Procedure to obtain higher than 14% efficient thin film CdS/CdTe solar cells activated with HCF₂Cl gas

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Abstract

This work reports a process used to obtain CdS/CdTe thin film solar cells with high efficiencies between 14% and 14.6%. The procedure consists of sequentially depositing by RF sputtering and close space sublimation (CSS) of several layers onto a glass substrate, configured as glass/ITO/ZnO/CdS/CdTe/Cu/Mo. The CdTe layer was deposited by CSS at low substrate temperature (500 °C) under Ar–O₂ atmosphere and the activation process is performed with a mixture of Freon gas (HCF₂Cl) and other gases.

Keywords: Solar cells; Heat treatment; Activation process; Chlorine

1. Introduction

Currently there is a technology to manufacture CdS/CdTe thin film solar cells for a large scale production (Razykov et al., 2011). These devices are already produced in modules of 60 × 120 cm² by two companies: Antec Solar in Germany and First Solar in the United States. The module conversion efficiency rose to 11.6% (http://investor.firstsolar.com/, 2010). However these companies use the vapor transport deposition (VTD) as deposition technique for CdS and CdTe films. Also the CdCl₂ treatment is performed with an aqueous solution sprayed on CdTe film and subsequently treated in a belt furnace (Biccari, 2011). In recent years, Romeo et al. development a new method to make the heat-treatment in Chlorine atmosphere. For the Cl-treatment the CdS/CdTe structure is placed in an ambient containing a non toxic gas such as HCF₂Cl. This innovation permits to obtain an efficiency of 15.8% (Romeo et al., 2006). Recently has been obtained a new world record efficiency 17.3% and was obtained by First Solar on production line (http://investor.firstsolar.com/releasesdetail.cfm?ReleaseID=593994, 2011). In the present work we report about our results in small CdS/CdTe solar cells (~1/4 cm²) using sputtered ZnO (buffer), CdS (window layer) and Cu/Mo (back contact). The CdTe absorber film is deposited by close space sublimation (CSS) at low substrate temperature (500 °C) and the activation process (chlorination) is performed with Freon gas mixed with another gas at 400 °C. Cells up to 14% efficiency are obtained with this procedure without a special treatment to CdS film.

2. State of the thin film cadmium telluride solar cells

Many research groups have as main goal to obtain high efficiency solar cells, higher or equal than 16.5%. This is the last world record efficiency reported before of the 17.3%. There are several works about procedure to obtain efficient...
solar cells, but most of them do not report its area size. We did a report selection based mainly on device area and efficiencies between values of $13–16.5\%$. In the Table 1, summarizes by four relevant aspects: the solar cell structure, the process of obtaining the CdS film, activation process and main parameters of solar cell.

As can be seen in Table 1, the window layer is obtained by different techniques, including the world record cells that use the humid process. The main disadvantage CdS deposit by humid process that is more complex at industrial scale. Also, the CdS is thermal treated under different atmospheres prior to CdTe deposition. One of the most important steps to achieve a high efficiency device is the activation heat treatment. Also it is performed for humid via, in the most of the cases. Only there is a work that reports a dry process (Romeo et al., 2010). We implement this process in our work, however in an atmosphere using a new blend of gases.

We found in our research to make the Table 1, a report about the guidelines to further increase the efficiencies of CdS/CdTe solar cell based on a new model (Dharmadasa et al., 2002). However the authors did not report the area of device.

### Table 1: Performance of thin film CdTe solar cells.

<table>
<thead>
<tr>
<th>Year</th>
<th>Type</th>
<th>CdS process</th>
<th>Activation Process</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Area (cm²)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td>Glass/SnO₂:F/CdS/CdTe/Au</td>
<td>Screen printing/Not treated</td>
<td>CdCl₂ dip and heat treatment</td>
<td>840</td>
<td>21.9</td>
<td>72.6</td>
<td>13.4</td>
<td>1.20</td>
<td>USF</td>
</tr>
<tr>
<td>1993</td>
<td>Glass/SnO₂:F/CdS/CdTe</td>
<td>CBD/Treated under H₂ atmosphere</td>
<td>CdCl₂ dip and heat treatment</td>
<td>843</td>
<td>25.1</td>
<td>74.5</td>
<td>15.8</td>
<td>1.05</td>
<td>USF*</td>
</tr>
<tr>
<td>1996</td>
<td>Glass/CdS/CdTe/C/Ag</td>
<td>CBD/Not treated</td>
<td>CdCl₂ solution and heat treatment</td>
<td>824</td>
<td>25.4</td>
<td>71.9</td>
<td>15.1</td>
<td>1.00</td>
<td>Matsushita</td>
</tr>
<tr>
<td>1997</td>
<td>Glass/ITO/CdS/CdTe/Cd/C</td>
<td>CBD/Not Treated</td>
<td>CdCl₂ solution and heat treatment</td>
<td>825</td>
<td>25.4</td>
<td>72.2</td>
<td>15.1</td>
<td>1.00</td>
<td>Matsushita</td>
</tr>
<tr>
<td>1998</td>
<td>Glass/CdS/CdTe/C/Ag</td>
<td>MOCVD/ Treated under air atmosphere</td>
<td>–</td>
<td>840</td>
<td>26.1</td>
<td>73.1</td>
<td>16.0</td>
<td>1.00</td>
<td>Matsushita</td>
</tr>
<tr>
<td>1999</td>
<td>Glass/SnO₂:F/SnO₂/CdS/CdTe/HgTe:Cu-Ag</td>
<td>CBD/Treated under H₂ atmosphere</td>
<td>CdCl₂ solution</td>
<td>820</td>
<td>21.8</td>
<td>70.6</td>
<td>12.6</td>
<td>0.86</td>
<td>NREL</td>
</tr>
<tr>
<td>2000</td>
<td>Glass/ITO/CdS/CdTe/C/Ag</td>
<td>MOCVD/Not treated</td>
<td>CdCl₂ solution and heat treatment</td>
<td>800</td>
<td>24.8</td>
<td>67.9</td>
<td>13.5</td>
<td>0.42</td>
<td>OU</td>
</tr>
<tr>
<td>2001</td>
<td>Glass/ITO/CTO/ZTO/CdTe</td>
<td>CBD/Not Treated</td>
<td>Vapor CdCl₂ and heat treatment</td>
<td>845</td>
<td>25.9</td>
<td>75.5</td>
<td>16.5</td>
<td>1.03</td>
<td>NREL*</td>
</tr>
<tr>
<td>2004</td>
<td>Glass/ITO/CdS/CdTe/Sb₂Te₃–Mo</td>
<td>Sputtering under CHF₃ atmosphere</td>
<td>Vapor CdCl₂ and heat treatment</td>
<td>862</td>
<td>25.5</td>
<td>72.0</td>
<td>15.8</td>
<td>1</td>
<td>UP</td>
</tr>
<tr>
<td>2005</td>
<td>Glass/ITO/CdS/CdTe/</td>
<td>MOCVD/Thermal annealing under air atmosphere</td>
<td>CdS:S nanoestruendo</td>
<td>822</td>
<td>26.0</td>
<td>71.7</td>
<td>15.3</td>
<td>0.10</td>
<td>OU</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO/CTO/ZTO/nano-CdS:O/CdTe/Cu/Te/ITO/Ni–Al</td>
<td>–</td>
<td>–</td>
<td>806</td>
<td>25.0</td>
<td>69.2</td>
<td>13.9</td>
<td>0.41</td>
<td>NREL</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO/CdS/CdTe</td>
<td>MOCVD dopado con (CH₃)₂SnCl₂</td>
<td>–</td>
<td>820</td>
<td>25.5</td>
<td>72.0</td>
<td>15.1</td>
<td>0.11</td>
<td>OU</td>
</tr>
<tr>
<td>2006</td>
<td>Glass/ITO: F/SnO₂/CdS/CdTe/Sb₂Te₃–Mo</td>
<td>Sputtering under CHF₃ atmosphere</td>
<td>Thermal evaporation CdCl₂ and air annealing</td>
<td>812</td>
<td>25.0</td>
<td>69.0</td>
<td>14.0</td>
<td>1</td>
<td>UD</td>
</tr>
<tr>
<td>2010</td>
<td>Glass/ITO/CdS/CdTe/Sb₂Te₃–Cu</td>
<td>Sputtering under CHF₃ atmosphere</td>
<td>From HCF₂Cl</td>
<td>862</td>
<td>25.5</td>
<td>72.0</td>
<td>15.8</td>
<td>1</td>
<td>UP</td>
</tr>
</tbody>
</table>


3. Experimental procedure

Our cell has a superstrate structure and it is fabricated by sequentially depositing several layers onto a Corning glass substrate, configured as glass/ITO/ZnO/CdS/CdTe/Cu-Mo. Fig. 1 shows the solar cell structure with the thickness of the different films that make up the cell. The thickness of these films was measured using a Vecco Dektak-8 Stylus Profiler.

We used as substrate a commercial Corning glass coated with ITO of one inch square (Delta Technology, USA). The films had a sheet resistance of $4–10 \Omega/\square$ and a transmittance of $90\%$. Next, a buffer layer of ZnO (200 nm) film was deposited by RF magnetron sputtering starting from a metal Zn target with 4 N purity. The ZnO films used has a resistivity of about $10^3 \Omega \text{cm}$ measured by four probe method and helps to reduce shunts caused by hole from CdS thin film. The CdS film was deposited also by RF sputtering using a CdS target with 4 N purity onto the ITO/ZnO structure at a substrate temperature of $250 \degree C$ in an Ar atmosphere.

The CdTe films were grown onto the glass/ITO/ZnO/CdS by CSS method. The $7–8 \mu m$ thick films were depos-
then Ar (0.4 mbar) and O₂ (0.1 mbar) are introduced. Next, the gas is removed and the high vacuum is restored, and are reaching the desired temperatures and they are stable. 

/C176 source slowly at 500°C for 20 min in an Ar atmosphere. A detailed study of our ohmic contacts was recently reported (Pen˜a et al., 2011). But, in our experimental system, the treatment of the substrate and is placed inside; the complete system consists of two graphite blocks (9 cm x 9 cm x 0.5 cm) both are heated by quartz lamps that do not produce contamination in the vacuum chamber. The separation between graphite blocks is 3–5 mm. The CdTe source used in this work was a target, manufactured with 5 N purity CdTe powder (e.g. provided by Cerac Inc.). For manufacturing the target, the powder is placed in a graphite crucible inside a vacuum chamber under a 500 mbar Ar pressure and the temperature is raised up to around 700 °C for few minutes and slowly is cool down to room temperature. For the CdTe film deposition, first we fix a high Ar pressure (~500 mbar). Next, we heated the substrate and source slowly at 500 °C and 580 °C, respectively. Once are reaching the desired temperatures and they are stable, the gas is removed and the high vacuum is restored, and then Ar (0.4 mbar) and O₂ (0.1 mbar) are introduced. Next the deposition process is performed. Finally it is cooled slowly until room temperature.

Our activation heat treatment is performed using Freon gas (HCF₂Cl) as Romeo (Mazzamuto et al., 2008; Vaillant et al., 2008). But, in our experimental system, the treatment is done in a quartz tube, with a graphite block as support for the substrate and is placed inside; the complete system is heated by halogen lamps. The activation process was made with 50 mbar partial pressure of Freon gas, with respect to the total pressure of 400–800 mbar of a gas mixture (argon–oxygen). The thermal treatment is done at 400 °C for 5 min. After this time the gas mixture is removed, high vacuum is restored and the samples are kept at the same temperature for another 10 min.

Finally, our ohmic contact on CdTe films was performed by etching the CdTe surface with Br₂:CH₃OH solution followed by two layers: Cu (5 nm) and Mo (750 nm), grown by RF sputtering in Ar atmosphere. Both measured with a Rate/Thickness Monitor INFICON SQM-160. After, the device is annealed at 200 °C for 20 min in an Ar atmosphere. A detailed study of our ohmic Cu/Mo contact was recently reported (Pen˜a et al., 2011).

Solar cell characterization was performed using an Oriel™ solar simulator (with a calibrated reference of Si cell) under an AM1.5. Also, the solar cell was measured directly at the sun, under 99.5 mW/cm² (http://www.mda.cinvestav.mx/weather) and with help of LabView program development in our laboratory. The current density–voltage (J–V) measurements were obtained using a Source Meter from Keithley 2420. From the J–V curve the principal photovoltaic parameters: open circuit voltage (V₉sc), short circuit current (Isc), fill factor (FF), efficiency (η), series resistance (Rₛ) and shunt resistance (Rₛ), were determined. The Rₛ and Rₛ were determinate by the slope of J–V characteristics at I ≥ 40 mA in forward and −0.2 V in reverse, respectively (Oman et al., 1999). The other Labview program it is used for the dark J–V curve and it gives the diode ideality factor (A) and saturation current diode (Jₐ0). The area of our cell was determined by using a picture from a digital microscope Model 111619172 of Labtronic Scientific with a zoom of 7×. By using Corel Photopaint© the interest area in the picture (Fig. 2) is selected. This area corresponds to solar cell area, and the number of pixels is equivalent to the real area. This method has a precision of 0.0001 cm².

4. Results and discussions

In general the use of ZnO high resistive transparent layer has allowed us to improve the reproducibility, stability and performance of our solar cells. Our detailed investigation on the benefits of ZnO as buffer layer is underway and will soon be published.

The Fig. 3 shows an AFM image of the CdS film used. A measurement of roughness of this sample gives 4.2 nm. We can see a CdS film compactness and with uniform grains. Tsuji et al. (2000) found that the grain size and shape of the CdS film greatly affect the electrical properties of solar cells, and the conversion efficiency strongly depends on the small roughness of the CdS surface. With a low roughness, the CdTe grown on this surface could have low stress and better morphological properties; therefore, the CdS–CdTe junction improves. The CdS film is not intentionally treated. However, receives a thermal treatment prior to the CdTe deposition process.

During the process of CdTe deposition, the CdS film was exposing to a pure oxygen atmosphere (0.1 mbar) during 25 s. Has been reported that oxidized CdS can suppress...
pinhole formation (Rose et al., 1996). The other important point is that oxygen present in the CdS layer significantly suppresses the interdiffusion (Wu, 2004; Yan et al., 2001). It allows us to have better control of the formation of intermixed (CdS\textsubscript{x}Te\textsubscript{1−x}) near the CdS/CdTe junction, giving benefit for the solar cell performance.

One of the crucial steps to achieve high efficiency is the activation process. We use Freon gas as Cl\textsubscript{2} source. In our case, in addition to using Ar–Freon mixture was necessary to use other gases for example the oxygen. This difference with respect to reported by Romeo, we attributed at the obtention process of CdS and CdTe films. In our case, the CdS film is deposited under Ar pure atmosphere and the CdTe film is deposited at low substrate temperature. This fact indicates that the activation process with Freon gas is not universal; it depends of obtention process of the CdS and CdTe films. After the treatment the CdTe morphology changed as show in Fig. 4. In Fig. 4 we can see that the grain size increases. This increase is about 2 \textmu m and it was measured by SEM micrographics. Our grain size is lower than shown by Romeo (Mazzamuto et al., 2008; Romeo et al., 2010) due to our CdTe film was deposited at low substrate temperature (500°C) with Ar–O\textsubscript{2} mixture atmosphere (0.5 mbar). It is know that O\textsubscript{2} presence reduces the grain size (Bosio et al., 2006).

In Fig. 5 we show the illuminated \( J−V \) curve for our best CdS/CdTe solar cell performed in simulator and sun conditions. We can see that the efficiency at sun illumination is higher. The decrease of \( V_{oc} \) and the increase of \( J_{sc} \) we correlate to an increase of cell temperature under the outdoor conditions and sun radiation heating (~37°C). The simulated measurements using the Oriel simulator are developed in a controlled temperature conditions (~25°C). The principal parameters for our cell are listed in Table 2.

The highest values ever reported for a CdS/CdTe cell are: \( V_{oc} = 845 \text{ mV}; \quad J_{sc} = 25.88 \text{ mA/cm}^2; \quad FF = 75.51\%; \quad \eta = 16.5\% \) (Wu et al., 2001). If we compare the results of Table 2 with the results reported by NREL, we can be seen that our values for \( V_{oc} \) and \( J_{sc} \) are near to reported for the record cell. However, the FF is lower than NREL, due to our \( R_s \) is ~4.3 \Omega cm\textsuperscript{2} and it limits principally the FF value.

In Fig. 6 we show the dark \( J−V \) characteristic. The linear part of this dark curve allows us to estimate the reverse

![Fig. 3. 5 × 5 \mu m\textsuperscript{2} AFM image of the CdS film.](image)

![Fig. 4. SEM photos of the surface of CdTe films: (a) morphology of an untreated CdTe film deposited by the CSS method and (b) morphology of the same film after thermal treatment in Ar + HCF\textsubscript{2}Cl atmosphere at a temperature of 400°C for 5 min.](image)

![Fig. 5. \( J−V \) curve for a 0.21 cm\textsuperscript{2} illuminated CdS/CdTe solar cell.](image)
saturation current density of cell diode $J_0 = 4.8 \times 10^{-11}$ A/cm$^2$ and the ideality diode factor $A = 1.65$. These values show the good diode quality of our cell (Oman et al., 1999). The deviation of linearity for low forward voltage is typical of thin film solar cells and in general is related to shunt effects. However this shunts effects seems to be not important in illuminated conditions due to $R_{sh}$ is high in our case ($>2$ k$\Omega$ cm$^2$). The differences in $\ln(J)$ vs. voltage dark curves at low forward voltages for cell with the same illuminated efficiencies, has been studied in the reference (Dongaonkar et al., 2010).

In a group of five ITO/ZnO/CdS/CdTe/Cu/Mo cells prepared with the process reported in the present work we obtained a good reproducibility.

In the Fig. 7 the behavior of the stability cells is shown. From this figure can be seen that the efficiency of our cells remains unchanged at least after the first month of its manufactured.

5. Conclusions

Our process to fabricated CdS/CdTe thin film solar cells is relatively simple. The films are grown by RF sputtering; except the CdTe film that is deposited by CSS. The CdS film is not intentionally treated. Although receives thermal treatment in oxygen prior to the CdTe deposition process in oxygen. Our deposition process of CdTe film allows us to have better control of the formation of intermixed (CdS$_x$Te$_{1-x}$) near the junction. Our process permits to obtain high efficient solar cells with a CdTe film deposited at low substrate temperature (500 °C). Treatment activation with Cl$_2$ of the cell is done using a gas that is inert and not toxic at room temperature mixed with a simple gas. A 14% in 0.21 cm$^2$ device was achieved.

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