

COMPARISON OF CSS-CdTe AND PVD-CdTe WITH DIFFERENT ACTIVATION PROCESSES

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ABSTRACT: CdTe polycrystalline thin film solar cells have a strong potential in scalability. They have shown long-term stable performance and high efficiency up to 16.5% under AM1.5 illumination. Amongst several attractive features high chemical stability of CdTe and a simple compound formation are the most important ones for large area production of solar modules. A further simplification has been done by substituting the CdCl₂ step by treating CdTe films in an atmosphere containing a non toxic gas that is inert at room temperature, like HCFCl₂, that belongs to the Freon[®] family. The treatment is typically done at a temperature of 400°C, for a few minutes and in an atmosphere of 100 mbar of Ar containing 15% of HCFCl₂. The change in the morphology of CdTe films after treatment is very similar to that obtained with CdCl₂ treatment and an increase in the size of small grains is always observed. This process has been applied by N. Romeo et al. CdTe thin films deposited by on close spaced sublimation (CSS) with very interesting results (15.8% efficiency). In this work the application of this novel "activation process" on physical vapor deposited cells will be described and a comparison of physical and electrical features with the standard process and with CSS deposited layers will be presented.

Keywords: CdTe, Recrystallization, Deposition

1 INTRODUCTION

The CdTe thin film solar cells have now reached long-term stable performance [1], high efficiency up to 16.5% under AM1.5 illumination [2] and easy scale-up for large area production [3]. High efficiency and fast deposition for CdTe by close space sublimation (CSS) allows high throughput and potentially cheap in-line production of solar modules. Even for low production volumes less than 20 MW/year, their cost would be lower than 1 Euro/Wp [4].

The highest efficiencies in CdTe solar cells have been obtained using CSS deposition method, which requires a high substrate temperature (~500 °C). Unfortunately the development of flexible CdTe solar cells on polymers is difficult with CSS process because of high substrate temperatures encountered during sublimation process.

On the other hand, conventional physical vapor deposition (PVD) process where CdTe is evaporated in a high vacuum evaporation (HVE) system at lower substrate temperatures (typically 300°C) has also provided solar cells with efficiencies exceeding 12% on low cost soda-lime glass substrates [5]. For these reasons HVE process is attractive for a very simple in-line deposition of large area CdTe solar modules on soda-lime glass substrates, as well as on polymer foils thereby facilitating the roll-to-roll manufacturing of flexible solar modules [6].

For high efficiency CdTe solar cells, it is generally known that an activation treatment prior to back contact deposition is necessary [7]. Typically heat treatment in chlorine atmosphere (CdCl₂ or HCl) may work as a flux which reduces atomic diffusion barriers at the grain

boundaries promoting grain growth (improving the crystalline quality), inter-mixing of CdS and CdTe films and removal of lattice defects at the junction region.

Most research groups use to carry out this step by depositing on top of CdTe a layer of CdCl₂ by simple evaporation or by dipping CdTe in a methanol solution containing CdCl₂ and then by annealing the material in air at 400°C for 15-20 min. In general, CdCl₂ handling and storage has several drawbacks. CdCl₂ has a relatively low evaporation temperature (about 500°C in air) and can be dangerous in case of fire when stored in large quantities, as required in a large-scale production plant, due to Cd release, which is highly noxious. Moreover, due to the high water solubility of CdCl₂, very severe measures have to be taken to avoid environmental pollution.

Alternative techniques such as reacting the CdTe/CdS stacks in either CdCl₂ vapor or Cl₂ vapor [7] has been shown to be suitable substitutes for large scale processing. Among these, the Cl₂ vapor offers advantages with respect to CdCl₂ vapor generation due to Cd toxicity.

A cheaper and secure method for applying the activation step has been introduced by N. Romeo et al. [8] where, to provide a Cl₂ vapor, a gas of the Freon family is flowed at high temperature on the CdTe layer.

2 FABRICATION OF SOLAR CELLS

2.1 CSS CdTe based solar cells

A transparent and conducting oxide (TCO) as front contact is made by two films: Indium Tin Oxide (ITO), 400 nm thick, deposited by DC-sputtering with a

sheet resistance less than 10 ohm/Sq and a ZnO 100nm thick acting as a buffer-layer deposited by reactive DC-sputtering.

The window layer, CdS film, is deposited by RF-Sputtering in Ar+CHF₃ atmosphere. The CdTe film is then deposited by CSS technique in Ar+O₂ atmosphere on top of the CdS layer.

Back contact is made of two different films: Sb₂Te₃, which guarantees the ohmic behavior of the contact, and a metallic film such as Mo or W [8].

2.2 PVD CdTe based solar cells

Commercially available soda-lime glass coated with fluorine doped tin oxide (FTO) is used as a substrate. CdS layer is grown in a high vacuum evaporation chamber at a substrate temperature of 150 °C and subsequently annealed at 450 °C for recrystallization, CdTe is then deposited at a substrate temperature of 300 °C in the same chamber without breaking the vacuum.

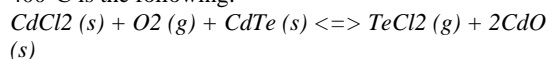
CdCl₂ treatment is applied by evaporating 400-600 nm on to the CdTe surface and then annealing the stack in air at 430 °C for 30 minutes. Standard back contact are made by evaporating Cu/Au, after bromine-methanol treatment of the CdTe surface, followed by a short annealing at 200 °C in air. Standard solar cells have a typical efficiency range of 11 to 12%, while highest efficiencies up to 12.5% have been obtained [5,6].

3 EXPERIMENTAL: THE ACTIVATION PROCESS

3.1 CdCl₂ based activation process

For PVD deposited layer, the CdTe is 4 µm thick. The 'CdCl₂ treatment' consists of physical vapour deposition of about 600 nm of CdCl₂ at a vacuum pressure of 10⁻⁶ Torr and no heating of the substrate. The CdCl₂/CdTe stacks are then put in a furnace at 430-440 °C for about 30 minutes in air. The remaining thin CdCl₂ layer that has not evaporated is then removed by bromine-methanol etching.

As shown by Mc Candless et al. [9] the reaction takes place between the two layers at temperatures above 400°C is the following:

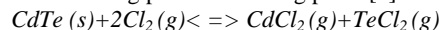


3.2 Freon[®] based activation process

CdTe/CdS/TCO system prepared as described above is placed in a quartz ampoule to which an inert gas containing Chlorine and Argon are inserted. Before each run the ampoule is evacuated with a turbo-molecular pump to 10⁻⁶ mbar. As a source of Chlorine-containing inert gas both Chloro-fluorocarbons and Hydro-chloro-fluorocarbons (gases of the Freon[®] family) may be used. The pressure range is normally 10-30 mbar for Freon[®] and 100-500 mbar for Argon. These pressures are independently measured by means of two different capacitance vacuum gauges and then monitored on a Varian MultiGauge.

The quartz tube is put into an oven where two thermocouples are installed; one is used for furnace temperature control and the other one for measuring sample temperature. Best results for samples with CSS deposited CdTe were obtained carrying out the treatment at 100 mbar of Argon containing 15% of HCF₂Cl (difluorochloromethane) at a temperature of 400°C for 5 minutes.

Since HCF₂Cl is decomposed at 400°C and CdTe starts to decompose at around 400°C, it is supposed that the following process is taking place [8]:



A vacuum for a few minutes, keeping the temperature at 400°C, is done after treatment in order to re-evaporate CdCl₂ formed on the CdTe surface and to clean the CdTe surface for the back contact.

4 DISCUSSION

4.1 Morphology of CdTe

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the surface morphology of CdTe layers. The morphology of as-deposited CdTe layers deposited by PVD and by CSS is quite different (Figure 1 and 2). The grain size of PVD CdTe is in the range of 0.5-1 micron and the structure is very compact. The CdTe deposited by CSS shows bigger grain size of 1 up to 3 microns. The difference in the microstructure of CdTe is due to the different deposition methods where for CSS the substrate temperatures and so the energies involved are higher. The as-deposited PVD CdTe layer is rougher than the CSS deposited one (see figure 4).

CdCl₂ treatment for the CSS- and for the PVD- CdTe layers has been performed. After recrystallization treatment a big change in shape and size of the CdTe grains is observed (see figure 1 and 2). In particular in the PVD CdTe the grains tend to coalesce together giving place to bigger grains (in the range of 2 to 5 microns) while some of the bigger grains divide into small grains and reorient themselves, as is also shown by the AFM pictures. For the CSS CdTe case instead, there is no enhancement of grain size but recrystallization actually shows that some of the bigger grains divide into small grains and reorient themselves (see figure 1, 2 and 4). In both cases an entirely different microstructure and morphology of CdTe is created.

Freon treatment of the CSS and PVD- CdTe layers has been applied. As shown in figures 1 and 2 also in this case a strong and effective recrystallization is observed. For the PVD CdTe layers enlargement of grain size is similar to the CdCl₂ case. The grains are clearly coalescing together to form bigger grains. The picture shown in figure 2 corresponds to a "mild" treatment (5 minutes) and it is clear that the recrystallization is not completed.

In figure 3 the comparison of a 5 minutes Freon treated CdTe and a 10 minutes Freon treated CdTe is shown: for the longer process smaller grains are substituted by bigger grains. There is, on the other hand, a different morphology with larger grain boundaries and different orientation. The CSS Freon recrystallized layers show a completely different morphology with rounded shape maze like grains, also in this case the enlargement of grain size is only slightly observed as in any case already generally accepted.

It is quite interesting to observe that the shape and orientation of grains in the recrystallized layers is strongly depending on the activation process. Most probably the two different chemical dynamics of the recrystallization reaction drive the recrystallization in a different way.

In any case, as shown by the AFM pictures in figures 4, 5 and 6, roughness of the layers is strongly depending on deposition process: PVD grains have a higher

roughness that is only slightly reduced after the treatment. Freon treatment shows to be more effective in this respect: the grains are much more rounded and the difference between the bottom and the top is reduced even for the CSS case. So the Freon treatment provides a much more compact layer especially for the CSS case, reducing the grain boundaries.

For PVD grown samples CdCl_2 treatment reduces the roughness because most of the "cone like" grains that are present in the as deposited case coalesce together giving place to a more homogeneous layer in height.

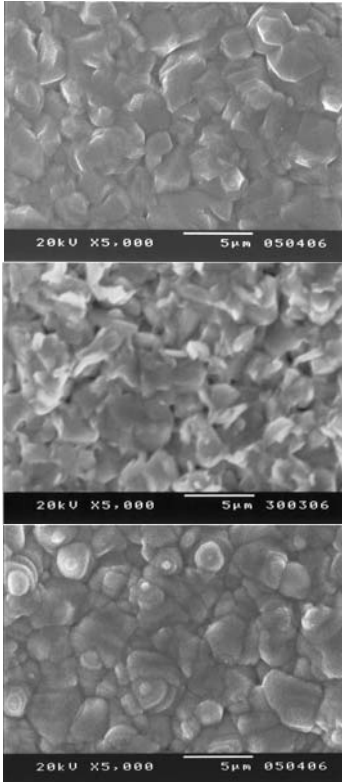


Figure 1: SEM pictures of as deposited, CdCl_2 treated and Freon treated CSS CdTe layers (from top to bottom).

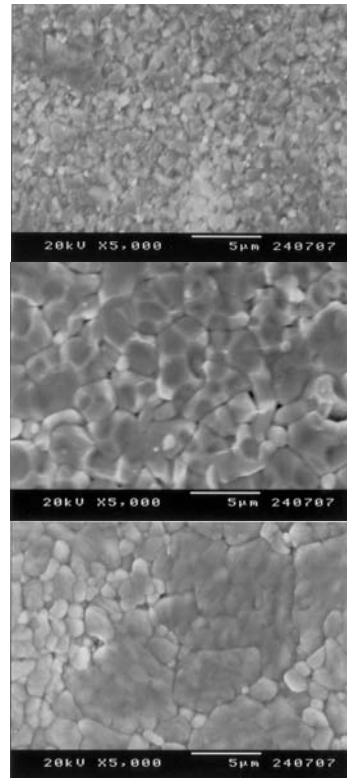


Figure 2: SEM pictures of as deposited, CdCl_2 treated and Freon treated PVD CdTe layers (from top to bottom).

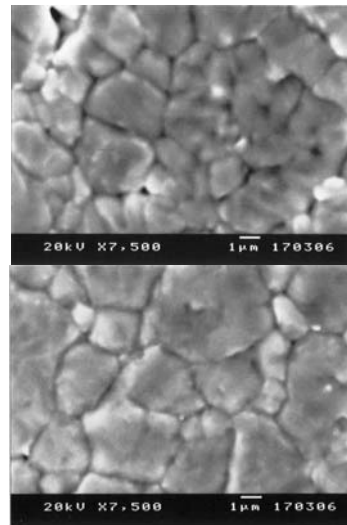


Figure 3: SEM pictures of a 5 minutes- and 10 minutes-Freon treated CdTe layer (from top to bottom).

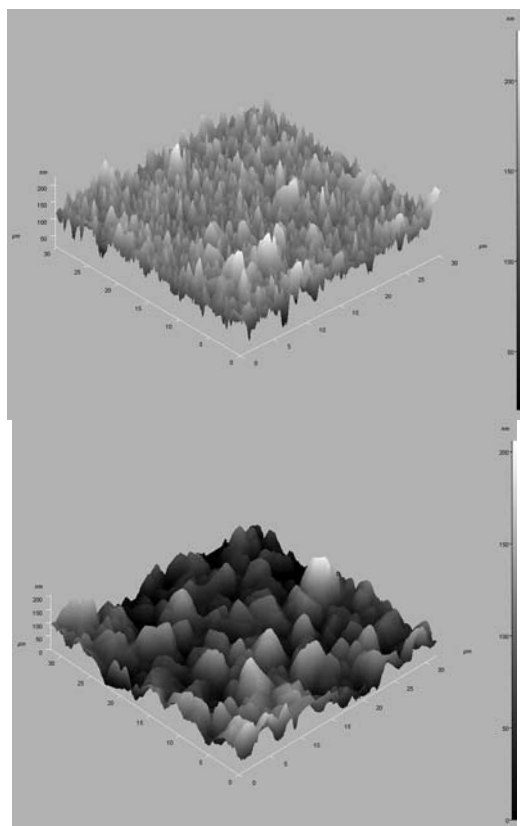


Figure 4: PVD and CSS as-dep CdTe layers (from top to bottom).

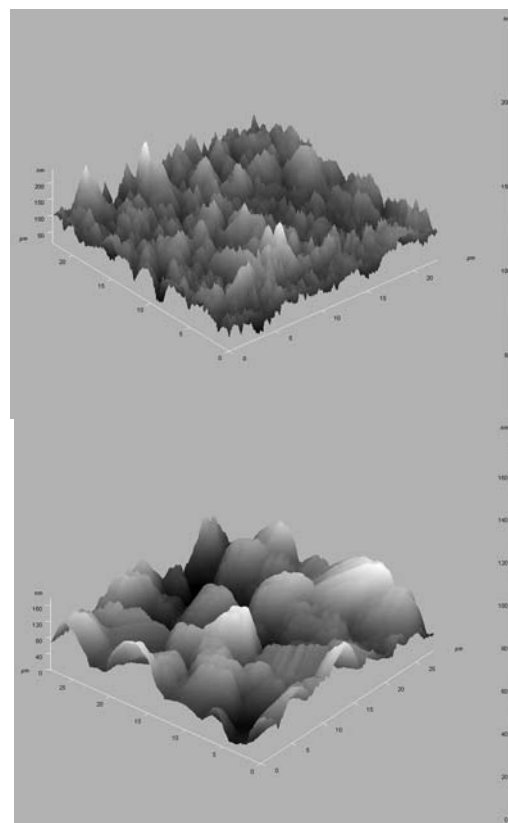


Figure 6: PVD and CSS Freon treated CdTe layers (from top to bottom)

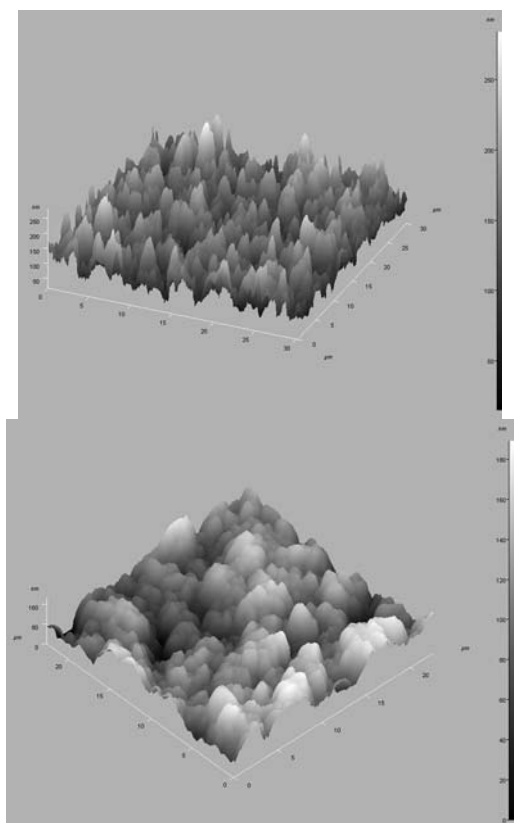


Figure 5: PVD and CSS CdCl₂ treated CdTe layers (from top to bottom).

4.2 X-ray diffraction of CdTe layers

The crystallographic orientations of different types of CdTe/CdS stacks were investigated with X-ray diffraction. The measurements were performed with a Siemens D-500 diffractometer and Cu-K α source.

As reported by the same authors [10], the as-deposited PVD CdTe exhibits a strong (111) preferred orientation which is gradually lost when the layer is processed for recrystallization. It is interesting to observe that if in case of CdCl₂ treated PVD CdTe the preferred orientation is totally lost since the (311) and the (422) peaks have very high intensities [10], the same happens when we provide recrystallization by Freon treatment using a longer process (figure 6): again the (311) and (422) peaks show high intensities compared to the (111) peak. If a milder Freon treatment is applied a more random orientation is shown: high intensity peaks are not only the (311) and (422) but also the (220) peak and other peaks have a stronger signal (see figure 7).

Practically we interpret this behaviour as the tendency, in the recrystallization process, in losing the initial orientation and then, if the energy and time is enough, to re-orient the poly-crystals, similar behaviour has been observed for CdCl₂ treatment previously [10].

As shown in figure 8, for the CSS deposited case what we can observe is that there is no re-orientation of the layers in this case since the preferential peaks remains the same after treatment. Especially for the CdCl₂ treatment we still observe the loss in the preferential orientation but in a lower effect compared to PVD CdTe layers (most probably due to the fact that CSS deposited

layers are grown with high substrate temperature and they have a higher stability).

In case of Freon treatment of CSS deposited layers there is no loss of preferential orientation but even a stronger preferential orientation on the (111) direction.

The big difference in behavior under recrystallization treatments between CSS and PVD CdTe deposited layers is due to the fact that in the CSS case the grains grow already very large and for this reason will not face a strong reorientation, since they have already a very low energy position.

For these reason the Freon and CdCl₂ treatment have, for the CSS case, the main task of passivating grain boundaries more than reducing them.

Both treatments do so that the main arrangement of the polycrystalline layer is increased, reducing the other random oriented grains.

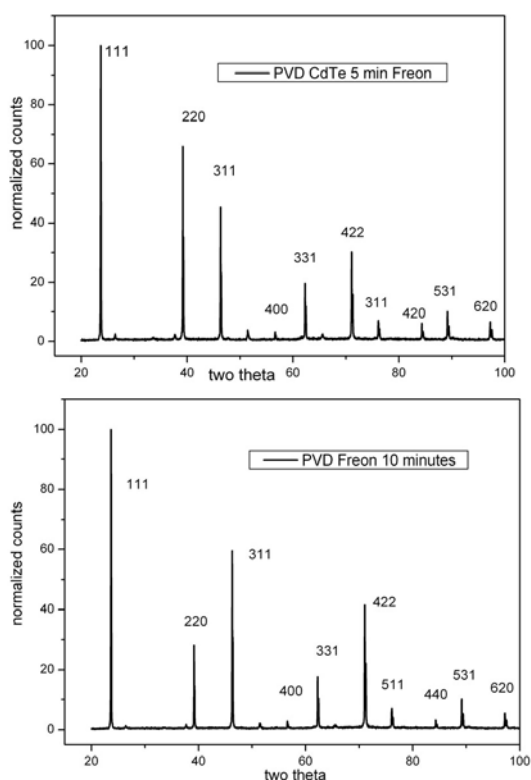


Figure 7: XRD spectra of PVD Freon treated CdTe layer with 5 minutes treatment and 10 minutes treatment (from top to bottom)

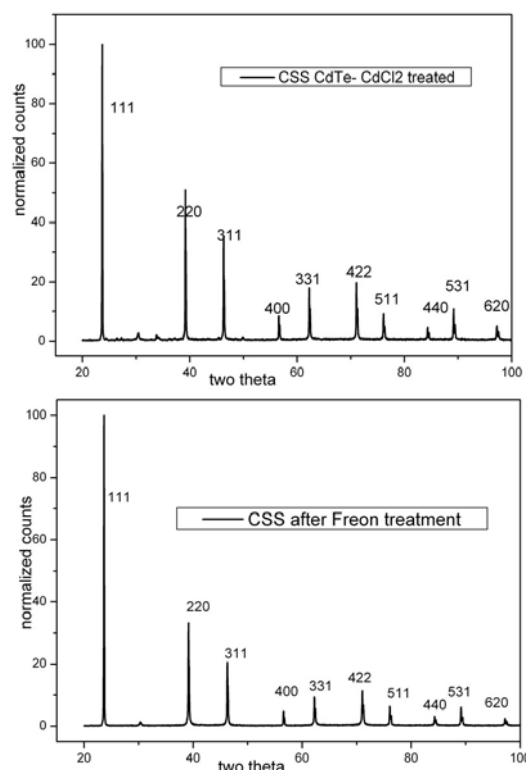
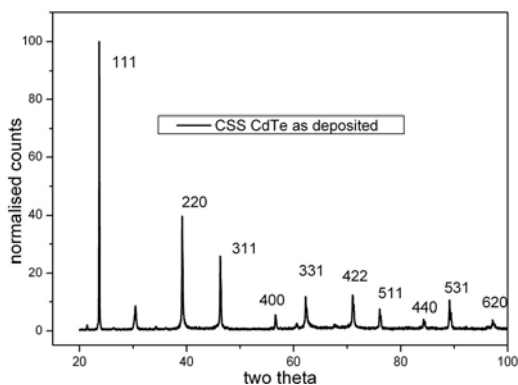


Figure 8: XRD spectra of CSS CdTe layer as dep , CdCl₂ treated and Freon treated (from top to bottom)

Table I: Lattice parameters of CdTe with different treatments

CdTe layer	Treatment	CdTe lattice parameter
PVD-CdTe	As deposited	6.499
PVD-CdTe	CdCl ₂ Treated	6.446
PVD-CdTe	Freon treated (5 minutes)	6.488
PVD-CdTe	Freon treated (10 minutes)	6.487
CSS-CdTe	As deposited	6.491
CSS-CdTe	CdCl ₂ treated	6.488
CSS-CdTe	Freon treated	6.489

4.3 Stress and intermixing

XRD measurements were analysed to study the intermixing and stress in the CdTe layers. The in-plane lattice parameters were accurately determined from the Nelson-Taylor plot [10]. As given in Table 1, the as-deposited layers have a high in-plane lattice constant compared to the recrystallized layers. As an example the lattice parameter of as deposited CdTe on PVD CdS decreases from 6.499 to 6.446 Å for the CdCl₂ treated layers. This is because of relaxation of the compressive stress which is generated by lattice and thermal mismatch between the CdTe and the underlying substrate. The lattice parameter may also decrease because of intermixing of CdS in to the CdTe layer.

A lower effect is observed for Freon treated layers, most probably due to the difference in the reaction process between the activating material and the CdTe/CdS stacks: for the CdCl₂ case there is a real diffusion of the material into the CdTe in the annealing step down to the junction as previously shown [5], in case of Freon treatment we

have to do with a gas which will not diffuse down to the junction as easily as the tiny particles of CdCl₂ that are deposited through the grain boundaries.

The relaxation of the compressive stress is lower for the CSS deposited layers, that is again due to the fact that depositing at higher temperature allows intermixing between CdS and CdTe already during CdTe deposition and the re-adjusting of the solid solution in the recrystallization step is very much reduced.

Freon treatment seems to be a milder process compared to CdCl₂ treatment and is optimal for CSS because in this case junction and grain enlargement is done in the deposition step. In the PVD process, the activation has the task of rearranging the grains and of regulating the CdTe/CdS intermixing, which is not obtained during the low substrate temperature deposition process. So the PVD process needs a stronger activation treatment like CdCl₂ or a longer Freon treatment.

5 CONCLUSIONS

Crystallization and morphology of the CdTe is strongly affected not only by the CdCl₂ treatment but also by the deposition method and the structure of the CdS windows on the TCO substrates, they also affect the influence of post-deposition treatment on CdTe. PVD CdTe grain size is small and post-deposition treatment is required to increase the grain size while the CSS grown grains have already the definitive stable large grain size. The CdCl₂ treatment causes growth or even disintegration of grains in the CdTe layers bringing the poly-crystallites to rearrange in orientation. The CdCl₂ and Freon treatments both reduce the texture but for the Freon case the reduction is less stressed, probably because the gas (with this set of parameters) is not reaching the junction. The recrystallization treatments tend, in a first step, to randomize the orientation and if energy is increased (either by increasing time or temperature) in a second step the (111) preferred orientation is partly regained. Intermixing of CdS and CdTe is milder for Freon treated devices and most probably in case of PVD layers where the intermixing is not applied during deposition but just by the recrystallization treatment a longer Freon treatment is required.

It is reported by previous works [2,6,8] that efficiency cells above 12% are made with CdCl₂ treated PVD-CdTe layers and that cells with efficiencies above 16% are made with either CdCl₂ or Freon treated CSS-CdTe layers. Nothing has been reported for cells made with Freon treated PVD-CdTe layers. We have started to fabricate finished devices with Freon treated PVD-CdTe layers and some preliminary results have brought to cells with efficiencies between 6 and 7% with best efficiency of 7.2 % (Voc=658mV Jsc=19.9 mA/cm² and fill factor of 55.3%). The Freon treatment has still to be optimized for the PVD CdTe cells, we believe that a too mild treatment has been applied and that transformation has not been completed at the junction region, this might give an explanation to the low fill factor of the devices.

What most important is that the Freon treatment is feasible for any kind of CdTe solar cell device and that is able to substitute CdCl₂ if optimized for each different process.

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