

# An innovative process suitable to produce high-efficiency CdTe/CdS thin-film modules

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## ARTICLE INFO

### Article history:

Received 9 September 2008

Received in revised form

14 May 2009

Accepted 1 June 2009

Available online 18 June 2009

### Keywords:

CdTe

Thin films

Solar cells

Modules

## ABSTRACT

A novel process, different in all steps from the common process usually used to fabricate CdTe/CdS thin-film solar cells, is described. This process on the one hand permits one to obtain high-quality layers and high-quality cells and on the other hand is particularly suitable to be scaled up at an industrial level. In fact, neither etching baths nor CdCl<sub>2</sub> deposition is used in this process. The back contact is made with a buffer layer capable of stabilizing Cu and, as a consequence, the devices are very stable.

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## 1. Introduction

CdTe with its energy gap of 1.45 eV is an ideal material to be used as an absorber in solar cells. Besides, its gap is “direct”, which means that only a few microns of the material are needed to absorb 90% of photons with energy greater than 1.45 eV. Its phase diagram is quite simple and only the stoichiometric compound can be formed at temperatures higher than 300 °C. At high temperature, namely 500–600 °C, that is used when it is deposited by closed-space sublimation (CSS), it grows p-type with a carrier concentration greater than 10<sup>14</sup> cm<sup>-3</sup> that are sufficient to form a good junction with an n-type partner. This is quite important since doping of polycrystalline thin films has to be avoided due to the fact that foreign elements, especially metals, tend generally to segregate into the grain boundaries. CdTe thin films can be prepared by several methods, such as simple evaporation [1], electrodeposition [2,3] and CSS [4]. Among these, CSS has been demonstrated to be most effective in giving high-efficiency solar cells since it allows the film to grow at high substrate temperatures (500–600 °C) at which CdTe grows polycrystalline with a large grain size (2–10 μm). High-efficiency thin-film solar cells are obtained using CdS as an n-partner (less than 100 nm thick) in the superstrate configuration. The highest efficiency so far reported for CdTe/CdS thin-film solar cells is 16.5% [5,6]. Here, the CdTe film is deposited by the CSS technique and CdS is deposited by chemical bath deposition (CBD), the front

contact is a layer of Cd<sub>2</sub>SnO<sub>4</sub> covered by a buffer of Zn<sub>2</sub>SnO<sub>4</sub> and the back contact is done with a layer containing a small amount of Cu. Due to the good photovoltaic properties of CdTe and the good scalability of the techniques used to produce CdTe/CdS thin-film solar cells, these devices are already produced in modules of 60 × 120 cm<sup>2</sup> by two companies, namely Antec Solar in Germany and First Solar in the United States. So far, CdTe/CdS modules exhibit efficiency between 7% and 10% [7]. An increase in the module efficiency can be obtained if the fabrication process is simplified in order to decrease the gap between the laboratory and the industrial scale. Here, we will describe a process that is notably simplified with respect to the ones that are currently used.

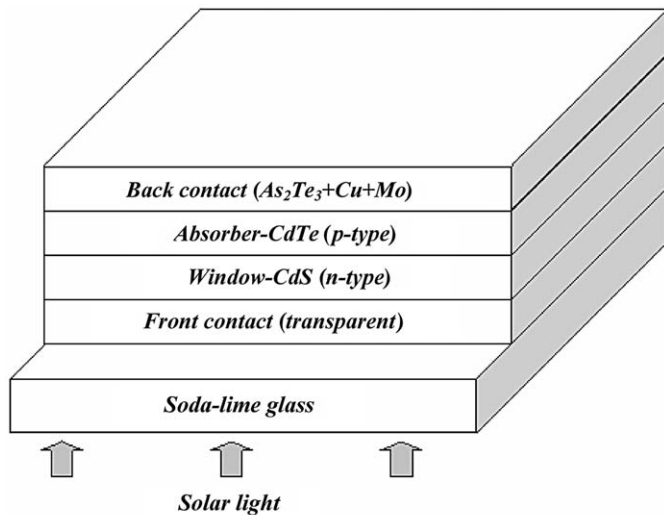
## 2. Structure of the cell

The CdTe/CdS thin-film solar cell is composed of four layers (Fig. 1):

- The TCO (transparent conducting oxide) layer that acts as the front contact.
- The CdS layer that is the n-type partner.
- The CdTe layer that is the p-type absorber.
- The back contact.

The configuration is of the “superstrate” type, which means that the light enters from the glass substrate. Both front and back contacts are composed of two sub-layers as it will be explained later on.

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**Fig. 1.** Sequence of the layers constituting the solar cell. The structure of CdTe/CdS solar cells has a superstrate arrangement.

### 3. The TCO layer

The most important characteristics that a TCO front contact must exhibit are a low sheet resistance and a high transparency in the visible region. Indium tin oxide with a 10 wt% of Sn fulfills these requirements. However, due to the high temperature at which CdTe is deposited and/or treated in the presence of chlorine, some In can diffuse from the ITO into the subsequent deposited layers. The use of a 100–200-nm-thick buffer layer between ITO and CdS, such as SnO<sub>2</sub> or ZnO, can hinder the In diffusion. Recently we have demonstrated, by SIMS depth profile measurement [8], that In has a concentration of  $5 \times 10^{15} \text{ cm}^{-3}$  in CdTe when SnO<sub>2</sub> is used as a buffer layer while its concentration rises to values of  $8 \times 10^{16}$ – $10^{17} \text{ cm}^{-3}$  when the buffer layer is not used. Besides, due to its relatively high resistivity, the buffer layer reduces the effect of a shunt resistance that could come from pinholes in the very thin CdS layer.

In prevision of an industrial production, the ITO is deposited by DC magnetron sputtering that is less expensive than RF magnetron sputtering while SnO<sub>2</sub> and ZnO are prepared by reactive DC magnetron sputtering in the presence of O<sub>2</sub> using pure Sn or Zn targets. In order to avoid the formation of nodules on the ITO target surface that could introduce a discharge instability, a rotating ITO target is being used.

### 4. The CdS layer

High-performance CdTe/CdS thin-film solar cells can be obtained with CdS prepared by three different techniques, namely chemical bath deposition, close-spaced sublimation and RF sputtering. We chose this last technique since it is the most suitable for industrial production. However, in order for a sputtered CdS film to give high-efficiency cells, it has to be made with some fluorine (F) in the sputtering chamber. We prepared F-doped CdS films by introducing in the sputtering chamber Ar containing  $\approx 3\%$  of CHF<sub>3</sub>. This gas is decomposed in the sputtering chamber and fluorine, being negative, is directed to the substrate. We expected that F will decrease the resistivity of the CdS film but this did not happen. On the other hand, F-doped CdS exhibits a forbidden gap a little larger than the un-doped CdS [9], a stronger cathodoluminescence emission [10], a stronger photoconductivity and, what is most important, gives higher

efficiency solar cells [11]. Possibly, fluorine, bombarding the CdS film during the growth, eliminates any excess of Cd and S and gives a more stoichiometric film. On the other hand, it could form some CdF<sub>2</sub>, which could passivate the grain boundaries. F-doped CdS has revealed to be more stable with respect to the CdS–CdTe mixing when the CdTe/CdS structure is treated at 400 °C in the presence of chlorine.

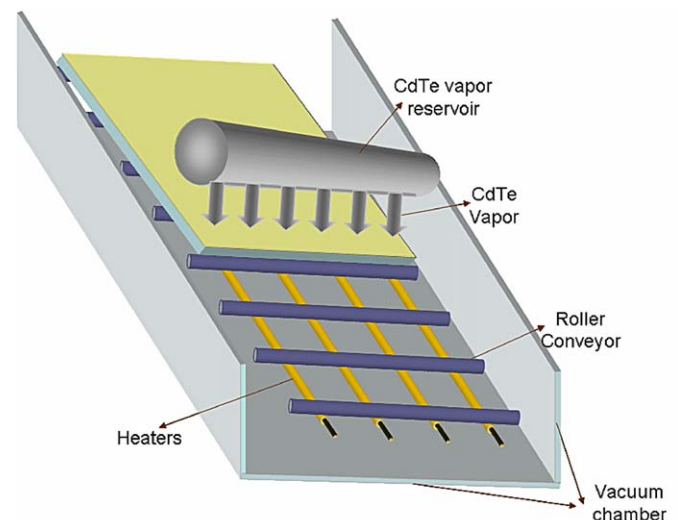
### 5. The CdTe layer

The most suitable method to deposit CdTe is close-spaced sublimation (Fig. 2), even though electrodeposition has also been demonstrated to be a very suitable technique [6]. However, CSS allows high deposition rates of the order of several microns per minute and it has been used for the preparation of the highest efficiency CdTe/CdS [5,11,12] solar cells. A slit 60 cm long and 2.5 cm wide was used and the vapour was supplied from top such that the glass substrate is well sustained on the carrying rollers. This is done in order to avoid the bending of the glass at 500 °C. The substrate temperature is typically 500 °C and the substrate-crucible distance is  $\approx 5$  mm. The deposition is done in an Ar atmosphere with a pressure of  $10^{-1}$ –1 mbar. With a crucible temperature of 700 °C, deposition rates between 1 and 4  $\mu\text{m}/\text{min}$  can be obtained.

### 6. Treatment of the CdTe/CdS structure in the presence of Cl<sub>2</sub>

Treatment of CdTe in the presence of Cl<sub>2</sub> is necessary in order for the solar cells to exhibit high efficiency. This treatment is generally done by depositing CdCl<sub>2</sub> on top of CdTe by evaporation or by dipping CdTe on a solution of CdCl<sub>2</sub>–methanol and with a subsequent annealing at 400 °C in air or in an inert gas such as Ar [11]. In view of the industrial production we found out another method to carry out the Cl<sub>2</sub> treatment that does not use any CdCl<sub>2</sub>.

The CdTe/CdS structure is annealed in a mixture of 100–500 mbar of Ar and 20–50 mbar of a non-toxic gas containing Cl<sub>2</sub> such as difluorochloromethane (HCF<sub>2</sub>Cl). The annealing duration was  $\approx 5$ –10 min at 400 °C. After the treatment the CdTe morphology is completely changed with an increase in size (Fig. 3). Since HCF<sub>2</sub>Cl is decomposed at 400 °C and CdTe starts to decompose at around 400 °C, we suppose that the following reaction happens



**Fig. 2.** Sketch of CSS as it is foreseen for a production line.

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