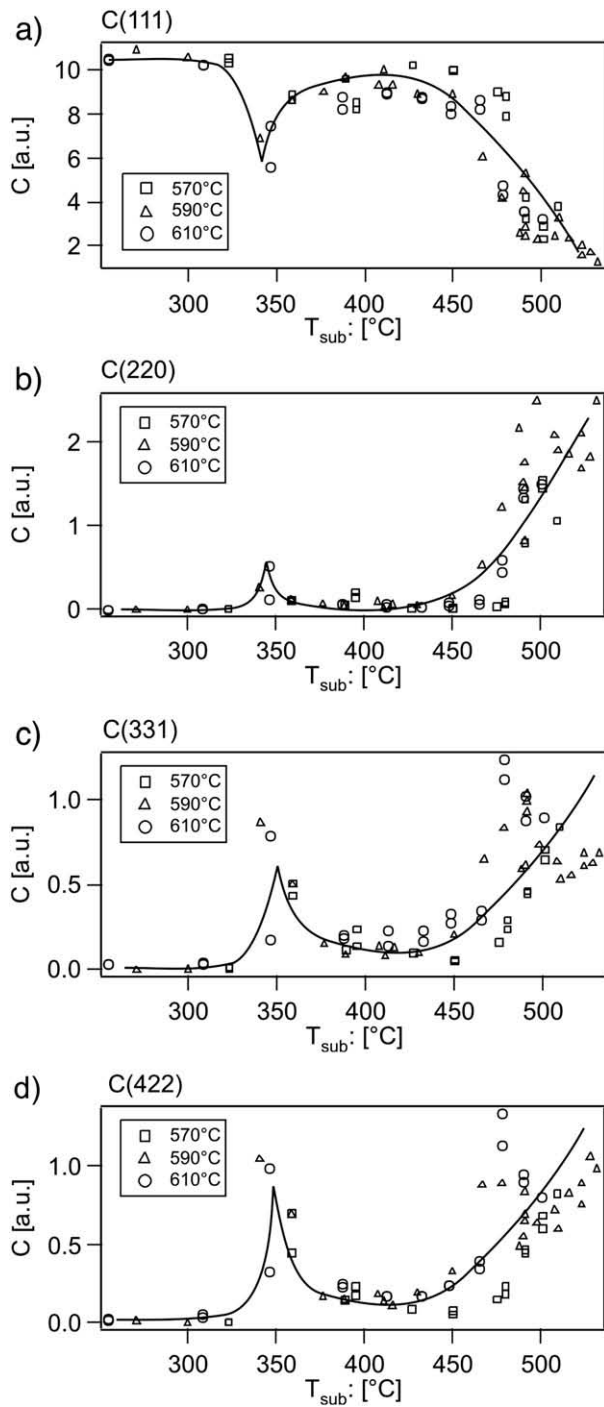


Fig. 3. Calculated texture coefficients of CdTe films deposited with source temperatures 570 °C, 590 °C and 610 °C. Lines indicate the general behaviour as guide to the eye. a) C (111), b) C(220), c) C(331), d) C(422).

(compare Fig. 3a). From this change of growth texture (also evident from the SEM images, Fig. 4) we have divided the growth in three different growth regimes. In the first regime up to about 320 °C the grains grow as columnar extended grains in (111) orientation onto the substrate independent on its crystalline orientation but related to the small grains of the TCO substrate. The formed film is very compact but at very low substrate temperatures cracks are formed in and on the layers. In the second growth regime (above 370 °C, the texture is again clearly in (111) direction but the grains are considerably larger and have lost the columnar morphology. At this temperature regime there is a strong tendency to form pinholes and voids in the growing CdTe

films. A random grain orientation is observed at higher deposition temperatures (above 520 °C), which is usually used for solar cell fabrication [15,16]. These CdTe films are formed from mostly 3D large and compact grains which, in their lateral size, are comparable to their vertical size. However, due to the different grain forms and

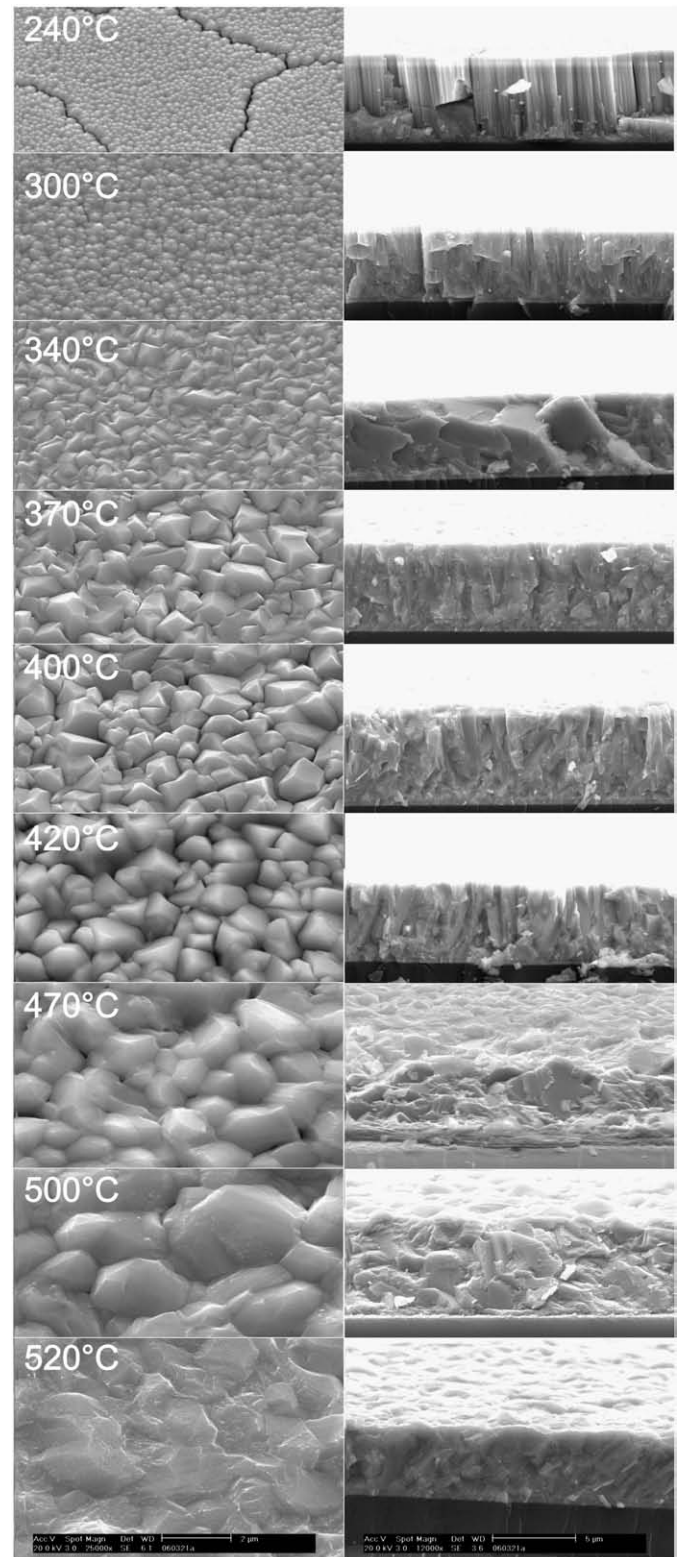


Fig. 4. SEM pictures with a 25000× magnification of CdTe films as formed at different substrate temperatures. Left: top view, right: side view. Compact and rather defect free grains are observed at elevated temperatures (520 °C) but also at the transition range between the first and second growth regime (around 340 °C).

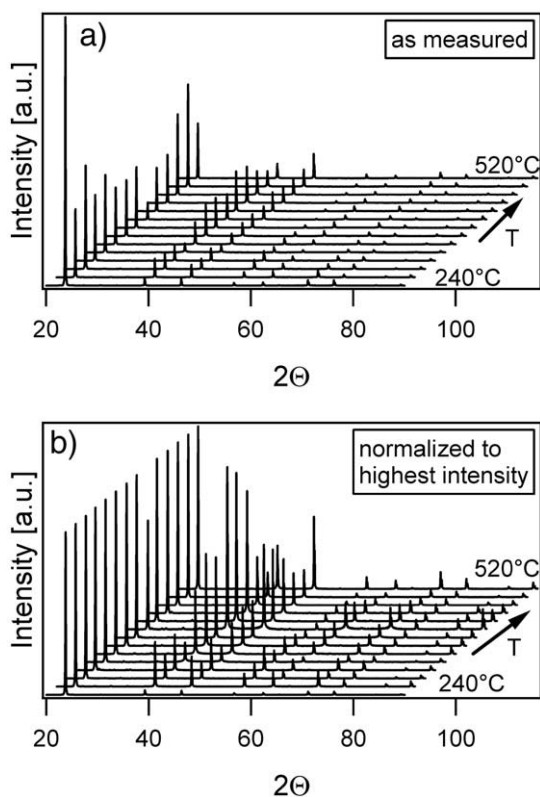


Fig. 5. XRD patterns of CdTe grown on CdS/SnO₂/ITO substrates (compare Fig. 2) after CdCl₂ activation with statistical pre-orientation of the CdS grains: a) as measured, b) normalized to the diffraction peak of highest intensity.

orientations there is still a strong tendency to form deep craters and grain boundaries of very different properties.

It is interesting to note that the films formed at the transition regime (340 °C) seem to expose very promising film morphology. The films are very compact without pin-holes and voids. But at the same time the grains seem to be rather compact and dense as also found for the high temperature growth regime, which is usually used for the manufacturing of solar cells. Therefore we have decided to investigate the properties of these films in more detail. It should be noted that the formed texture and growth regimes have been found to depend also on the CdTe deposition rate. The results show that for low rates a preferential (111) texture is formed which is lost for elevated temperatures. This result can be explained by a faster nucleation of CdTe (111) on (0001) oriented CdS surfaces as well as by the preferred preorientation of the CdS films. This correlates well with the larger growth rate of CdTe found in junction formation experiments using (0001) oriented CdS single crystal surfaces compared to (10–10) oriented surfaces [19].

As usual the structural properties and texture obtained after preparation are strongly changed after the CdCl₂ activation process, the effect of activation on the structural properties was also studied. In Fig. 5 we show the changes of XRD patterns as obtained after a standard activation procedure. The activation was performed with the exposure of the CdTe layer to drops of CdCl₂ dissolved in methanol and annealing in air at 410 °C for about 20 min.

It is clearly evident that the preferential (111) orientation as observed in Fig. 2 is lost for all deposition temperatures in agreement to the results reported in literature (see Introduction). However, it is also clear that the

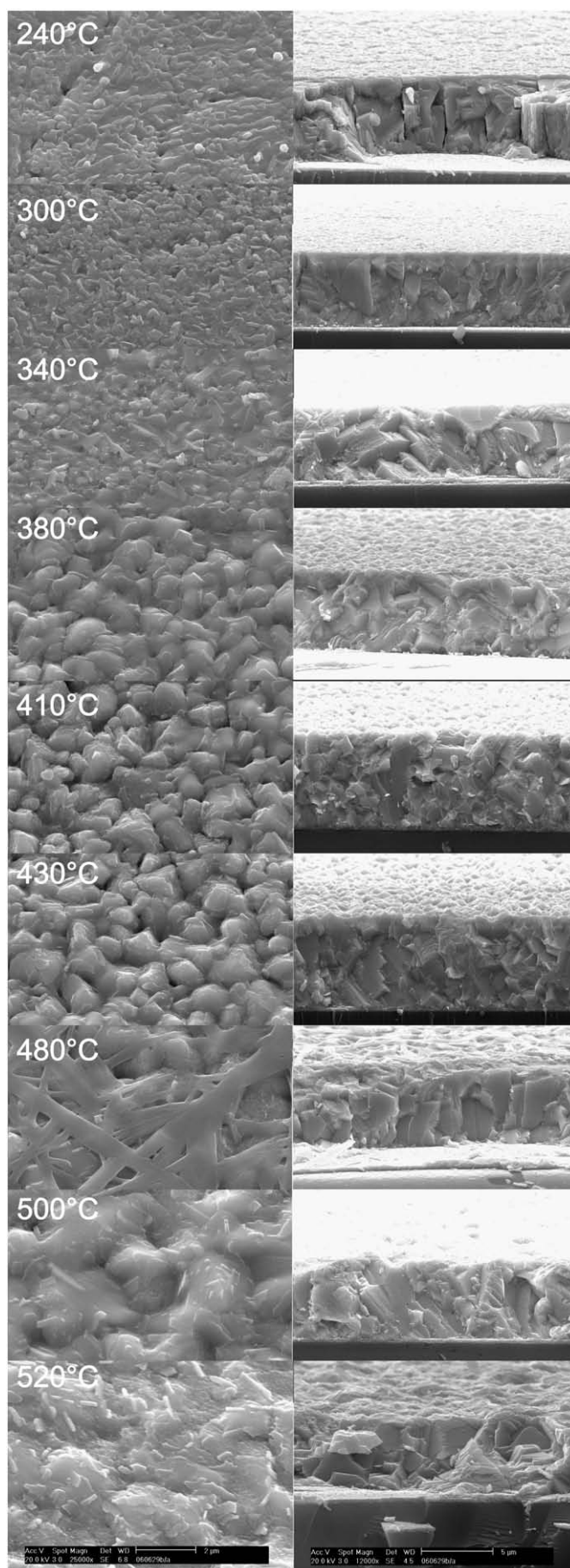


Fig. 6. SEM pictures with a 25000× magnification of CdTe films as formed at different substrate temperatures and after CdCl₂ activation (similar to Fig. 4). Left: top view, right: side view. Compact and rather defect free grains are again observed at elevated temperatures (above 500 °C) but also at the transition range between the first and second growth regime (around 340 °C).

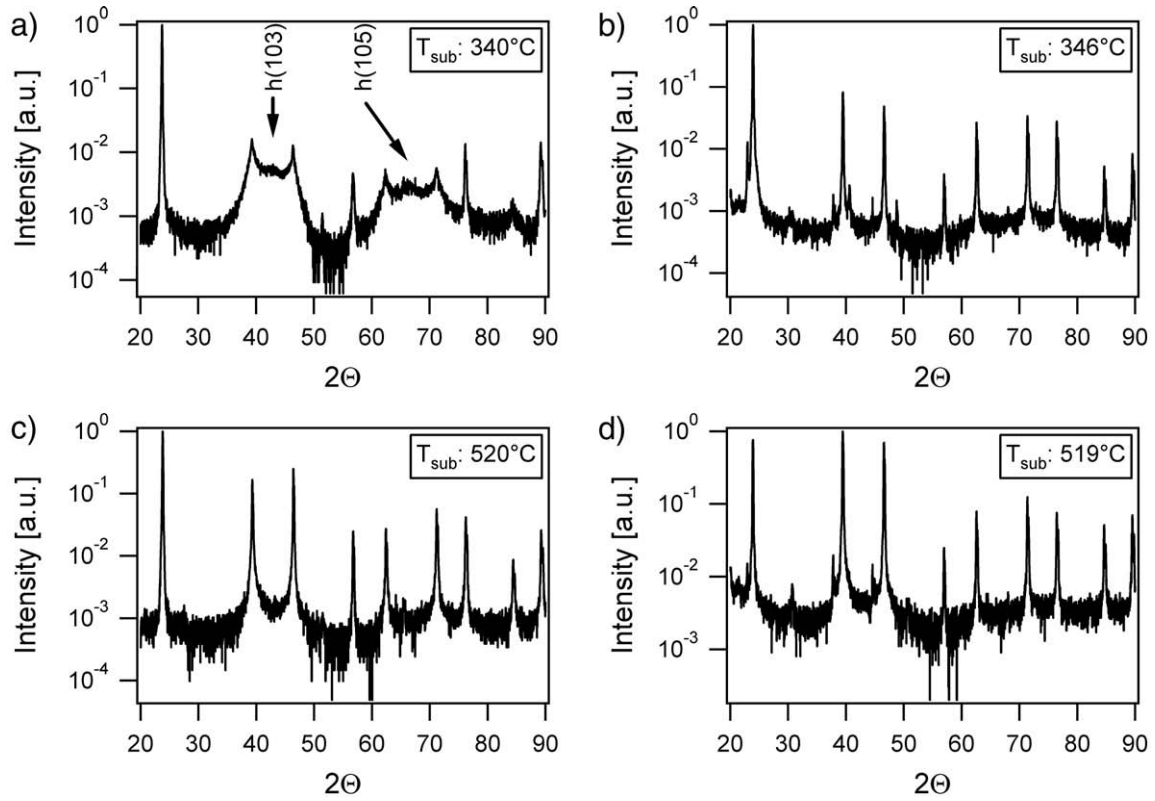


Fig. 7. Detailed XRD patterns of CdTe grown on CdS/SnO₂/ITO substrates at 340 °C and at 520 °C before (a,c) and after CdCl₂ activation (b,d). The broad additional diffraction intensity fitted with a hexagonal CdTe phase observed for low temperature growth is lost after activation and at elevated growth temperatures. Reflexes of the hexagonal CdTe phase are indicated in Fig. 7a.

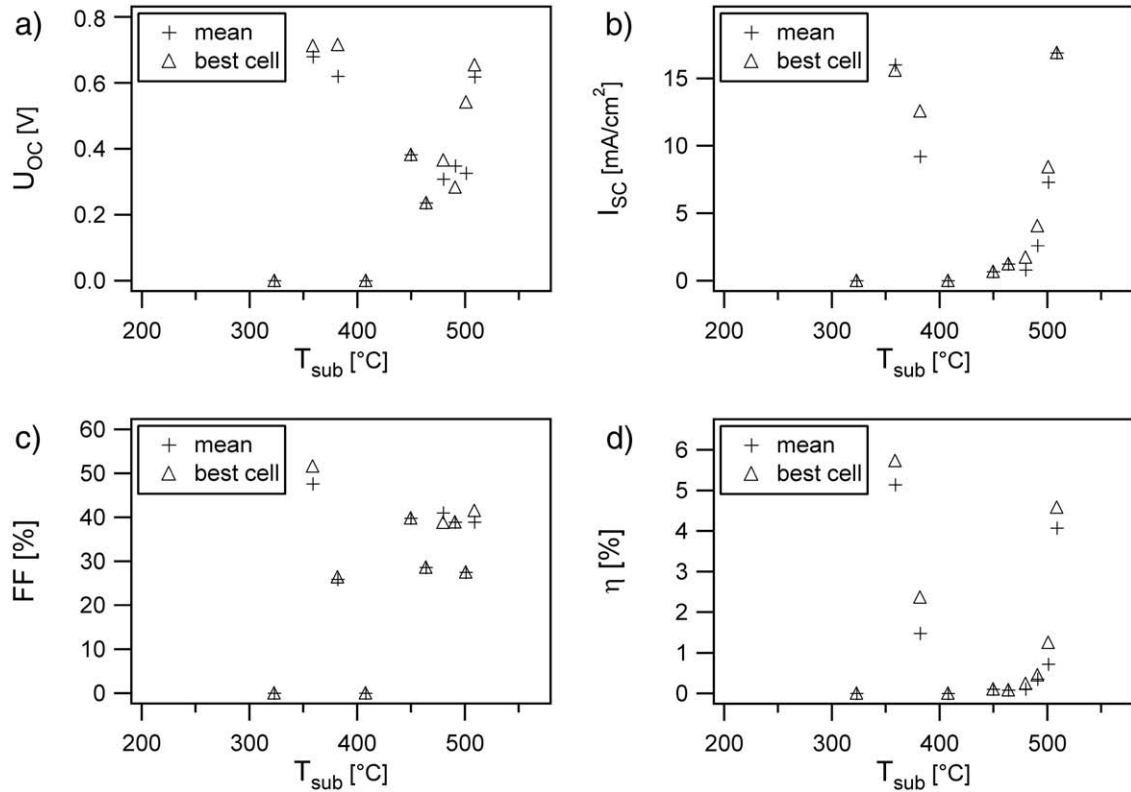


Fig. 8. Electrical characterization of CdTe cells produced with standard activation procedure. Mean values (cross) and the value of the cell with the highest efficiency (triangle) are shown. a) open circuit voltage (U_{oc}), b) short circuit current (I_{sc}), c) filling factor (FF), d) conversion efficiency (η).

texture is not identical for all films which indicates that the number of grains with different orientation depends on the previous growth history and is not only dependent on the activation treatment. This is again evident from the SEM pictures shown in Fig. 6 for films grown at different substrate temperatures and after the CdCl_2 activation. Two growth temperatures seem to produce CdTe films of morphology in close correspondence to the SEM images shown in Fig. 4 obtained before activation. The high temperature regime with substrate temperature above 500 °C as well as the transition regime identified above seems to produce favourable film morphology with compact layers consisting of large grains with the size of film thickness and minor concentrations of voids and craters. This should also influence the electronic properties as is evident from the performance of solar cells prepared with the different films (see below).

Detailed investigations of the XRD patterns before and after activation show that the number of defects in the films strongly depends on growth temperature and activation treatment. In Fig. 7 XRD patterns are shown in logarithmic scale showing films grown at the transition regime at 340 °C and at high temperatures at 520 °C before and after activation. The CdTe films grown at low sample temperatures show a broad and rather high concentration of scattering intensity between the main cubic CdTe diffraction patterns. We assign these scattering intensity to the contribution of planar defects, which are related to twin boundaries and stacking faults formed along the (111) direction. As also found for other fcc crystals [20–23] there is a strong tendency to form different layer sequences along the (111) direction of fcc cubic crystals deviating from the ideal ...ABCABCABC... sequence. With the addition or missing of layers intrinsic ...ABCABABC... and extrinsic ...ABCABACABC... stacking faults may form but also lamellar twin boundaries as ...ABCABACBA... may form. Finally also a number of hexagonal layer sequences ...ABABAB... may exist. As these default layer sequences are expected to form only short periodicities a broad diffraction line may be expected which for simplicity can just be fitted by a hexagonal contribution to the overall XRD pattern. It can be assumed that the additional energy needed to form such planar defects may be small for CdTe. However, we have only found these defects in the temperature regime around 450 °C. At elevated growth temperature the defects are not observed in high concentrations as also shown in Fig. 7. But also the activation treatment leads to a loss of the defects related scattering intensity in the CdTe films. Therefore it seems to be safe to conclude that for the structural integrity of CdTe absorber layers with preferable electronic properties well defined grains without planar defects are needed.

In order to relate the changes in structure and morphology to electrical properties solar cells have been produced from the different films with standard conditions in deposition but using non-adapted constant activation conditions. These conditions seem to be a good compromise for the different CdTe films prepared. However, it has been found that especially the activation treatment needs detailed optimization for films prepared outside the standard temperature regime. For this reason the obtained efficiencies are lower than the typical values prepared in our set-up, which are in the range of 10.5% (without containing Cu and with simple Te/Au back contacts). In Fig. 8 we show the solar cell parameters of CdTe solar cells prepared in dependence on substrate temperature after the activation treatment. Without activation, no reasonable efficiencies could be obtained. As expected, the conversion efficiency of activated samples increases for growth temperatures exceeding 500 °C. However, very similar conversion efficiencies are also obtained for films grown at the transition regime of 340 °C. It appears that the major impact on efficiency comes from the loss of photocurrent due to shunt related recombination pathways which also influences open circuit photocurrent Voc and fill factor FF.

The above presented results suggest that films grown at lower temperatures by CSS may also provide good conversion efficiencies if the post-deposition treatment, especially the activation, is further

optimized. On the other hand the films formed at this low substrate temperature seem to provide advantages for the compactness of the absorber layer, which would be preferential for thinner solar cells by avoiding pin-holes. We speculate that the found dependencies on film morphology and planar defects are of general importance. But for gaining optimized performance the processing steps must be optimized in relation to each other, which have not yet been achieved. On the other hand it has already been proven by other deposition techniques as magnetron sputtering [24,25], PVD [26] or electro-deposition [27–29] that high performance cells can be reached at lower substrate temperatures with smaller film thicknesses. But the results presented here suggest that similar results are also possible with CSS based deposition techniques.

4. Summary and conclusions

We have systematically studied the structural and morphological properties of CdTe solar cells in dependence on deposition temperature. The results clearly show that high performance cells are related to films which have lost their (111) growth texture. The (111) growth orientation is related to the formation of a high concentration of planar defects related to stacking faults and twin boundaries which evidently impair the electronic bulk properties. In addition, also the interface orientation may be a critical issue [19]. It is found that compact layers with preferential structural and electronic properties can also be formed at low sample temperature in dependence on the texture of the CdS films.

Based on the given results it is concluded that the activation treatment also strongly affects structural defects within the bulk of the CdTe grains. But for elevated temperatures there is also a strong tendency of forming non-oriented 3D grains as thermodynamic stable form of compounds with an fcc cubic lattice. This tendency may contribute to the formation of low shunt resistances in the cell due to pin-holes, unfavourable grain boundaries, and/or weak diodes which are major losses in thin cells in the range of 1 µm thickness.

Textured layers of similar oriented grains, which may be a precondition of preparing thinner CdTe absorber layers, need a better understanding of the control of nucleation and growth of CdTe films on the given substrates. The growth processes are strongly influenced by kinetic factors but also by the orientation of the CdS layer and thus most probably also by the TCO layer and its structural properties. Therefore, there is a strong need for investigating the orientation dependence of growth processes in the deposition sequences of the CdTe solar cells starting from the glass substrate, covering the TCO and the CdS layer, and finally the CdTe absorber film. In addition, one needs a better understanding of the orientation dependence of surface and interface properties from a structural as well as from an electronic point of view. Therefore we feel that despite the promising recent results of CdTe reaching economic competitiveness there are still major fundamental questions open for improving CdTe cells in order to further approach the theoretical limits in efficiency.

Acknowledgements

The presented work at University of Darmstadt is supported by the Bundesministerium für Umwelt (BMU) and by the Bundesministerium für Bildung & Forschung (BMBF).

Thanks go to Christina Spanheimer for SEM measurements and Sebastian Gottschalk for supporting the XRD measurements.

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