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Last Progress in CdTe/CdS Thin Film Solar Cell Fabrication Process

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Abstract

In the past, we described a dry process for the fabrication of CdTe/CdS thin film solar cells. In this process, most of the layers composing the cell, namely ITO, ZnO, CdS and back contact are deposited by sputtering and CdTe is deposited by close-spaced sublimation. The treatment of CdTe is done at 400°C, for 10-20 minutes, without CdCl₂, by using a Freon gas, dichlorofluoromethane, as a Cl supplier. Back contact is made by depositing onto a not-etched CdTe film surface a buffer layer of As₂Te₃, followed by a thin layer of Cu and Mo. Recently, we modified the Cl-treatment and we improved the quality of the back contact. Since dichlorofluoromethane is an ozone depleting agent and its use is now forbidden, we replaced it with a gas, like Ar, containing 4%HCl and mixing it with a Fluorine-containing gas, such as CHF₃. Both these gases are not depleting agents and they aren't forbidden. By adjusting the relative amounts of the chemical species into this mixture, we got results which are very similar to those obtained with dichlorofluoromethane. Concerning the back contact, we discovered that, by using as a buffer layer As₂Te₃, or Bi₂Te₃ and by making an annealing in air at 200°C for 15-30 minutes, a stable and ohmic contact, without any rollover in the solar cell I-V characteristic, is obtained.

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1. Introduction

CdTe/CdS and Cu(In,Ga)Se₂/CdS thin film solar cells have shown on laboratory scale efficiency values higher than 17% [1] and 20% [2] respectively. Both kinds of solar cells are now considered as good candidates for large scale module production.

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However the CdTe fabrication technology seems to be more suitable for large scale production, since it is based on the use of thin film deposition techniques such as sputtering and “close-spaced sublimation”, which are fast, reproducible and able of producing homogeneous thin films over areas as large as 1 m^2 , or more. An important step in the CdTe-based solar cell fabrication process is the treatment of the CdTe film in presence of Cl, at about 400°C . If this treatment is not performed, the solar cell efficiency is generally lower than 5%. It is generally accepted by the scientific community that the Cl-treatment increases the grain size of CdTe, passivates the grain boundaries and promotes a mixing between CdS and CdTe at their interface.

At the beginning, this treatment was done by dipping the CdTe film in a saturated CdCl_2 -methanol solution, in order to deposit a CdCl_2 film on top of CdTe. After the CdCl_2 deposition, the bi-layer CdTe/ CdCl_2 is put in an oven, where it is annealed at about 400°C for 20 minutes. In order to remove the CdCl_2 residuals from the CdTe surface, it is needed to make an etching in a Br-methanol solution, or in a mixture of nitric and phosphoric acids.

Alternatively the CdCl_2 film can be deposited by vacuum evaporation [3].

Another method is that of exposing the heated CdTe surface to a CdCl_2 vapour in a vacuum chamber [4].

In order to avoid the use of CdCl_2 , which is highly toxic, we proposed another way to treat CdTe films in presence of Cl [5]. This novel method consists in treating the CdTe in an atmosphere composed of 20-40 mbar of a non-toxic gas containing Cl and 300-500 mbar of Ar. As a gas containing Cl we chose one of the Freon family, namely CHF_2Cl (chlorodifluoromethane), called also R-22. As it is reported in ref. [5], this treatment gives the same results as the one made with CdCl_2 . Solar cells with an efficiency higher than 15% were obtained by using this treatment. However R-22 is an ozone-depleting agent and it is now banned.

In this paper we report the use of another gas containing Cl, that is effective in treating CdTe and it is not an ozone-depleting agent.

Another important step in the fabrication of CdTe/CdS solar cells is the preparation of a stable and not-rectifying back contact.

In this case we also proposed a novel approach, which consists in the deposition of a thin layer of As_2Te_3 on top of a not-etched CdTe surface, followed by the deposition of a few nanometers of Cu.

Since Cu is deposited at a substrate temperature of 250°C , a solid-state reaction with As_2Te_3 happens during the Cu deposition and a Cu_xTe layer is formed at the CdTe surface. When the coefficient x is lower than 1.4, the Cu_xTe is considered a good and stable ohmic contact for CdTe [6].

In this paper we report a more detailed study of the back contact in which, besides As_2Te_3 , also Bi_2Te_3 and Sb_2Te_3 have been used as buffer layers and a further improvement of the back contact was obtained by performing an annealing of the Cu- As_2Te_3 or the Cu- Bi_2Te_3 back contacts, at 200°C in air.

An explanation of this improved contact will be given in the text.

2. Solar cell preparation

The structure of the CdTe/CdS thin film solar cell prepared in our laboratory is shown in Fig. 1. We start with a 1 inch square soda lime glass, which is covered in sequence by a 300 nm thick ITO and a 100 nm thick ZnO films, both deposited by sputtering at a substrate temperature of 400°C . While ITO is prepared by D.C. magnetron sputtering, ZnO is deposited by R.F. reactive magnetron sputtering, in an atmosphere of Ar containing about 20% O_2 , by using a pure Zn target.

On top of ZnO a 100 nm thick CdS film is deposited by R.F. magnetron sputtering, at a substrate temperature of 250°C and in an atmosphere of Ar containing about 4-5% of a F-based Freon gas, such as CHF_3 (trifluoromethane), called also R-23.

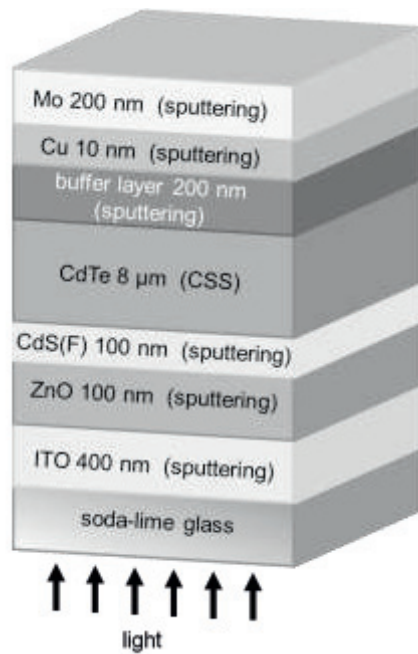


Figure 1. Structure of a CdS/CdTe solar cell.

As it is reported in ref. [7], the presence of F in the sputtering discharge improves the quality of CdS film, since, being F⁻ ions electronegative, they bombard the CdS surface during the growth, eliminating any excess of Cd or S and making the material more stoichiometric and much more stable during the Cl-treatment of CdTe. This is demonstrated by the fact that, if CdS is prepared without any F in the sputtering discharge, some bubbles and a lift off of CdTe are observed after the Cl-treatment.

CdTe is deposited by close-spaced sublimation (CSS). Our CSS system is composed of two graphite blocks, put at a distance of about 1 cm one from each other (fig. 2).

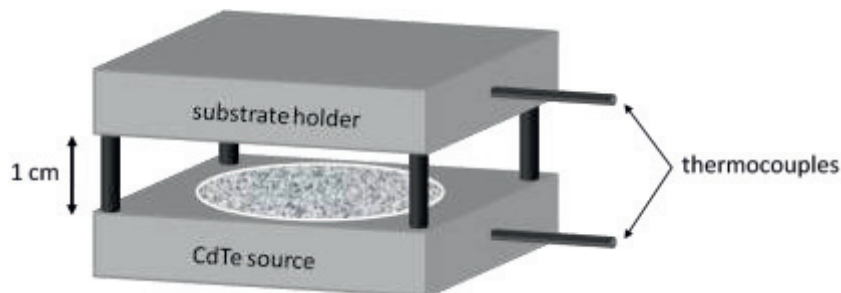


Figure 2. CSS system configuration.

The bottom block contains the CdTe source, since it is covered by a thick layer (500 μm) of CdTe, previously deposited on top of it. The upper block contains the glass substrate.

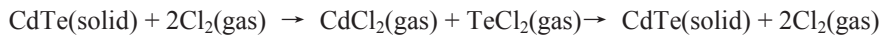
Two thermocouples are imbedded into the graphite blocks in order to control both CdTe and substrate temperatures.

The deposition of the CdTe film is done in an atmosphere of Ar whose pressure is typically fixed at 1 mbar. While the substrate temperature is generally fixed at 500°C, the source temperature is maintained at 600-620°C. A few minutes are enough to obtain a CdTe thickness of 8 µm.

3. Treatment of CdTe in presence of Cl

As reported in ref. [5], in order to make a dry process and to avoid the use of CdCl₂, which is a poisoning material, we made the CdTe treatment by putting the sample in an atmosphere made up of 400-500 mbar of Ar mixed with 20-40 mbar of a gas of the Freon family, containing Cl, namely CHF₂Cl (chlorodifluoromethane) or R-22. This gas is not toxic and it was used for long time for the refrigeration even though it is now banned, since it is an ozone depleting agent. The experimental results obtained with this treatment demonstrated to be very good and solar cells approaching 16% were obtained.

It has been supposed that the following reaction happens during the treatment:



In this case Cl₂ is supplied by CHF₂Cl which is decomposed at 400°C, the temperature at which the treatment is done. Following the reaction, small grains especially in the grain boundaries go into vapour phase, since they are not strongly bonded and they react with Cl₂ giving place to two other gases, namely CdCl₂ and TeCl₂. After that, Cd and Te recombine on the CdTe surface, enlarging further the larger grains (see Fig. 3a and 3b). In this way, the defective zones in CdTe are removed, giving finally a better crystallized material.

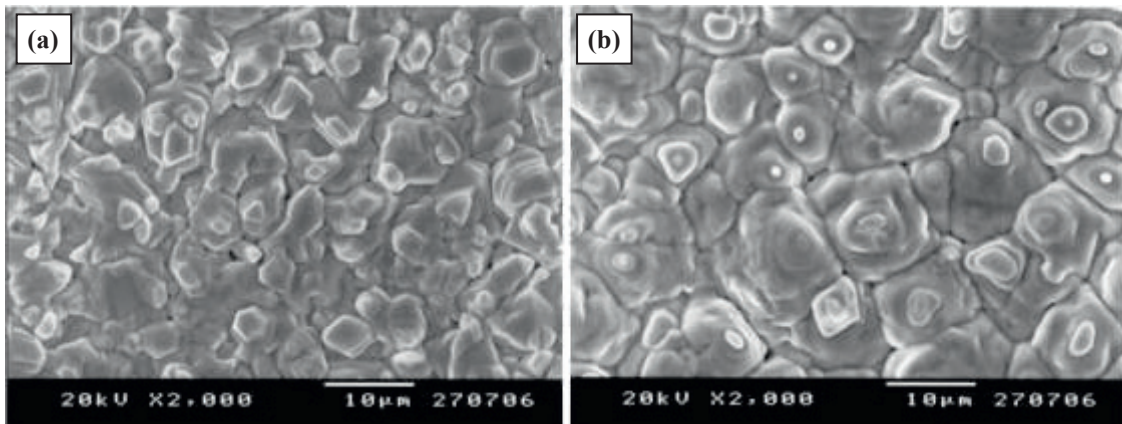


Figure 3. SEM image of CdTe film morphology **a)** before and **b)** after Cl-treatment.

However, since R-22 is banned and it can't be used anymore, one has to find another gas, which is permitted and which can play the same role as R-22. Mc Candless and al. [8] have tried in the past to use HCl as a treating gas, but their results were not conclusive and, after this work, nobody has reported the use of HCl, probably because this gas is highly aggressive.

We found out that HCl can work well if it is used mixed with Ar in a low percentage and mixed further with a gas containing fluorine or O₂, such as air. We used, as a source of Cl₂, Ar containing 4% HCl, which is commercially available and, as a gas containing fluorine, CHF₃ (trifluoromethane) also called R-23. Another gas containing fluorine, which is cheaper than CHF₃, namely C₂H₂F₄, also called R134a can be used at place of CHF₃. A mixture of 20 mbar of Ar containing 4% HCl and 300-400 mbar of CHF₃ has shown to be effective in treating CdTe. The results were very similar to those obtained with R-22 + Ar. Also in this case solar cells exhibiting a conversion efficiency close to 16% were obtained. If CHF₃ is substituted with Ar, the treatment is always too aggressive, digging out the grain boundaries. It seems that the presence of fluorine decreases the aggressiveness of HCl.

The same or better happens if air, which contains O₂ is used in place of CHF₃. After treatment, just in order to make a thoroughly dry process, we do not make any etching of the CdTe surface before making the back contact. We only leave the CdTe sample in vacuum for a few minutes, at the same temperature of the treatment, in order to remove any residual of CdCl₂, which could form on the CdTe surface.

4. The back contact

The preparation of an ohmic, non-rectifying back contact on the CdTe/CdS solar cell has resulted to be, so far, a difficult task. A metal with the high work function needed to make a good contact on CdTe does not exist. For this reason, other routes have been followed. The most common way, used by most researchers, consists in etching the CdTe surface in a mixture of HNO₃ and HPO₃, called NP etch, in order to produce a Te-rich surface and to deposit subsequently a few nanometers of Cu. The explanation of how this way of making the contact works has been given by Wu et al. [6]. Following these authors, Cu reacts with the Tellurium surface, forming a Cu_xTe compound. This material seems to make a non-rectifying contact with CdTe. However, the same authors report that, in order for Cu_xTe to be stable and not to free Cu, the stoichiometric coefficient x should be lower or equal to 1.4 and this is not a simple task to fulfill.

In the past we tried to make a Cu-free back contact on a not-etched CdTe surface. By using sputtered Sb₂Te₃ as a buffer layer in the back contact, we were able to obtain solar cells with efficiency close to 16%, with fill factors higher than 70%. However, this way of making the back contact resulted to be not reproducible, since it depended on the way the sputtering target was prepared. More recently, we proposed another method to prepare the back contact. This consists in the use of a 200 nm thick As₂Te₃ layers a buffer, covered by a 10 nm thick Cu film. Both layers were deposited by sputtering. If Cu is deposited on top of As₂Te₃ at 250° C substrate temperature, Cu reacts with As₂Te₃ forming a Cu_xTe with $x \leq 1.4$. This was demonstrated by doing x-ray diffraction (XRD) spectra on a sample of As₂Te₃+Cu deposited on a glass substrate [5].

Despite we were able to obtain high efficiency solar cells with high fill factors, in some cases a roll-over in the J-V characteristic appeared. Very recently we found that, by doing an annealing at 220°C in air for a few minutes, the roll over disappears (see Fig. 4).

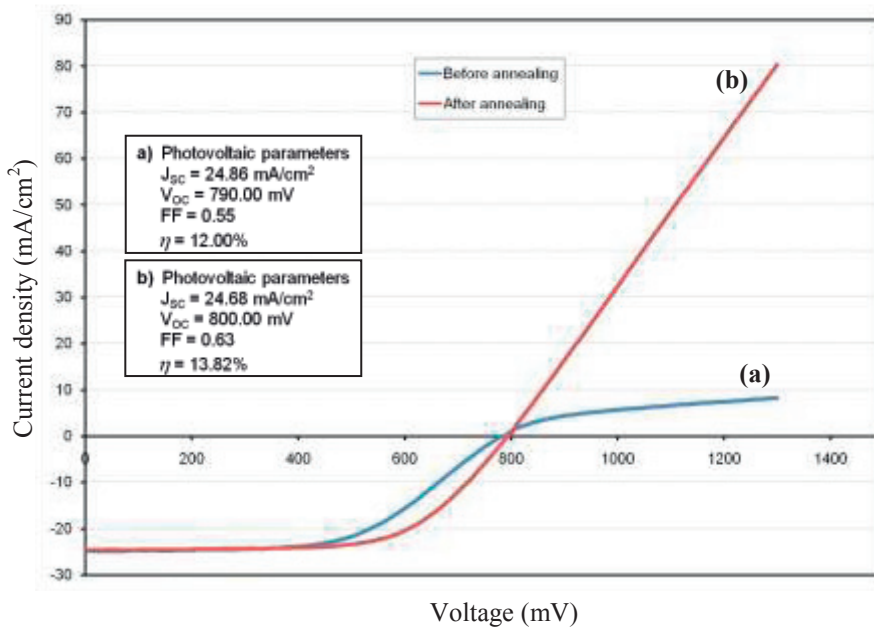


Figure 4. J-V characteristic of a CdTe solar cell **a)** before and **b)** after the annealing in air.

At this point, we tried to understand what was happening by depositing the As_2Te_3/Cu bi-layer directly on a glass substrate and by doing an XRD spectrum before and after the air annealing.

XRD measurements were performed with a Bruker D8 diffractometer (Cu $K\alpha$ radiation) in Debye-Scherrer mode. Samples were aligned in a configuration parallel to the beam and then their positions were modified over the azimuthal angle in order to cross layers in a grazing incidence condition. Diffraction pattern were collected in the X-Y range.

As one can see in the XRD spectra, after annealing new diffraction peaks appear, which were identified as elemental Tellurium (Fig. 5a and 5b).

This was interpreted in the following way: during annealing, Oxygen reacts with As_2Te_3 , setting Te free.

Concerning the back contact, Te, which is set free during the annealing in air, reacts now with the Cu, which was not completely bounded with Te during deposition, forming a complete layer of Cu_xTe . This process has been repeated by using, instead of As_2Te_3 , two other compounds of the V-VI group of elements, namely Sb_2Te_3 and Bi_2Te_3 .

While the process works well by using Bi_2Te_3 , it doesn't work with Sb_2Te_3 .

Again we performed XRD spectra on both Bi_2Te_3/Cu and Sb_2Te_3/Cu bi-layers, deposited directly on glass. We found out that free Tellurium appears in the air-annealed Bi_2Te_3/Cu sample, but free Te is absent in the air-annealed Sb_2Te_3/Cu sample.

We interpreted this fact by considering that O_2 doesn't react with Sb_2Te_3 , since this material is much more stable, but it reacts with As_2Te_3 and Bi_2Te_3 , since both these materials are less stable than Sb_2Te_3 .

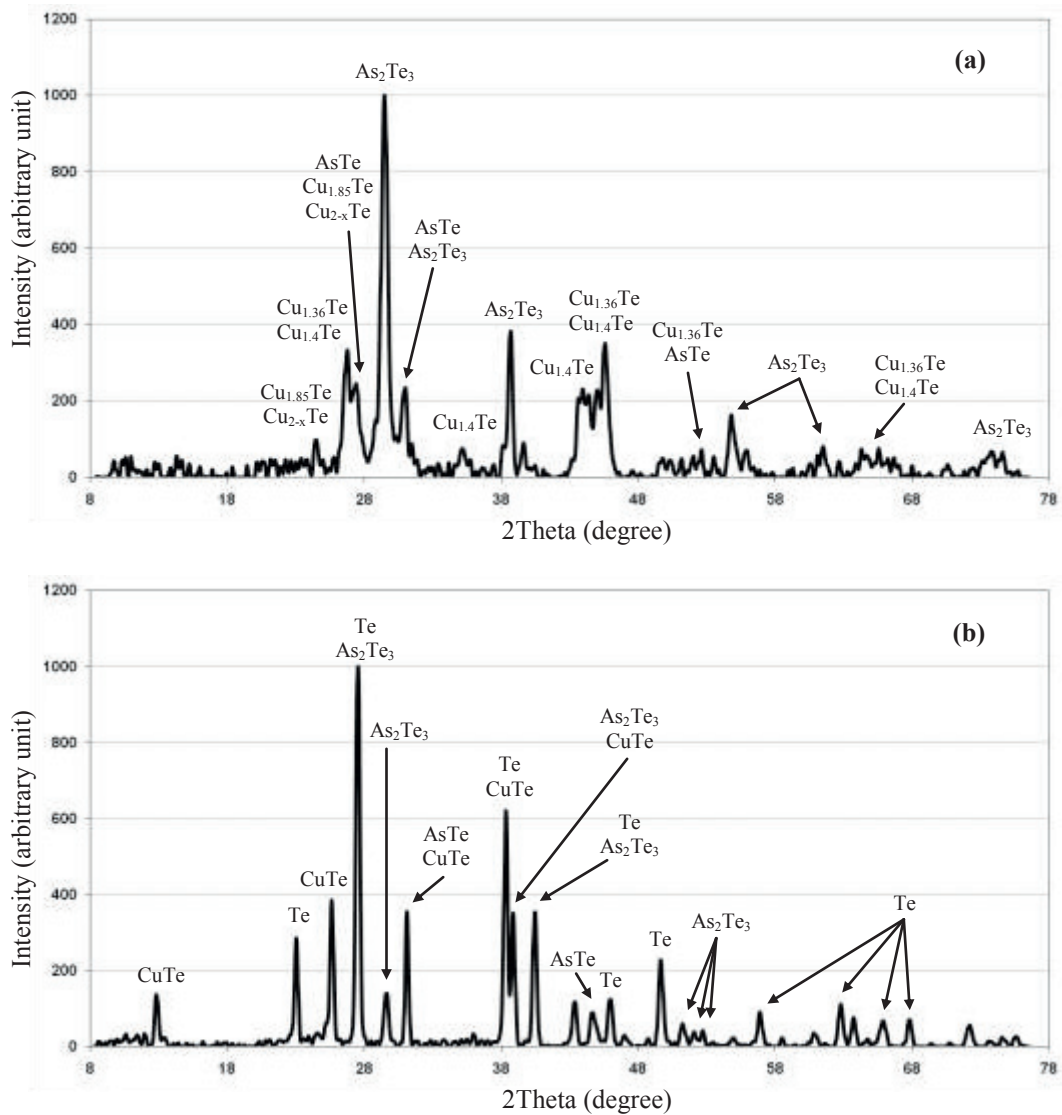


Figure 5. XRD spectrum of $\text{As}_2\text{Te}_3/\text{Cu}$ structure deposited on glass **a)** before and **b)** after annealing in air.

Conclusion

Two improvements in the fabrication process of CdTe/CdS thin film solar cells are reported in this article. The first one concerns the CdTe treatment in presence of Cl . Here we demonstrate that Ar containing 4% HCl , which is commercially available, mixed with CHF_3 , or air, can be effectively used to treat the CdTe .

The obtained results are comparable or even better than those obtained by using CdCl_2 . This process is dry and doesn't use any CdCl_2 , then it is more compatible with an industrial process. The second one

concerns the preparation of the back contact. In this case, we report that a buffer layer made of $\text{As}_2\text{Te}_3/\text{Cu}$ or $\text{Bi}_2\text{Te}_3/\text{Cu}$ deposited on top of CdTe and followed by an annealing in air at 220°C for a few minutes can produce a stable and non-rectifying contact on CdTe.

The back contact process is completely dry and the layer deposition is done by sputtering. No etching is done on the CdTe surface before the back contact.

Also this process can be easily integrated in a large-scale industrial production.

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