High Efficiency CdTe/CdS Thin Film solar Cells by a Process Suitable for Large Scale Production.

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ABSTRACT: It has been demonstrated that CdTe/CdS thin film solar cells can exhibit an efficiency around 16.5%. However this efficiency has been obtained by adding some Cu at the back contact. Cu behaves as a shallow acceptor in CdTe and then it can increase the hole carrier density in CdTe. On the other hand, Cu is a fast diffusor in CdTe and at a long run it can segregates at the grain boundaries damaging the solar cell. In our process we did not use any copper but we developed a new ohmic contact which is very stable. This consists in a thin layer of 1000-2000 Å of Sb_2Te_3 deposited by sputtering directly on top of the CdTe surface. With this new contact we were able to obtain an efficiency of 14% or more in CdTe/CdS solar cell whose area is 2 cm^2. These cells kept under 20 suns for several days at 100°C not only do not degrade but they improve their efficiency. The process consist in a subsequent deposition of 5 different layers, 4 of which, namely TCO, CdS, Sb_2Te_3 and Mo are deposited by sputtering and CdTe by CSS. The treatment with $CdCl_2$ is done by depositing 1500 Å of $CdCl_2$ on top of CdTe and with an annealing at 400°C in 500 mbar of Ar. After the treatment, Ar is pumped away keeping the substrate at 400°C. In this way, $CdCl_2$ is completely re-evaporated from the CdTe leaving a perfectly cleaned surface. Before the deposition of the contact, no etching is done on the CdTe surface. Due to the fact that no acids nor other kind of liquids such as Br-methanol are used in this process and considering that both sputtering and CSS are very scalable techniques, this process results to be very suitable for large scale production.
Keywords: CdTe; CdS; PV Materials; Thin Film.

1 INTRODUCTION

CdTe/CdS thin film solar cells have a good possibility to be produced on large scale. A record 16.5% conversion efficiency has been recently reported from the NREL (National Renewable energy Laboratory) group (1). However, this high efficiency has been obtained by using a borosilicate glass as a substrate and by making a contact to CdTe with a paste containing copper. Borosilicate glass has to be avoided since it is too expensive while copper has the drawback to be a fast diffusor in CdTe and therefore it makes the cell to degrade in the long run.
We developed a process, which uses cheap soda-lime glass as a substrate with a stable contact that does not contain any copper. No liquids or acids are used. This process is capable to produce solar cells with efficiency of 14% or more.

2 BRIEF DESCRIPTION OF THE PROCESS

The CdTe/CdS solar cells fabricated in our laboratory are made up of 5 layers (Fig. 1).

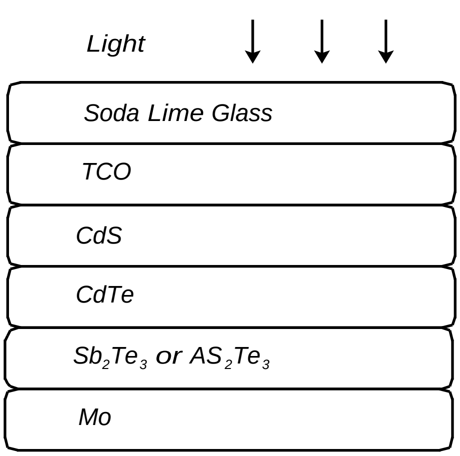

Figure 1: CdTe/CdS thin film solar cell structure

First, the soda-lime glass is covered by a 500 nm thick layer of a transparent conducting oxide (TCO) which in our case is fluorine doped In_2O_3. On top of the TCO a 100 nm thick layer of CdS is deposited by sputtering or close-spaced-sublimation. Before the deposition of CdTe, CdS is annealed for 15 min in an atmosphere containing O_2. CdTe whose thickness is around 8 µm is deposited by closed-space-sublimation. Before making the top contact, CdTe is treated with $CdCl_2$ at 400°C in a chamber containing 500 mbar of Ar and then annealed in vacuum for a few minutes in order for the residuum $CdCl_2$ to be completely removed by evaporation. The top contact is made by depositing in sequence 150 nm of Sb_2Te_3 or As_2Te_3 and 150 nm of Mo by sputtering. No acids are used during the overall process. The sequence of the process is shown in fig. 2.

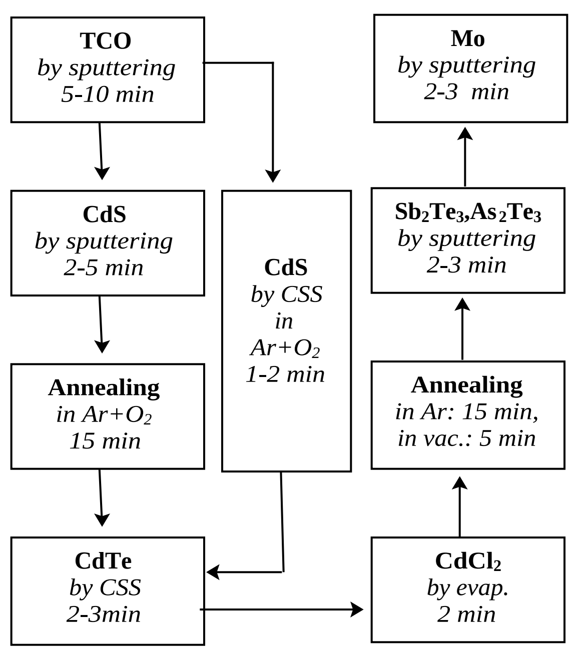

Figure 2: Block sequence of the CdTe/CdS thin film solar cell fabrication process

3 DETAILED DESCRIPTION OF THE PROCESS

3.1 The transparent conducting oxide (TCO)

The most common TCO is In_2O_3 containing 10% of Sn (ITO). This material has a very low resistivity on the order of 3 x 10^{-4} Ωcm and high transparency (> 85 %) in the visible spectrum. However, this material is made by sputtering and the ITO target after several runs forms some noodles which contain an In excess and a discharge between noodles can happen during sputtering which can damage the film. Another material, which is commonly used, is fluorine doped SnO_2 which however exhibits a higher resistivity close to 10^{-3} Ω cm and as a consequence a 1 μm thick layer is needed in order for the sheet resistance to be around 10 $\Omega/_{square}$. A high TCO thickness decreases the transparency and then the photocurrent of the solar cell. Finally a novel material, namely Cd_2SnO_4, has been developed by the NREL group (2). Also this material has some drawbacks since the target is made up of a mixture of CdO and SnO_2 and, being CdO highly hygroscopic, the target is not much stable. A new TCO has been developed in our laboratory which is highly transparent and exhibits a resistivity of 2.5 x 10^{-4} Ω cm. This TCO is simply In_2O_3 which is doped with fluorine during the growth. The In_2O_3 target differently from ITO does not form any noodle. A very low resistivity is obtained by introducing in the sputtering chamber a small amount of fluorine in form of CHF_3 and a small amount of H_2 in form of a mixture of $Ar+H_2$ in which H_2 is 20% in respect to Ar. A typical example is a 500 nm film of In_2O_3 deposited with a deposition rate higher then 10 Å/sec at a substrate temperature of 500 °C, with an Ar flux of 200 sccm, a CHF_3 flux of 5 sccm and a $Ar+H_2$ flux of 20 sccm. This film exhibits a sheet resistance of 5 $\Omega/_{square}$ and a transparency higher than 85% in the wavelength range of 400-800 nm. Another characteristic of this film is its good stability and the ability to stop Na diffusion from the soda-lime glass. This has been demonstrated by making CdTe/CdS solar cells on top of this type of TCO which have shown to be very stable even if heated up to 180°C when illuminated by "ten suns" for several hours.

3.2 The CdS layer

CdS is prepared by sputtering or Close-Spaced-Sublimation (CSS) This last technique allows the preparation of thin films at a substrate temperature much higher than that used in simple vacuum evaporation or sputtering. This because substrate and evaporation source are put very close one to each other at a distance of 2-6 mm and the deposition is done in presence of an inert gas such as Ar, He or N_2 at a pressure of 10^{-1} – 100 mbar (fig. 3). The higher substrate temperature allows the growth of a better crystalline quality material. An important characteristic of the close-spaced-sublimation is a very high growth rate up to 10 μm/min, which is suitable for large-scale production.
However, this technique has a drawback: when small pieces containing dust are used as sublimation source, due to a different thermal contact, some micro-particles can be overheated and then spit on to the substrate together with the vapor. In order to avoid this drawback, complicated metallic masks are used in some cases. In our case we used a new sublimation source

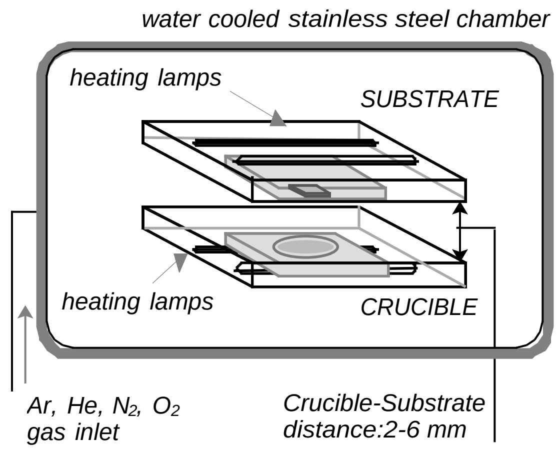

Figure 3: Schematic diagram of the Close-Spaced-Sublimation (CSS) system

which consists in a compact block obtained by melting and solidifying the material in an oven able to substain a temperature higher than the melting point of the material. The procedure to prepare the CdS compact block is as follows: pieces of CdS are put in a graphite container of the desired volume; the pieces are completely covered by boron oxide (B_2O_3) which is a low melting point material (≈ 450°C) and exhibits a very low vapor pressure when melted. In this way CdS covered by B_2O_3, if it is put into an oven containing an inert gas at pressure higher than 50 atm, does not evaporate even at a temperature higher than its melting point. Since CdS melts at a temperature of 1750°C, the oven is heated up to a temperature of 1800°C or more and then cooled down to room temperature. In this way, a unique compact block of CdS is obtained which has demonstrated to be particularly suitable to be used as a sublimation source in a closed-space-sublimation system. CdS films prepared with this type of source resulted to be very smooth and completely free of dust. The CdS films used to prepare the CdTe/CdS solar cells are typically 100 nm thick. The substrate temperature is kept at 300°C when CdS is prepared by sputtering and at 500°C when it is prepared by close-spaced-sublimation. The sputtered CdS layer needs an annealing at 500°C in an atmosphere containing O2 in order for the CdS/CdTe solar cell to exhibit a high efficiency. In the case CdS is prepared by closed-space-sublimation, O_2 is introduced in the sublimation chamber during the deposition. The role of O_2 is not known but presumably it could be useful to passivate the CdS grain boundaries.

3.3 The CdTe layer

CdTe films are deposited on top of CdS by close-spaced-sublimation at a substrate temperature of 500°C. The CdTe source is a compact block obtained by melting and solidifying pieces of CdTe in an oven under high pressure as described previously. Since CdTe melts at 1120°C, the oven needs to be heated up to 1200°C in order to have a complete melting of the CdTe pieces. Deposition rates during the CdTe growth are typically 4 μm/min. In this way 8μm of CdTe are deposited in 2 min.

3.4 Treatment of CdTe with $CdCl_2$

An important step in the preparation of high efficiency CdTe/CdS solar cells is the treatment of CdTe with $CdCl_2$. Most research groups use to make this step by depositing on top of CdTe a layer of $CdCl_2$ by simple evaporation or by dipping CdTe in a methanol solution containing $CdCl_2$ and then anneal the material in air at 400°C for 15-20 min. It is generally believed that the $CdCl_2$ treatment improves the crystalline quality of CdTe by increasing the size of small grains and by removing several defects in the material.

After $CdCl_2$ treatment, CdTe is commonly etched in a solution of Br-methanol or in a mixture of nitric and phosphoric acid. This etching is necessary in the case the $CdCl_2$ treatment is done in air since CdO or $CdTeO_3$ are generally formed on the CdTe surface. CdO and/or $CdTeO_3$ have to be removed in order to make a good back contact onto CdTe. Besides it is believed that the etching, producing a Te-rich surface, facilitates the formation of an ohmic contact when a metal is deposited on top of CdTe (3).

We developed a new method to make the $CdCl_2$ treatment, which avoids the etching and contemporarily allows to make a good contact. The procedure is as follows:

100-150 nm of $CdCl_2$ are deposited by evaporation on top of CdTe with the substrate kept at room temperature. An annealing of 15-20 min is done at 400°C in a vacuum chamber in which 500 mbar of Ar are introduced. After the annealing the chamber is evacuated keeping the substrate at 400°C for 5 min. since $CdCl_2$ has a high vapor pressure at 400°C, any $CdCl_2$ residuum re-evaporates from the CdTe surface.

CdO or $CdTeO_3$ are not formed since the annealing is done in an inert atmosphere which does not contain O_2. We found that a Te-rich surface is not needed to make a not-rectifying contact if the contact is made by depositing on top of CdTe a thin layer of a highly conducting p-type semiconductors such as Sb_2Te_3 or As_2Te_3.

3.5 Back contact

A good not rectifying contact is obtained on a clean CdTe surface if 150 nm of Sb_2Te_3 or As_2Te_3 are deposited by sputtering at a substrate temperature respectively of 300°C and 250°C. Sb_2Te_3 grows naturally p-type with a resistivity of 10^{-4} Ωcm while As_2Te_3 grows p-type with a resistivity of 10^{-3} Ωcm. The contact procedure is completed by covering the low resistivity p-type semiconductor with 150 nm of Mo.

4 CdTe/CdS SOLAR CELLS CHARACTERISTICS

By following the procedure described before several solar cells have been prepared by using as a substrate a 1 inch square low-cost soda-lime glass.

A typical area of these cells is 1-2 cm^2. The finished cells are generally put under 10-20 suns for several hours at a temperature of 180°C in the open-circuit-voltage conditions. No degradation has been notified but rather a 20% or more increase in the efficiency has been found.

The efficiency of these cells is in the range of 12% - 14% with open-circuit-voltages (V_{oc}) larger than 800 mV, short-circuit-currents (J_{sc}) of 22-25 mA/cm^2 and fill-factors (ff) ranging from 0.6 to 0.66. As an example a cell exhibiting a 14% efficiency has been prepared in the following way: a soda-lime glass has been covered by 500 nm of In_2O_3:F (fluorine-doped) deposited at 500°C substrate temperature as it has been described in section 3.1; 100 nm of CdS have been deposited by sputtering at 300°C substrate temperature and annealed for 15 min at 500°C in 500 mbar of Ar containing 20% of O_2; 8μm of CdTe have been deposited on top of CdS by CSS at a substrate temperature of 500°C as described in section 3.3; a treatment with 150 nm of $CdCl_2$ has been done in an Ar atmosphere as described in section 3.4; without any etching, a contact, depositing by sputtering in sequence 150 nm of Sb_2Te_3 and 150 nm of Mo has been made.

After one hour under 10 suns at a temperature of 180°C in open-circuit conditions the solar cell exhibited the following parameters:

$V_{oc} \approx 852$ mv	$J_{sc} \approx 25$ mA/cm^2
ff ≈ 0.66	efficiency ≈ 14%

The techniques used in this process such as sputtering and close-spaced-sublimation are both fast, reproducible and easily scalable. At least three innovation have been introduced with this process:

- the TCO, which is fluorine-doped In_2O_3;
- a compact CdTe and CdS source for the close-spaced-sublimation;
- a $CdCl_2$ treatment and back contact which does not make use of acids or liquids, rendering the process even faster and avoiding the danger and the law restrictions due to the use of acid tanks.

We can conclude that the process described above can be used for the fabrication in-line of CdTe/CdS photovoltaic modules at a high production rate.

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