

The thin film solar cell based on CdTe: toward the industrial production.

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Abstract: The recent progress on developing CdTe/CdS thin film solar cells is described with emphasis to a fabrication process aimed at a large scale production. A completely dry process in which neither CdCl_2 nor etching acids, developed in our laboratory, is reported. Small area 1cm^2 stable solar cells with an efficiency of 15.8% can be obtained with this process. Neither copper nor any other element of the first group of the periodic table is used in the back contact in order to avoid the degradation, which is known to be caused by the diffusion of these elements through the grain boundaries.

1. Introduction

Single crystal solar cells, such as Si and/or III-V compound solar cells have showed, in the laboratory scale, efficiencies close to their respective theoretical limits. Si modules with an efficiency around 15% can be easily bought at an average cost of 5€/W, that is quite far from being competitive with the cost of electrical energy obtained from fossil fuels.

A further cut of Si modules cost could be obtained both by reducing the thickness and enlarging the area of Si wafers and by increasing the production by automating the fabrication process. However, it will be quite difficult to decrease the price under 2€/W. The only way to reach a module cost competitive to that of electrical energy obtained from fossil fuels is that of using modules based on thin film solar cells. There are at least three reasons why thin film modules could be cost competitive:

- a) The amount of source material is at least 100 times less than that used for single crystal modules and is a negligible part of the overall cost.
- b) The fabrication process can be completely automated and a production yield of one module per minute can be obtained.
- c) Low cost soda lime glass can be used as a substrate

Production cost of less than 0.5\$/W have been foreseen by K.Zweibel [1] for thin film modules, a cost that is close to be competitive with the electrical energy obtained from fossil fuels. So far, three kinds of thin film solar cells are considered for production:

- 1) Amorphous silicon : α -Si maximum efficiency of ~13% [2]
- 2) $\text{CuInGaSe}_2/\text{CdS}$: maximum efficiency of 19.2% [3]
- 3) CdTe/CdS : maximum efficiency of 16.5% [4]

Among these, the CdTe/CdS thin film solar cell is the most favoured since, due to the simple techniques used for thin film deposition, it can be more easily brought from laboratory scale to industrial scale.

Nowadays there are two companies producing CdTe/CdS modules namely First Solar in the United States and Antec Solar in Germany.

2. The CdTe/CdS thin film solar cells

The CdTe/CdS thin film solar cell is composed of four layers, namely the TCO (Transparent Conducting Oxide) which acts as the front contact, CdS which is the n-type partner, CdTe which is the p-type partner, and the back contact (see Fig.1). Both TCO and back contact are constituted of two sub-layers. As a substrate, a soda lime glass is normally used.

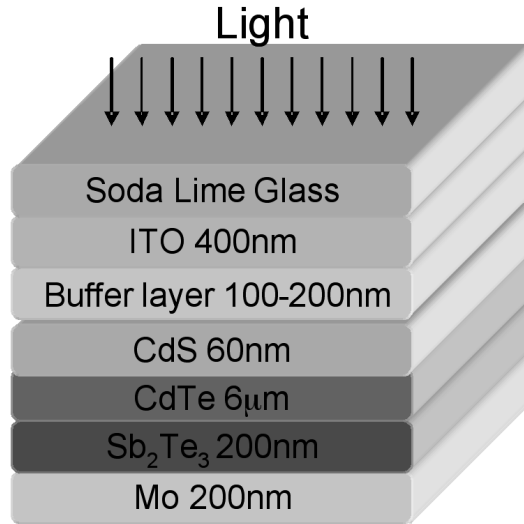


Figure 1: Structure of the CdTe/CdS thin film solar cell

3. The TCO layer

The characteristics which a TCO layer must exhibit are:

- 1) A low sheet resistance less than 10 Ohm-square in order for it not to add a series resistance to the solar cell
- 2) A high transparency more than 90% in the wavelength region of interest that is between 400nm and 800nm for CdTe/CdS solar cells.

Indium tin oxide can fulfil these requirements. However, due to the high temperature at which CdTe is deposited and/or treated in presence of Cl, some In can diffuse from the ITO into the subsequent deposited layers. In order to avoid the In diffusion, a buffer layer such as SnO₂ or ZnO is interposed between ITO and CdS.

A buffer layer thickness of 100-200nm can be sufficient to hinder the In-diffusion.

We demonstrated, by SIMS depth profile measurements, that the In concentration in CdTe decreases from $\sim 10^{17} \text{ cm}^{-3}$ to $5 \cdot 10^{15} \text{ cm}^{-3}$ when the buffer layer is introduced between ITO and CdS/CdTe. The buffer layer has another role: due to its relatively high resistivity, in the order of 10^2 - $10^3 \text{ } \Omega\text{cm}$, it can reduce the shunt that could form between CdS and ITO since CdS has to be very thin (~ 60 - 80nm). Having in mind an industrial production, both ITO and buffer layer are deposited by DC sputtering. ITO is deposited in an atmosphere of Ar+1% of O₂ while SnO₂ or ZnO are deposited by using metal targets in an atmosphere of Ar+20%O₂.

4. The CdS Layer

CdS films can be prepared by several methods. Among these, Chemical Bath Deposition (CBD) and Close-Spaced Sublimation (CSS) demonstrated to be suitable to prepare high efficiency cells. However, for an industrial production, sputtering is considered the most suitable technique. Simple radio frequency sputtering does not produce CdS films that give high efficiency cells. However, high quality CdS films can be obtained by sputtering if some F is introduced in the

sputtering chamber. We prepared F-doped CdS films by introducing in the sputtering chamber Ar containing 3% of trifluoromethane (CHF_3). This gas is decomposed in the sputtering discharge and fluorine, being negative is directed to the substrate. We expected that fluorine, being a donor for CdS, decreased the film resistivity, but this did not happen. On the other hand, CdS films prepared in an atmosphere of $\text{Ar}+\text{CHF}_3$ exhibit a forbidden gap larger than that of CdS films prepared in an atmosphere of simple Ar (see Fig.2).

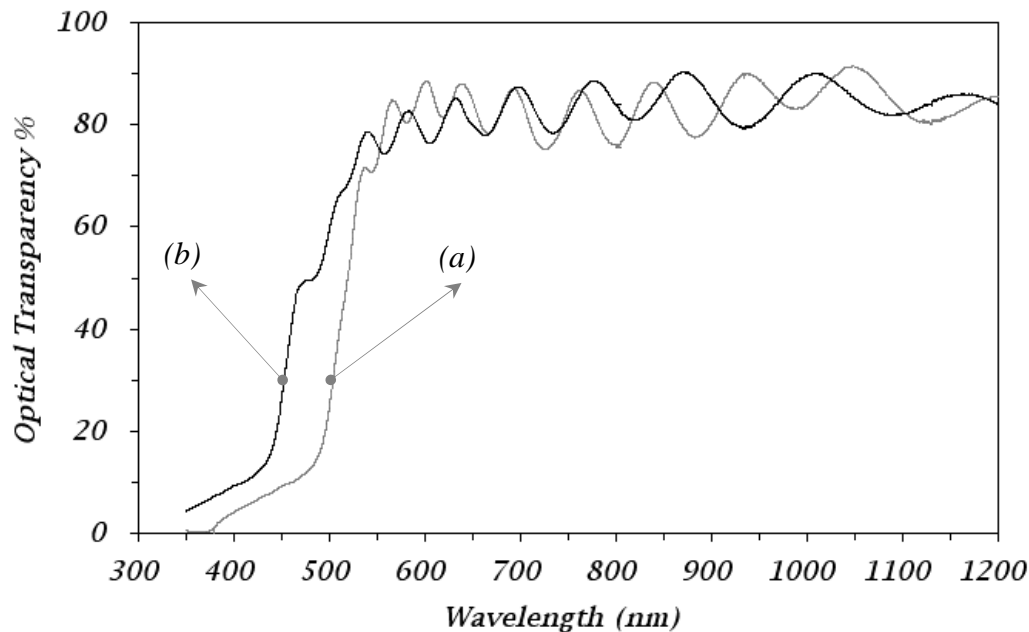


Fig 2: Transparency spectrum of the CdS film prepared by sputtering in: (a) only Ar, (b) in $\text{Ar}+\text{CHF}_3$

They exhibit a stronger cathodoluminescence, a stronger photoconductivity and, what is more important, they give higher efficiency solar cells. Probably, the effect of fluorine is that, since it bombards the CdS film during the growth, it eliminates any excess of Cd and S and produces a more stoichiometric film. Besides, some CdF_2 could form during the growth that can passivate the grain boundaries. We observed that this type of CdS is harder to mix with CdTe when the CdS/CdTe structure is treated at 400°C in presence of chlorine. This argument will be afforded more in details below.

5. The CdTe Layer

CdTe films can be prepared by several methods such as simple evaporation, electrodeposition, sputtering and CSS. The choice of the right method has to be made by making the following considerations:

- a) For industrial applications the deposition rate should be very high on the order of a few $\mu\text{m}/\text{min}$ since a minimum thickness of $3\text{-}4\mu\text{m}$ is needed in order to avoid shunts through the grain boundaries. In this case electrodeposition and sputtering are excluded.
- b) The crystalline quality of the film, namely the grain size, should be quite high. This can be obtained only if high substrate temperature is used. The simple evaporation in high vacuum limits the substrate temperature to $300\text{-}350^\circ\text{C}$, since at higher temperatures CdTe tends to re-evaporate. The grain size of evaporated CdTe films is always less than $1\mu\text{m}$ and it is quite difficult to obtain CdTe/CdS thin film solar cells with efficiency higher than 12% by depositing CdTe by simple evaporation.

The only method that is able to grow CdTe at high substrate temperature (up to 650°C) and that gives CdTe films with a grain size much larger than 1µm is the close-spaced sublimation (CSS) Fig.3. Efficiencies up to 16.5% [4] can be obtained if CdTe is deposited by CSS.

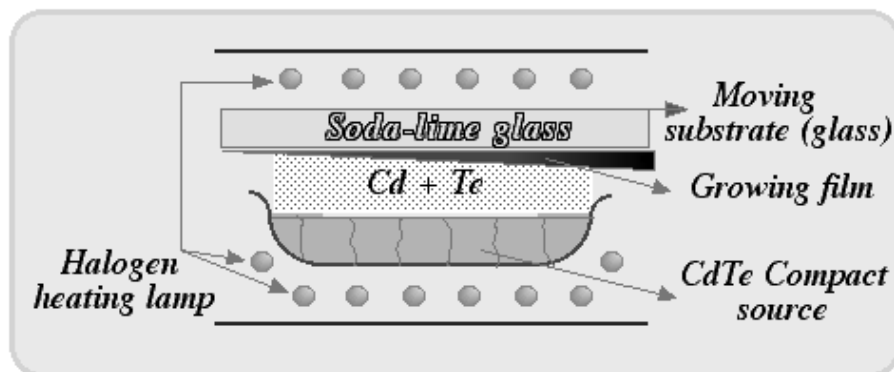


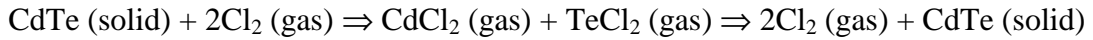
Fig 3: CSS scheme for CdTe deposition

A peculiar characteristic of CSS is that it permits to deposit films at substrate temperatures much larger than that used with other techniques giving the possibility to get more crystallised and better quality thin films. The CSS is made up of a crucible containing the material to be evaporated and a substrate that is put very close to the crucible (2-8 mm). The evaporation is done in presence of an inert or reactive gas whose pressure can be varied between 1 and 100mbar. Since the crucible temperature is kept always higher than that of the substrate, material is transferred from the crucible to the substrate by sublimation. The presence of a gas inside the CSS chamber can help the deposited material not to re-evaporate even at temperatures at which the material evaporates when it is in a high vacuum chamber. In our case the CSS is made up of two graphite blocks that act respectively as crucible and substrate holder and they are put one over each other at a distance of 4mm. The graphite blocks are heated up by lamps that are kept close to them. The temperature of both crucible and substrate is controlled by thermocouples immersed in the graphite blocks. As a gas inside the chamber, we used either Ar or O₂, or Ar mixed with O₂. Depending on substrate temperature a CdTe grain size ranging from 1 to 10 µm can be obtained. When O₂ is put in the CSS chamber, the grain size is always smaller, but we found out that CdTe(O)/CdS solar cells exhibit generally a larger V_{OC} and fill factor. We explained this fact considering that CdTe, growing in presence of O₂, tends to have a larger number of Cd-vacancies, since Cd reacts more than Te with O₂, and some Cd is lost in form of CdO. More Cd-vacancies means more p-type carriers.

6. CdTe-treatment in presence of Cl₂

An important step in the fabrication of CdTe/CdS thin film solar cells is the CdTe treatment in presence of Cl₂. This is generally made by covering the CdTe surface with a layer of CdCl₂ that can be deposited both by dipping the CdTe film in a solution containing CdCl₂ or by evaporating 100-200nm of CdCl₂ on the CdTe surface. After the deposition of CdCl₂, the CdTe film is put in an oven and it is treated for 20 minutes at 400°C. At this temperature CdCl₂ is decomposed and reacts with CdTe bringing CdTe small grains in the vapour phase. In this way, CdTe is reordered and most defects are removed. If this treatment is not done, the efficiency of CdTe/CdS solar cells is never higher than 5%. In view of an industrial production, we invented a completely new way of treating CdTe in presence of Cl₂ that avoids any use of CdCl₂. We treat CdTe in presence of a gas containing Cl₂ mixed with Ar. This gas could be anyone of the Freon family but we chose the one that contains less chlorine such as CHF₂Cl (difluorochloromethane) since it is the less dangerous for the ozone belt. This gas is inert and not toxic at room temperature and it is contained in low-pressure cylinders; therefore it can be handled very easily. A mixture of ~100mbar of Ar and

20mbar of CHF_2Cl at 400°C is sufficient to give the same effects as the treatment with the CdCl_2 . Since at 400°C CHF_2Cl is decomposed and CdTe starts to decompose, we suppose that the following reaction happens:



In this way, the small CdTe grains go into vapour phase and become solid again only if they are more strongly bound and then more ordered. An increase of the average grain size can be seen in Fig. 4 and Fig. 5 where the CdTe surface is shown before and after treatment. The use of this new method for treating CdTe gives a strong advantage for an industrial production. First of all, the step of depositing CdCl_2 is eliminated. CdCl_2 , differently from CdTe , has a high vapour pressure at temperature as low as $400\text{--}500^\circ\text{C}$ and, in case of fire, Cd can be freed that is very dangerous for the human health.

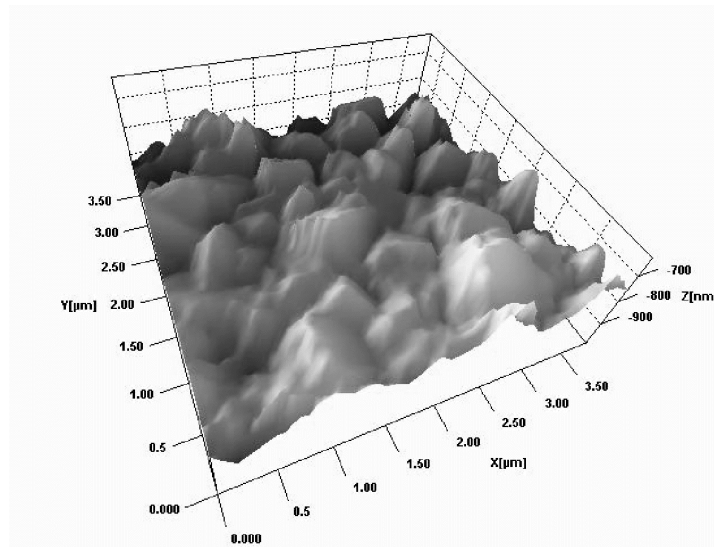


Fig. 4: AFM image of not treated- CdTe

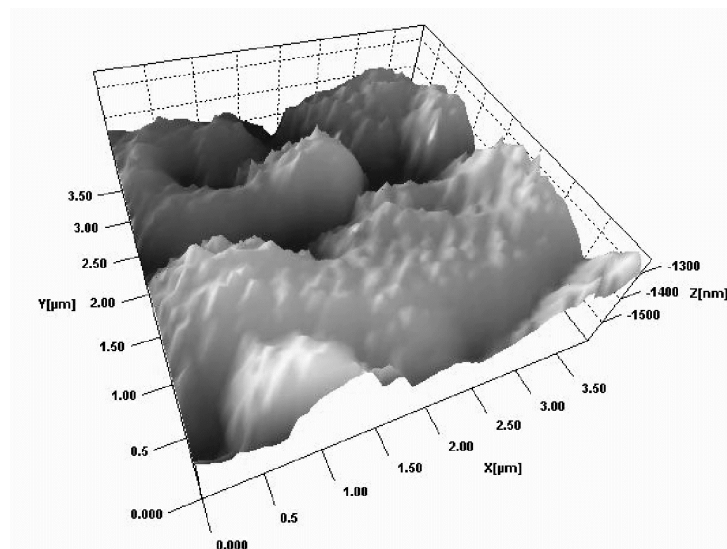


Fig 5: AFM image of CHF_2Cl treated CdTe

After the treatment, keeping the sample at 400°C , a vacuum is made in order that any CdCl_2 that could form onto the CdTe surface is removed. In this way, the CdTe surface remains clean and it is ready for the back contact. The process here described has been patented.

7. The back contact

Making an ohmic contact to CdTe is a quite difficult task. Most researchers deposit a few nanometers of Cu on top of CdTe in order to strongly dope p-type the CdTe surface. Before depositing Cu, an etching in Br-methanol or in a mixture of HNO₃ and HPO₃ is done in order to make the CdTe surface rich in Te. In this way a Cu₂Te thin film is formed which could limit the Cu-diffusion into CdTe. The contact is then completed with graphite past. This type of contact works quite well but it introduces another drawback that is Cu, being a very fast diffuser in CdTe, migrates through the grain boundaries reaching the junction where it can create shunting paths. If the solar cell has to live almost 20 years, Cu has to be avoided.

We invented a new back contact, which does not contain copper or any element of the 1st group of the periodic table. Our contact is made by sputter depositing 200nm of Sb₂Te₃ onto the CdTe surface at a substrate temperature of ~300°C. Sb₂Te₃ has a forbidden gap of ~0.3eV, is p-type and exhibits a resistivity of less than 10⁻³Ω·cm. We made this choice since Sb₂Te₃ contains Sb, a group V element, which, if it dopes CdTe close to the surface, it dopes p-type. This type of contact resulted to be very stable even if the solar cell is exposed to a 20 suns light soaking at a temperature of 100°C or more. Instead, an improvement of the solar cell parameters has been seen after light soaking. The contact is completed by depositing 200nm of Mo on top of Sb₂Te₃.

One important consideration to be made is that we do not etch CdTe before making the contact since we do not need to create a Te-rich surface on top of CdTe. The ohmicity of Sb₂Te₃ has been also verified by using it as a contact for CdTe single crystal [5].

8. The CdTe/CdS solar cell

The parameters of the CdTe/CdS solar cells prepared by the process described before have been determined by measuring the I-V characteristic under an AM1.5, 100mW/cm² simulated solar light. Open circuit voltages ranging between 840 and 870mV, short circuit currents between 24 and 26 mA/cm² and fill factors between 0.6 and 0.72 are obtained.

The highest efficiency that we were able to obtain on an area of 1cm² is 15.8%. The I-V characteristic of this cell is shown in Fig.6. Cell parameters are: V_{OC}=0.862mV, J_{SC}=25.5mA/cm², ff=72% and η=15.8%.

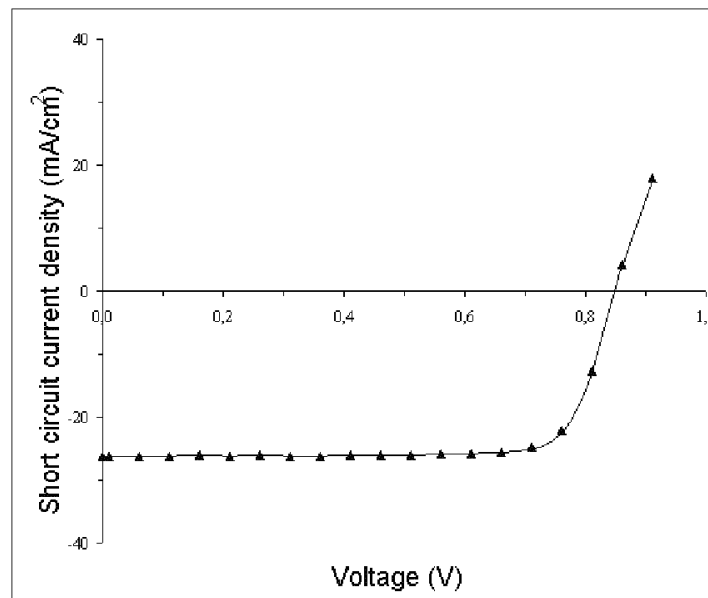


Fig6: I-V characteristic of our best completely dry-processed cell.

9. A possible industrial in-line dry process

The techniques that we use in our process are sputtering and CSS both fast and easily scalable. A possible industrial dry process is shown in Fig.7. Modules of $0.6 \times 1.2 \text{ m}^2$ can be processed in a few minutes.

The glass, moved on a rail, enters in a washing and drying machine after which it is heated up to 400°C and goes into a sputtering chamber, where 500nm of TCO are deposited. The temperature is decreased again to RT and a laser scribing is done in order to eliminate the TCO along parallel lines 1cm distant one from each other. The temperature is then risen on to 250°C and $60\text{-}80\text{nm}$ of CdS are deposited by sputtering. In sequence the substrate temperature is risen up to 500°C and $5000\text{-}6000 \text{ nm}$ of CdTe are deposited by CSS. After decreasing the temperature to RT a second laser scribing is done in order to remove CdS and CdTe in parallel lines close to the ones made before.

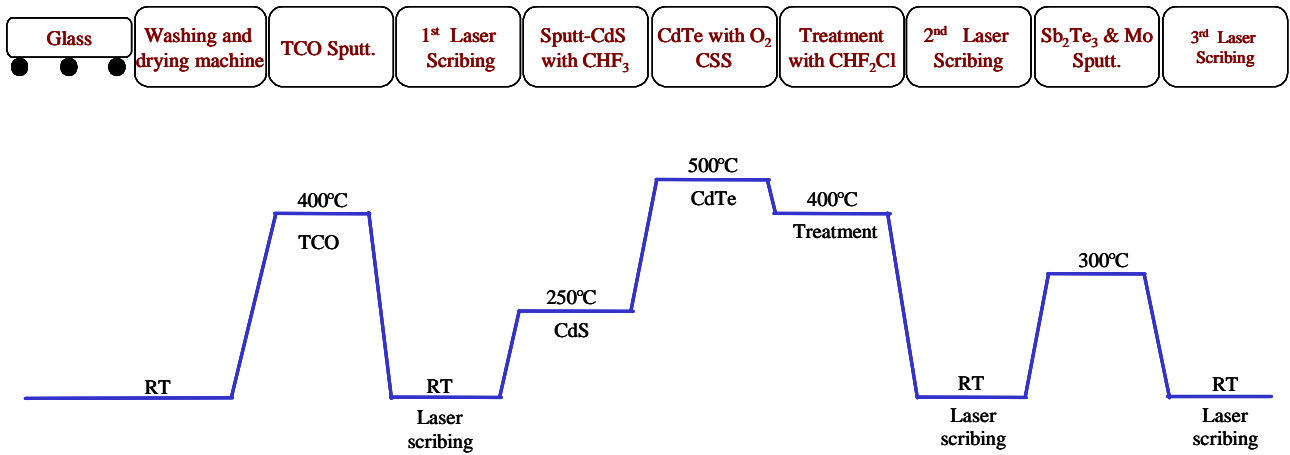


Fig 7: Block diagram and temperature profile of the industrial in-line dry process

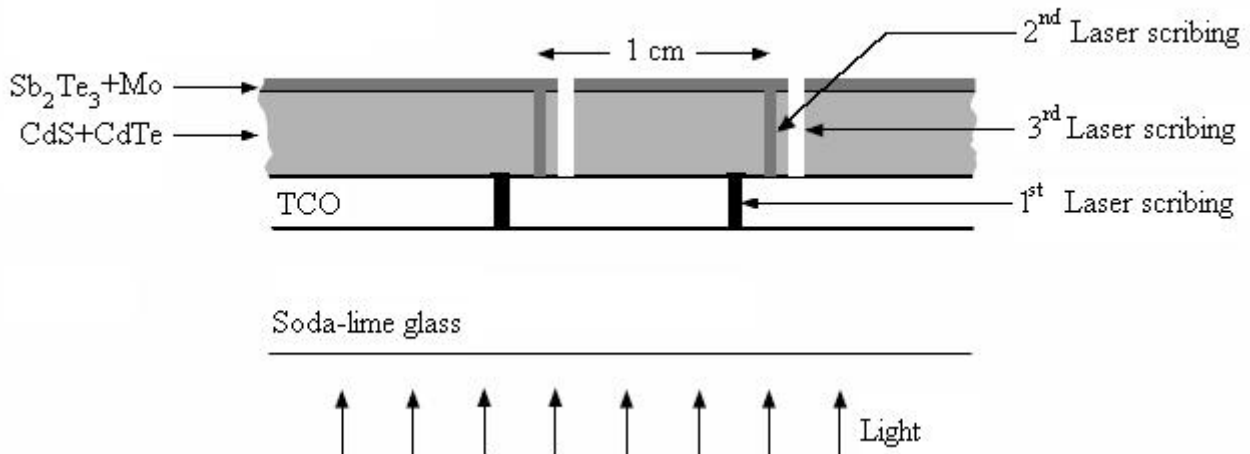


Fig 8: Typical interconnects scheme for a CdTe/CdS solar cell module

The temperature is risen again to 300°C at which 300nm of Sb_2Te_3 and 300nm of Mo are deposited in sequence by sputtering. Finally, a third laser scribing is done in parallel lines close to

those made by the second laser scribing in order to have a module made up of solar cells 1cm large and as long as the length of the glass all put in series. (see Fig. 8).

This process is the simplest process to fabricate CdTe/CdS photovoltaic modules since differently from Antec or First Solar it does not use CdCl₂ to treat nor acids to etch the CdTe surface.

10. Environment issues

Since CdTe contains Cd, a tale wanders around that CdTe-based photovoltaic modules could be dangerous. As sodium chloride (kitchen salt) is not sodium, CdTe is not Cd. The melting point of CdTe is 1041°C and it starts to evaporate at 1050°C at atmosphere pressure. In case of fire, the covering glass melts and encapsulated everything. This experiment was already done.

Cd is a by-product of Zn, Pb and Cu mining. Most of Cd, since it is not used in the market, is buried or stored for future use or disposed of in landfills as hazardous waste.

The Cd world consumption is on the order of 20000 tons per year while for 1000MW of power generated from 10% efficient CdTe modules only 700 tons of Cd are needed (only 4% of total consumption of Cd).

Paradoxically, using Cd to form CdTe and then to make photovoltaic modules removes Cd from the environment and reduces the risk of pollution [6, 7].

11. Conclusion

The technology to fabricate CdTe/CdS thin film solar cells can be considered mature for a large scale production of CdTe-based modules. A stable efficiency of 15.8% has been demonstrated for 1 cm² laboratory cell and it is expected that an efficiency of 12% can be obtained for 0.6×1.2m² modules. A fully automated in-line process could produce 1 module every 2 minutes at a cost substantially less than 1€/W.

We have contributed to strongly simplify the process:

1. By developing a new way of depositing CdS, namely sputtering in presence of CHF₃
2. By using a gas such as CHF₂Cl instead of CdCl₂ for treating CdTe
3. By eliminating the CdTe etching step from the production process
4. By inventing a new ohmic and stable contact for CdTe

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