

High Efficiency CdTe/CdS Thin Film Solar Cells Prepared by Treating CdTe Films with a Freon Gas in Substitution of CdCl₂

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ABSTRACT: CdTe/CdS thin film solar cells have reached a sufficient conversion efficiency to be considered for an industrial application. The fabrication process is quite fast and it is one of the easiest to be transferred to a large-scale production. In the past, we have simplified the fabrication process by eliminating the etching step by making a completely dry process. 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, namely HCFC1₂. This belongs to the Freon[®] family. The best treatment conditions are as follows. Treatment temperature is typically 400°C. Time of treatment is on the order of a few minutes and the atmosphere containing Cl is typically 100 mbar of Ar containing 15% of HCFC1₂. 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. Solar cell efficiency obtained with this treatment, close to 16%, is comparable if not larger than that reached with CdCl₂ treatment. The Cl₂-treatment can be made with any gas of the Freon family and the only need is that the gas contains chlorine. This method is very effective in producing high efficiency cells. It avoids the use of CdCl₂ that could be dangerous and instead it uses a gas that is stable, inert and not toxic at room temperature. Besides it eliminates the step of CdCl₂ evaporation and, as a consequence, it is much more suitable for an industrial production. This process has been patented.

Keywords: CdTe - Cl₂ treatment - solar cells efficiency

1 INTRODUCTION

An important step in the preparation of high efficiency CdTe/CdS solar cells is the activation treatment of CdTe film. 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. To avoid the deposition of CdCl₂, it has been recently proposed to use vapor of CdCl₂ to treat CdTe. In this case CdCl₂ vapor is obtained by a source facing the CdTe film or conveyed from a remote source by a carrier gas. Alternative techniques such as reacting the CdTe/CdS in either CdCl₂ vapor or Cl₂ vapor [1, 2, 3, 4] has been shown to be suitable substitutes and are more amenable to large scale processing. Among these, the Cl₂ vapor offers advantages with respect to CdCl₂ vapor generation due to Cd toxicity. The use of HCl has also been proposed as an alternative to CdCl₂ treatment. [5]

Treatment of CdTe/CdS thin film structures in dilute mixtures of HCl vapor at 380°C to 440°C promotes similar micro-structural changes in the structure to that obtained by treatment with CdCl₂. The structural properties of the CdTe/CdS system are sensitive to both HCl concentration in the treatment atmosphere and treatment temperature.

It is generally believed that the heat treatment in chlorine atmosphere (CdCl₂ or HCl) may work as a flux which breaks down atomic diffusion barriers at grain boundaries and thereby promotes:

- grain growth improving the crystalline quality
- mixing between CdS and CdTe films

- removing several defects in the junction region.

Industrial interest towards thin film solar cells is increased in recent years also in view of the high conversion efficiency reached so far. A record 16,5% conversion efficiency has been recently reported. [6] Therefore several efforts have been made to provide processes suitable for large-scale in-line production of CdTe/CdS thin film solar cells. However, a number of problems still hinder the achievement of this result, in particular the crucial step of treatment of the CdTe film. Most of the presently available treatment processes involve a step of CdCl₂ evaporation which is carried out at low temperature. This has the disadvantage that the CdTe film must be first cooled down to below 100°C from 500°C at which it is deposited otherwise CdCl₂ vapors do not stick onto the CdTe film surface. After the low temperature deposition, the CdTe-CdCl₂ system must be heated again up to more than 400°C in order to make a treatment in Ar or air atmosphere followed by a vacuum annealing to remove any residual CdCl₂. The above steps significantly affect the production cost.

As a further disadvantage, since CdCl₂ is usually available in a very fine powder form, it cannot directly be evaporated in an industrial production line, as the finest grains would be entrained in the vapor giving rise to a locally uneven deposition. For this reason CdCl₂ powder must be sintered in the form of ingots before evaporation and this is a very expensive step in view of the safety precautions to be taken to carry it out.

Furthermore, 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 quantity, as

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required in a large-scale production plant, due to Cd release, which is highly noxious. Moreover, due to the high water solubility of CdCl_2 , very severe measures have to be taken to avoid any environmental pollution and health damage.

2 EXPERIMENTAL CONSIDERATIONS

2.1 Sample preparation

The CdTe/CdS solar cell is composed of 4 principal layers that are: (see Figure 1)

- A transparent and conducting oxide (TCO) which acts as a front contact; TCO layers are made by two films: the first one is Indium Tin Oxide (ITO), 400 nm thick, with a sheet resistance less than 10 ohm/Sq and the second one that behaves as a buffer-layer is ZnO with a thickness of 100nm.
- A CdS film made by RF-Sputtering in Ar+ CHF_3 atmosphere which is the so called window layer;
- A CdTe film which is the absorber layer made by CSS technique in Ar+ O_2 atmosphere on top of CdS;
- The back contact on top of CdTe film. Also this layer is made by two different films: the first one is Sb_2Te_3 , which guarantees the ohmic behavior of the contact, and the second one is a metallic film such as Mo or W.[7]

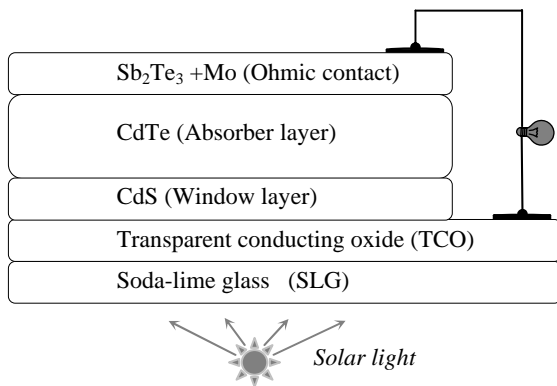


Figure 1: Sequence of the layers constituting the solar cell. The structure of CdTe/CdS solar cells is of the superstrate arrangement, which means that the solar light enters the cell through the glass substrate.

2.2 Experimental apparatus

CdTe/CdS/TCO system prepared as described above is placed in an evacuable quartz ampoule to which an inert gas containing Chlorine and Argon are admitted. Before each run the furnace 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 Ar. These pressures are independently measured by means of two different capacitance vacuum gauges and then monitored on a Varian MultiGauge.

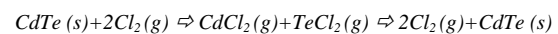
The quartz tube is put into an oven where two thermocouples are installed; one is used for furnace temperature control and the other one for measuring sample temperature. Typical heat treatments parameters are summarized in Table I. Best results were obtained

carrying out the treatment by means of 100 mbar of Ar containing 15% of HCF_2Cl (difluorochloromethane) at a temperature of 400°C for 5 minutes.

Table I: Typical parameters of the heat treatment in Ar+ HCF_2Cl (Freon) atmosphere.

| | Ar (mbar) | Freon(mbar) | Temp. °C | Time (min) |
|------|-----------|-------------|----------|------------|
| min. | 100 | 5 | 380 | 5 |
| max. | 500 | 20 | 420 | 20 |

Since HCF_2Cl is decomposed at about 400°C and CdTe starts to decompose at around 400°C, we suppose that the following process happens especially for the small grains that are the first-ones to decompose:



A vacuum for a few minutes, keeping the temperature at 400°C, is done after the treatment in order to make CdCl_2 formed on the CdTe surface to re-evaporate and to have a clean CdTe surface ready for the back contact. The Cl_2 -treatment can be made with any gas of the Freon[®] family. The only need is that the gas contains chlorine.

3 RESULTS AND CONCLUSIONS

The behavior of CdTe films thermal treated with Freon[®] or with any other chlorine sources is quite the same from many points of view because the reaction mechanism is similar. Actually, during thermal treatment in chlorine ambient the smallest and more unstable CdTe grains are vaporized and, when they re-crystallize, larger, more stable CdTe grains are formed. The effect is very evident when CdTe is deposited by high vacuum evaporation in view of the fact that the average grain size is lower than one micron. If treated CdTe was produced by CSS (Close-Spaced Sublimation), starting grains are larger, more than some microns, and a re-crystallization of the grain edges is appreciated. The surface of the as-deposited CdTe film is shown in figure 2 (a). The single crystals on the surface are very angled and between the grains it is possible to see very deep grain boundaries.

The CdTe polycrystalline film grows in the zinc-blende structure. The (111) plane exhibits a hexagonal symmetry. This is clearly observed in figure 2(a). After Freon treatment the edges of the grains on the surface of CdTe layer are more round and the morphology appears to be smoother than before treatment. In figure 2(b) one still can see the (111) hexagonal crystal structure but after treatment one observe a pyramid-like crystal with a hexagonal base. This indicates that some CdTe evaporates and gets lost during the treatment process leaving an etched-like surface. This behavior is typical of all the CdTe films heat treated in chlorine atmosphere. In general non-homogeneous distribution of the grain size is found, while larger grains are observed in the treated films.

Also for Freon[®] based process, the introduction of oxygen into the CSS chamber during the deposition of CdTe films, permits to execute the thermal treatment in chlorine ambient in an inert gas such as Ar or N_2 instead

of an oxidizing atmosphere, i.e. air. This fact is very important because the presence of oxygen during the CdTe deposition or during the Cl₂ treatment can increase the number of *p*-type majority carriers.

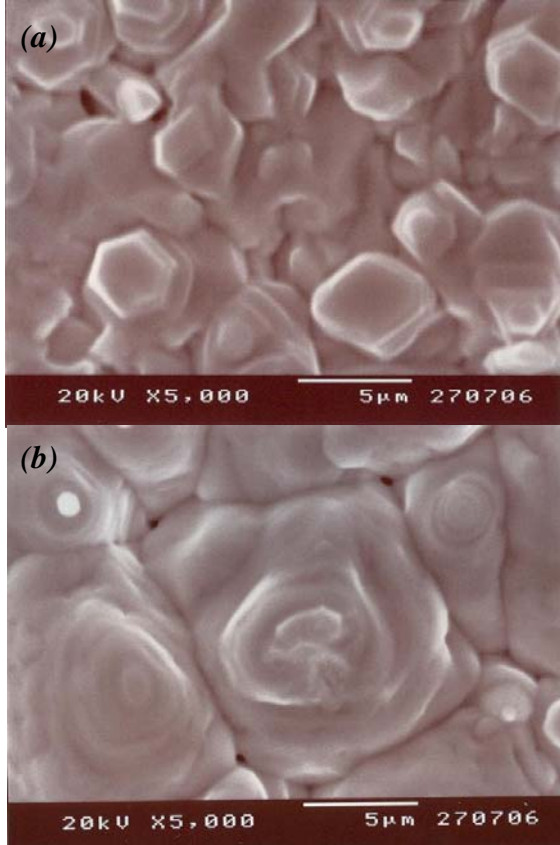


Figure 2: SEM photos of the surface of CdTe films. (a) morphology of an untreated CdTe film deposited by CSS method; (b) morphology of the same film after thermal treatment in Ar+HCF₂Cl atmosphere at a temperature of 400°C for 5 min.

Similarly to what happen with CdCl₂ treatment, also in these films the presence of a ternary oxide (CdTeO₃) is detected by X-ray analyses. Since this insulating material is principally localized into the grain boundaries, the attendance of CdTeO₃ allows the surface self-passivation which prevents the recombination of the photo-generated carriers. In figure 3 are shown the results of the XRD analysis. The peaks are normalized to the (111) and the CdTeO₃ peaks are omitted for a better comprehension.

Only to give an idea about preferred orientations the texture coefficients *C_i* and their standard deviation *σ* are reported in table II.

Table II: The texture coefficients *C_i* and the standard deviation *σ* of the CdTe crystalline structure before and after Freon treatment.

| | <i>C_i</i> | | | | | | | | | <i>σ</i> |
|--------|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|----------|
| | (111) | (220) | (311) | (400) | (311) | (422) | (511) | (440) | (531) | |
| before | 0,5 | 0,8 | 1,2 | 0,3 | 0,7 | 0,7 | 1,0 | 2,0 | 1,6 | 0,5 |
| after | 0,9 | 0,5 | 0,6 | 0,8 | 0,9 | 1,0 | 1,5 | 1,5 | 1,4 | 0,3 |

After treatment, the preferential orientation shifts

slightly to the (111) direction but the overall orientation tends to be more random as the value of the standard deviation decreases.

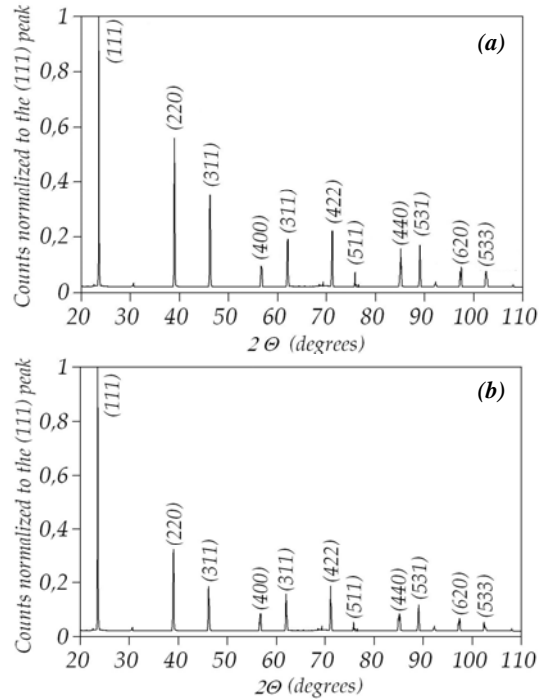


Figure 3: X-Ray diffraction pattern of the CdTe layer (a) before and (b) after Freon heat treatment.

Depth-dependent cathode-luminescence (CL) analyses demonstrates that the impurities introduced during the Freon[®] heat treatment are non-homogeneously distributed along the deposition direction of CdTe. In particular, chlorine concentration is higher near the CdTe surface and the CdS/CdTe interface and no evidence of any incorporation of fluorine is observed. [8]

However, if the penetration of Cl into the grains is small, migration through the grain boundaries can be much faster. In this way Cl atoms could reach the CdS/CdTe interface and be incorporated as donors in the S-rich part of CdS_xTe_{1-x} alloy region, while in the Te-rich part, chlorine can form complexes with Cd-vacancies which have acceptor behavior. It is moreover known that the formation of this interfacial layer reduces structural defects due to the lattice mismatch between the semiconductors and leads to a lower defect density in the critical region near the interface. The value of X and the extension of the intermixed layer could depend both on the CdTe deposition parameters and on Freon[®] heat treatment temperature. The best energy conversion efficiency reached so far in our laboratory obtained optimizing the thermal treatment in Freon atmosphere is around 16%. Two typical characteristics are reported in Figure 3. We have taken the I-V characteristics by illuminating the cells by means of an Oriol[™] solar simulator with 100mW/cm² incident power and AM 1.5 solar light spectrum. The measurement system has been calibrated with a 14% efficient CdTe/CdS thin film solar cell previously certified at an authorized laboratory. Part (b) of figure 3 shows parameters of one of the best device: an efficiency of 15.6% with a V_{oc} (open circuit

voltage) of 849 mV, a J_{sc} (short circuit current density) of 25,58 mA/cm² and a ff (fill factor) of 0.718 over an area of the device of 1 cm². In Figure 3 (a) it is depicted a device behavior after treatment in Freon atmosphere at 420°C for 20 min. The I-V characteristic puts in evidence an increase of the diode reverse saturation current that is responsible of a drastic reduction of fill factor. This performance demonstrates that the formation of CdS_xTe_{1-x} intermixed layer is strongly influenced by chlorine reaction during the heat treatment. In this case the intermixed layer and, as a consequence, the junction region is too large to give a good rectifying device. The cell parameters are: efficiency around 10% with a V_{oc} of 712 mV, a J_{sc} of 25,2 mA/cm² and ff of 0.56.

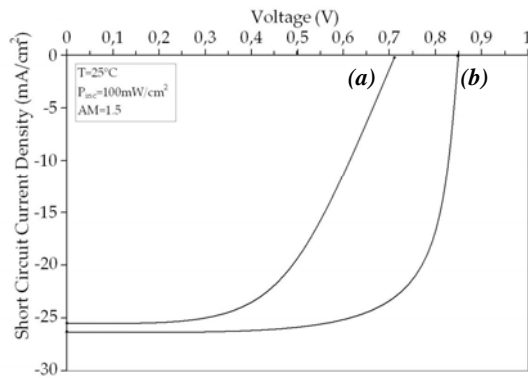


Figure 4: J versus V characteristics of the CdTe/CdS solar cells taken in standard conditions after thermal treatment in Freon atmosphere. (a) behavior of a device obtained by using 100 mbar of Ar containing 15% of HCF₂Cl at a temperature of 420°C for 20 minutes. (b) behavior of a device obtained by using 100 mbar of Ar containing 15% of HCF₂Cl at a temperature of 400°C for 5 minutes.

In conclusion, as a source of Chlorine-containing inert gas suitable to make CdTe films thermal treatment, both Chlorofluorocarbons and Hydrochlorofluorocarbons may be used. These are non-flammable, non-corrosive, non-toxic and odorless gases. Even if Chlorofluorocarbons are considered dangerous for the ozone layer surrounding the Earth, they could be used in an industrial process being easily recoverable in a closed circuit plant without any pollutant emission in the earth atmosphere.

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