



Polycrystalline CdTe thin films for photovoltaic applications

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Abstract

The CdTe/CdS thin film solar cells can be most conveniently fabricated in the form of thin films. Solar cells based on CdTe have been studied for several years now and the technology seems to be ripe for starting significant industrial production. Recently CdTe thin film solar cells have achieved an energy conversion efficiency record of 16.5% on a laboratory scale.

In this paper we review the process needed to prepare high efficiency CdTe/CdS solar cells from the point of view of thin film deposition techniques.

Furthermore we show that thin film CdTe technology is sufficiently mature to be easily transferred to form the basis of a large-scale module production.

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PACS: 84.60.Jt; 81.15.ez; 81.15.Gh; 85.30.ez; 81.10.Bk

Keywords: A3. Thin film/epitaxial growth; A3 CVD techniques; B1 CdS; B2. Semiconducting CdTe; B3. Solar cells

1. Introduction

Crystalline solar cells, particularly those made with silicon (Si) and gallium arsenide (GaAs), have achieved energy conversion efficiencies approaching the theoretical limits for their respective band gaps. Furthermore, the small remaining losses are reasonably well

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understood, and any additional effort would appear to offer only a modest improvement. However, during the last 15–20 years the photovoltaic world has been enriched with other interesting materials such as CdTe and CuInSe₂. Both these materials are considered very suitable for the fabrication of solar cells because of their direct band gap. As a consequence of the direct energy gap, the absorption edge is very sharp and thus, more than 90% of the incident light is absorbed in a few micrometers of the material. The maximum photocurrent available from a CdTe cell under the standard global spectrum normalized to 100 mW/cm² is 30.5 mA/cm² and the theoretical maximum efficiency of CdTe is over 27%. Recently an energy conversion efficiency record for CdTe of 16.5% has been reported [1]. This record, despite its achievement on a laboratory scale, demonstrates that CdTe thin film technology has arrived at a level comparable with the more sophisticated technologies typical of single crystal materials. One of the best characteristics of this semiconductor is that it is possible to fabricate a complete photovoltaic device using only thin film technology. This extraordinary fact has been well known ever since 1972 when Bonnet and Rabenhorst [2] published an interesting paper on CdTe/CdS thin film solar cells reporting an efficiency of 6%. There followed a period during which several research groups tried to develop a solar cell fabrication process based on related thin film deposition techniques. However, it was only in the 1980s before the 10% efficiency value was overcome by Tyan and Albuernie [3]. Subsequently an efficiency of 15.8% was reached by Ferikides et al. [4] and most recently a research group of NREL reported a record efficiency of 16.5% [1].

Most surprisingly CdTe/CdS solar cells fabricated using thin film technology exhibit higher efficiencies than those fabricated from single crystal materials. In fact, solar cells with an efficiency around 10% or higher have been made as hetero-junctions, homojunctions, buried homojunctions and MIS junctions, using CdTe single crystal. The higher 13.4% efficiency concerns an n-ITO/p-CdTe single crystal buried homojunction [5]. Best performances are shown in Table 1.

All researchers who work on thin film CdTe solar cells are in agreement concerning the few important controlling characteristics, namely: stoichiometry, growth morphology and the quality of the grain boundaries, doping and contacting [8].

Table 1
Representative data for single crystal and all thin film p-CdTe solar cells

Type of cells	Open-circuit voltage V_{oc} (mV)	Short-circuit current J_{sc} (mA/cm ²)	Energy conversion efficiency (%)	Ref.
CdTe single crystal				
Buried homojunction:n-ITO/p-CdTe	890	20 ^a	13.4	[5]
Heterojunction:n-ZnO/p-CdTe	540	19.5 ^a	8.8	[6]
CdTe homojunction:p-CdTe by CSVT on n-CdTe single crystal	820	21 ^a	10.7	[7]
Thin films				
All thin film CdTe solar cell			6	[2]
(CdS and CdTe by low temperature CSS)	750	17 ^b	10.5	[3]
(CdS by CBD and CdTe by high temperature CSS)	843	25.1 ^a	15.8	[4]
(CdS by CBD and CdTe by low temperature CSS)	845	25.88 ^a	16.5	[1]

^a Under simulated AM 1.5 solar illumination at 100 mW/cm².

^b Under simulated AM 2 solar illumination at 75 mW/cm².

Stoichiometry can be easily achieved if the films are deposited or post-annealed at elevated temperatures where the compound can exhibit a very low vapor pressure in comparison to the single elements. CdTe growth characteristics are principally controlled by its crystal structure; in particular, if viewed perpendicular to the (111) plane the direct lattice shows alternate layers of hexagonally arranged Cd and Te ions. Since these planes have a strong tendency to grow parallel to the substrate film growth can develop completely independent of the substrate.

Furthermore, in II–VI compounds polycrystalline thin films, the grain boundaries are often very narrow and have little influence on the overall electronic properties.

As to doping, the deposition of CdTe is always performed at a temperature below 600 °C. This temperature is not sufficient to permit a uniform level of doping inside the polycrystalline thin film. This means that a partition coefficient exists between the doping concentrations in the bulk and in the grain boundaries. In fact, it is well known that, in II–VI semiconductor materials, the grain boundaries can accommodate segregation in several orders of magnitude more than the bulk for all the metallic elemental species capable of doping the compound either p-type or n-type. The principal suggestion is to avoid the use of In, Ga and Al that introduce donor levels and to use Sb, Na, Ag or Cu to introduce acceptor levels. Other kinds of doping elements like P, As, N, Cl, Br, and iodine have so far been demonstrated to be very efficient for doping II–VI single crystals. In the case of polycrystalline thin films, due to the unfavorable energetic conditions caused by the low deposition temperature, they do not enter into the ionic matrix of the crystal lattice avoiding the doping action of these species. At a temperature of 500–600 °C, native p doping is observed, probably due to Cd vacancies, which are probably enhanced by the presence of oxygen during the growth. Also for this reason thin film technology is winning since the thickness of the CdTe film can be made as low as possible in order to prevent significant series resistance effects without being constrained to use high doping levels.

All photovoltaic devices involving CdTe as an absorber material contain a highly transparent and n-conducting partner, which promotes the creation of a depleted region in the p-conducting CdTe film. In highly efficient CdTe based solar cells this partner is CdS and, despite the lattice mismatch which is 9.7%, the interface shows a good behavior without the typical recombination losses associated with junction interface states [9]. The CdS, with a forbidden energy gap of 2.42 eV, acts as a filter for solar light having a cut off at 514 nm; for this reason this device loses part of the solar spectrum which corresponds to a theoretical loss in the short-circuit current of about 5 mA/cm². The electrical resistance of the CdS film may become an important factor that affects the whole solar cell behavior. Generally the thickness of the CdS film is minimized having in mind the need to preserve the best properties of the cell such as the open-circuit voltage.

The dark resistivity of as-deposited CdS films is usually in the range of about 10⁴–10⁶ Ω cm. These CdS films are suitable for solar cell purposes because they increase their conductivity under illumination. This effect is due to the excess carriers in the bulk introduced by the absorption of the radiation with energy larger than the band gap and to the lowering of the potential barriers at the grain boundaries. In order to increase the photocurrent, the CdS film thickness has to be as small as possible. For this reason an additional transparent electrode must be used. This electrode called a “Transparent Conducting Oxide” (TCO) is generally a semiconducting material such as SnO₂ or ITO (indium–tin–oxide). When the transparent layer is on top of the device, the cell is in the so-called “frontwall” configuration and can be fabricated on a non-transparent substrates.

Otherwise, if the TCO is deposited directly on the substrate, the device is said to be in the “backwall” configuration and the solar cell fabrication needs a transparent substrate.

Nowadays, highly efficient solar cells based on CdTe as an absorber material coupled with CdS as a window layer are made in the backwall configuration and soda-lime glass is used as a transparent substrate. The schematic diagram of all the stacked layers of the CdTe/CdS system is shown in Fig. 1.

Despite the good performance and efficiency, the preparation of these thin film solar cells based on CdTe/CdS heterojunction still exhibits quite a few open problems and it is therefore subject to a margin of uncertainty in its progress. One of the major open questions is certainly the back contact, which is crucial for the time stability of the solar cell.

In fact, in order to obtain a low resistance or possibly ohmic contact with a p-type CdTe film, use is made of various metals like Cu, Hg, Pb, Ag or Au which, due to their ability to diffuse into the different layers may deteriorate the device [10–14]. All the devices described in Table 1 were completed with these kinds of back contact and nothing is reported about their time stability.

The device back-contact problem was solved, several years ago, by using a different type of material such as Sb_2Te_3 or As_2Te_3 [15–17]. These semiconductors demonstrate ohmic behavior and a very low contact resistance when coupled with p-type CdTe.

Commonly, in efficient solar cells, CdS films are prepared by RF sputtering, Close-Spaced Sublimation (CSS) or Chemical Bath Deposition (CBD) [18–20]; CdTe films are deposited by CSS, electrodeposition or metal-organic chemical vapor deposition (MOCVD) [9,21–23].

Since any mature solar cell technology tends to the stage where costs are determined by those of constituent materials, this means that highly efficient processing operations that produce solar cells with high-energy conversion efficiency are favored.

Each technique as described above has its own merits but in order to produce a device that is easily scalable for industrial needs (i.e. the costs of the equipment, the deposition rate and the final cell performance) the CSS and sputtering techniques seem to be the most advantageous processes.

A big challenge for thin film photovoltaics is the development of large area semiconductor technology. In fact, one of the advantages of the thin film technology is the potential increase in the manufacturing unit from a silicon wafer ($\approx 100\text{--}200\text{ cm}^2$) to a glass sheet ($\approx 10^4\text{ cm}^2$) that is about 50–100 times larger. In order to achieve this goal, high quality materials and high throughput on large areas have to be obtained.

In this paper we want to review the typical thin film techniques that are able to produce highly efficient CdTe/CdS solar cells and especially those that are ready for industrial production. In particular we want to show an all in-line process, starting from a laboratory scale and based on classical thin film technology, in order to demonstrate that it is possible to produce large area photovoltaic modules with high throughput.

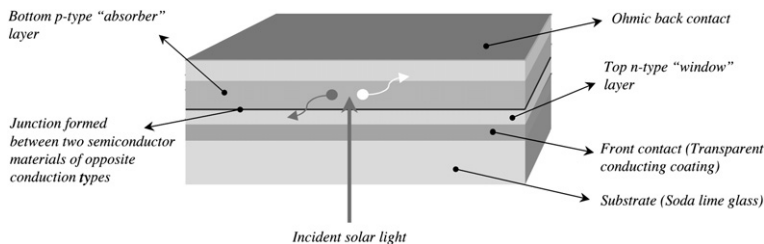


Fig. 1. A CdTe/CdS thin film solar cell structure in the backwall configuration.

2. Transparent conducting oxides (TCOs)

In recent years there has been a great interest in metallic oxides thin films due to their many industrial applications [24–26].

Thin films of these materials (TCOs) are produced by several deposition techniques. The most studied TCOs are: $\text{SnO}_2\text{:F}$ (FTO), ZnO:Al (AZO), $\text{In}_2\text{O}_3\text{:Sn}$ (ITO), and Cd_2SnO_4 (CTO) [27]. These metallic oxides exhibit very good optical transparency nearly or more than 90% for visible light and near infrared radiation and very high n-type conductivity. For these reasons TCOs are generally nearly degenerate semiconducting materials with a free carrier concentration between 10^{18} cm^{-3} and 10^{20} cm^{-3} . The high transparency and also the high electrical conductivity make the TCOs suitable for a great variety of applications. In fact they are used in optoelectronic devices and as transparent electrode in photovoltaic modules. Also they have been employed in glass coatings, for example as transparent heating elements for planes and car windows.

Because of their high reflectivity in the IR part of the spectrum they could also be used as transparent heat-mirror coatings for buildings, cars and energy saving light bulbs. Since it is not possible to obtain both high electrical conductivity and optical transparency in any intrinsic material, one way to reach this aim is to create electron degeneracy in a wide band-gap oxide. This could be made in two different ways:

- Introducing donor elements into the oxide matrix.
- Exploiting deviation from correct stoichiometry by, for example, using structural defects and/or oxygen vacancies.

The first point is explained by considering the substitution of a higher valence cation by a donor impurity in the oxide, e.g. tin or antimony in indium oxide or fluorine in tin oxide, increases the electron concentration and so the n-type conductivity. On the contrary, the replacement of a lower valence cation by an acceptor impurity generates a hole (broken bond) that works like a trap (deep level in the energy gap) in the n-type metallic oxide decreasing its n-conductivity.

Since the mean grain size of TCO thin films is in the range of 10–100 nm depending on the deposition method, the high electrical conductivity of doped and undoped films depends mainly on carriers (electrons) concentration and not on their mobility. This is due to the fact that the mobility in these films is considerably lower than that in the bulk materials, because it is limited by grain boundaries.

In the last few years a lot of new TCOs have been developed starting from multicomponent oxides such as: GaInO_3 , ZnSnO_3 , $\text{Cd}_2\text{Sb}_2\text{O}_6\text{:Y}$, Zn_2SnO_4 , MgIn_2O_4 , $\text{In}_4\text{SnO}_{12}$ [28]. All these metallic oxides can exhibit high n-type conductivity following the behavior described above.

In addition, a new p-type TCOs has been intensively studied in recent years in order to make a p–n junction. In 1997 it was reported for the first time that a CuAlO_2 thin film exhibits p-type conductivity.

After that, a new series of materials based on copper was discovered such as: CuGaO_2 and SrCu_2O_2 [29,30]. In 2000, a UV-emitting diode based on a p–n heterojunction composed of p- SrCu_2O_2 and n- ZnO was successfully fabricated using heteroepitaxial thin film growth.

Anyway, the major area of interest is in n-type TCOs due to their utilization in industrial applications. One of these applications is in photovoltaic (PV) module fabrication. In this case, it is necessary to reach a very low resistivity. This direction has been strongly accelerated by the rising demand for enlargement of the module size.

In PV module production the specification needed for TCOs not only concerns the very high electrical conductivity and very high optical transparency but also their chemical and physical stability [31].

2.1. Fluorine doped tin oxide (FTO) films

SnO_2 (TO) is the first transparent oxide to have received relevant commercialization. Nowadays TO films are used in products like “low-emissivity” windows, photovoltaic modules, flat-panel displays, heated windows, etc. In general commercial TO thin films are produced by Chemical Vapor Deposition (CVD) [32–34]. In CVD a solid film is deposited onto a substrate, typically glass, from gas or liquid reactants that are contemporaneously supplied and premixed close to the deposition zone. Many inorganic and metal-organic precursors are used for the deposition of pure TO films. The most industrially used are tin tetrachloride (SnCl_4 , TTC), dimethyltin dichloride ($((\text{CH}_3)_2\text{SnCl}_2$, DMTC), tetramethyltin ($\text{Sn}(\text{CH}_3)_4$, TMT) and O_2 or O_3 containing about 3–10 mol.% O_3 . When TO films are used as transparent conducting oxides (TCOs) such as in solar cells, a very high electrical conductivity is needed. In TO films the n-type conductivity is primarily due to O-vacancies, and often a mixture of two phases: SnO and SnO_2 are involved. $\text{Sn}_{1-x}^{4+}\text{Sn}_x^{2+}\text{O}_{2-x}^{2-}$ oxide can be formed where x is the fraction of SnO in the mixture. This oxide contains x oxygen vacancies and x Sn^{2+} atoms that donate two electrons for conduction. But this mechanism does not provide films with sufficient conductivity that are suitable for solar cells. In this case the CVD process is provided with precursors containing HF (hydrogen fluoride)-acid. In fact it is well known that fluorine can dope TO films producing very low resistivities.

Some useful properties of the CVD TO films are as follows:

- High transparency in the visible part of the light spectrum (more than 90%);
- High reflectivity for infrared light;
- Low electrical resistivity (on the order of $10^{-4} \Omega \text{ cm}$ for fluorine doped TO);
- Good environmental steadiness;
- High mechanical hardness;

Despite these remarkable features, most on-line coated glass is still produced by sputtering techniques. Only about 25–30% of all coated float glass is produced by CVD. In part this is due to the fact that the sputtering techniques were developed for large area coating before the CVD technique, and furthermore the development of a successful on-line CVD process is very difficult. CVD is a complicated process since it involves liquid and gas phases and surface chemistry as well as the hydrodynamics of the whole reactor system. For this reason it is not possible to plan an industrial CVD process based only on theoretical considerations or chemi-physical models, but rather on technological results and experience. This means that optimal conditions of film deposition are not always achieved and, as a consequence, low process yields and high product rejection rates are usual (principally due to optical nonuniformities) in the glass coating production process.

Besides this, the utilization efficiency of reagent species in an industrial CVD reactor is around 10%; this implies the need for very expensive chemical scrubbing units that can create more than one hundred thousand of tons of waste per year.

Meeting these problems, one can readily appreciate that CVD methods do not only need a lot of expertise in chemical reactions, fluid dynamics, mass and heat transfer and material

science, but also many years of development to implement more reliable techniques for the glass coating industry. Thus it is clear why sputtering is the most utilized technique for the deposition not only of TO films, but also for many other TCO.

For this reason, typical sputtering parameters were studied in order to prepare several TCO thin films with very high quality for photovoltaic application. In this section we briefly described the main characteristics of the TCOs tested in our laboratory when used as a front contact in photovoltaic devices.

Pure TO thin films, prepared by sputtering in an Ar atmosphere, starting from an oxide target, exhibit a resistivity of $10^{-1} \Omega \text{ cm}$ and an optical transparency up to 90% in the visible region of the light spectrum.

The films were doped by mixing the Ar sputtering gas with CHF_3 in the range 1–10% with respect to the total $\text{Ar} + \text{CHF}_3$ gas pressure. The minimum resistivity that we were able to obtain by making use of the maximum quantity of CHF_3 in the sputtering chamber during the SnO_2 deposition was about $8 \times 10^{-4} \Omega \text{ cm}$. A disadvantage of the use of pure TO thin films in comparison with the other TCOs is that the resistivity of the $\text{SnO}_2\text{:F}$ is 3–4 times greater. This means that, in order to obtain the same sheet resistance as that of the TCO films, one has to deposit an $\text{SnO}_2\text{:F}$ film 3–4 times thicker with a loss in the transparency. As a consequence, we did not prepare any solar cell with $\text{SnO}_2\text{:F}$ alone but we used this material as a buffer layer against Na diffusion from soda-lime glass. For example we deposited an $\text{SnO}_2\text{:F}$ film, 100–500 nm thick on top of an ITO film prepared as will be described later. The final performance of the solar cell did not change if compared with that of the device fabricated by making use of ITO alone.

2.2. The In_2O_3 (IO) family

The In_2O_3 (IO) films are normally polycrystalline with cubic structure and a typical grain size of about 10–50 nm depending on the deposition technique. The most common techniques used for deposition of IO thin films are the following: reactive R.F. sputtering, chemical vapor deposition, spray pyrolysis, glow discharge and activated reactive evaporation. IO films often exhibit superior electrical and optical properties with respect to the other transparent conductors; this fact is principally due to the higher mobility in IO. In fact In_2O_3 films prepared using various deposition methods have mobilities in the range $10\text{--}75 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ that is very high considering that they are polycrystalline thin films.

IO films exhibit a direct optical band gap, which lies between 3.55 and 3.75 eV, which was shown to increase with increasing carrier concentration owing the Burstein–Moss shift. For films with thicknesses below $1 \mu\text{m}$ the optical transparency in the visible and near IR regions is about 80–90%. For this reason IO has been widely used as a transparent conductor.

2.3. The tin doped In_2O_3 (ITO) films

ITO films prepared in our laboratory were obtained by R.F. magnetron sputtering from several targets with different stoichiometry; in particular we studied four kinds of ITO: In_2O_3 containing, respectively, 1, 2, 4, and 10 weight% of SnO_2 . Some ITO films were deposited in a sputtering gas mixture containing $\text{Ar} + \text{O}_2$; the O_2 partial pressure was varied between 2 and 20% in respect to $\text{Ar} + \text{O}_2$ total pressure. All these films exhibit a very low resistivity ($2 \times 10^{-4} \Omega \text{ cm}$); the resistivity of the ITO films does not depend on the stoichiometry of

the target and on the sputtering deposition parameters, such as the substrate temperature, deposition rate, Ar pressure and power density. This probably means that Sn is an effective dopant and the doping level does not depend on the typical sputtering parameters. Since the optical transparency of the ITO layers is more than 80%, the films are sufficiently transparent to be used as front contacts for CdTe/CdS solar cells. However, we found out that the efficiency of the solar cells, when using an ITO film thicker than 1.2 μm , could be quite high (above 14%) but were not very reproducible. We explain this by the fact that all ITO targets modify their surface after several runs forming some In-rich nodules which can cause some occasional discharges during sputtering deposition [35]. This discharge instability produces a non-stoichiometrically uniform ITO film. In order to improve the reproducibility of the ITO film we introduce in the sputtering chamber, during the film deposition, a small amount of H_2 and trifluoromethane (CHF_3). The H_2 partial pressure was changed in the range of 1–10% and the CHF_3 in the range of 1–10% with respect to the total $\text{Ar} + \text{H}_2 + \text{CHF}_3$ pressure. With the maximum quantity of CHF_3 we did not observe any indium-rich nodule formation on the surface of the ITO target. This is probably due to the fact that the free indium atoms can react with fluorine on the surface of the target forming a stable compound. Therefore this reaction prevents the segregation of In into superficial nodules and, as a consequence, the sputtering discharge is more stable producing stoichiometric and more uniform ITO films.

From the point of view of the stability of the whole device, the quality of the ITO layers is better for films prepared in $\text{Ar} + 4\%\text{H}_2 + 10\%\text{CHF}_3$ gas. This kind of film, being very compact and dense, offers a better shield against Na diffusion from the soda-lime glass. Since the presence of Na atoms favors the reactivity of all the present elemental species, this can cause the formation of undesirable compounds. For example, the formation of CdSO_4 has been observed, when a CdS film is deposited in the presence of oxygen on top of ITO layer if it is not sufficiently dense to avoid the diffusion of alkaline atoms from the soda-lime glass [31].

2.4. Germanium doped indium oxide (IGO) films

Germanium doped indium oxide (IGO) films are normally prepared by R.F. sputtering from a target of In_2O_3 containing 4% weight of GeO_2 . A typical deposition rate was larger than 1 nm/s. The surface of this target did not present any formation of In-rich nodules and the film deposition was much more stable and reproducible. The preparation of an IGO film is carried out by using pure argon or a mixture of Ar, H_2 and CHF_3 as a sputtering reactive gas. In the first case it is obtained as an IGO film with a resistivity on the order of $8.5 \times 10^{-4} \Omega \text{cm}$ and a very good transparency in the visible region of the spectrum. This means that germanium has the same behavior as tin in an In_2O_3 matrix and acts as an effective dopant for In_2O_3 . The IGO films deposited by reactive sputtering by using a mixture of $\text{Ar} + \text{H}_2 + \text{CHF}_3$ as sputtering gas presented a resistivity of $2 \times 10^{-4} \Omega \text{cm}$ (Fig. 2).

This result shows that hydrogen can create some oxygen vacancies in the In_2O_3 matrix giving more possibility for fluorine to substitute oxygen and therefore to better dope the IGO film during the deposition. The H_2 and CHF_3 gas pressures were both 5% with respect to the total $\text{Ar} + \text{H}_2 + \text{CHF}_3$ gas pressure. The IGO film stability and its very low resistivity permit the use of a thickness as low as 400 nm for the TCO layer. With this TCO we fabricated solar cells with an efficiency up to 14% and with very good reproducibility.

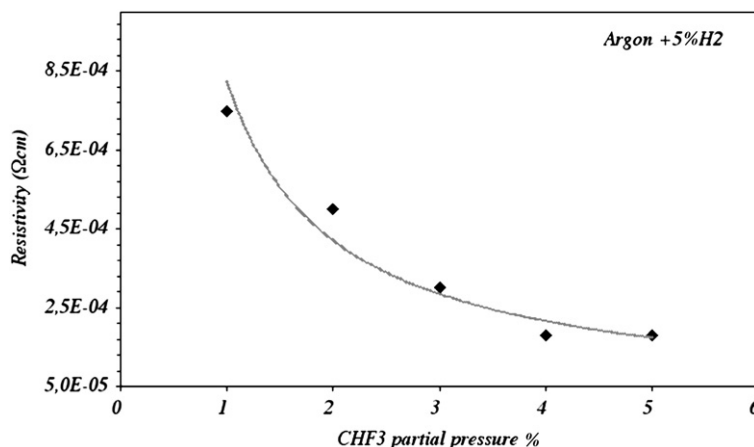


Fig. 2. Variation of the IGO:F film resistivity as a function of the percentage of the trifluoromethane (CHF_3) with respect to the total $\text{Ar} + \text{CHF}_3$ pressure used in the sputtering chamber during the film deposition. The hydrogen was fixed at 2% with respect to the total $\text{Ar} + \text{H}_2$ pressure and the substrate temperature was kept at 450°C for all the deposited IGO films.

2.5. Fluorine doped indium oxide (IFO) films

Another TCO of the IO family is fluorine doped indium oxide (IFO). In_2O_3 can be sputtered at a relatively high deposition rate ($\geq 10 \text{ Å/s}$) without any change on the target surface. When In_2O_3 is not intentionally doped during sputtering deposition it grows with a resistivity of the order of $1 \times 10^{-2} \Omega \text{ cm}$. In this case the conductivity is due to native defects, such as oxygen vacancies (Fig. 3a). It is possible to prepare IFO films with a resistivity of $\approx 2 \times 10^{-4} \Omega \text{ cm}$ by introducing Ar containing 5% of H_2 and 5% of CHF_3 in the chamber during sputtering deposition (Fig. 3b). The IFO films obtained in this way are very smooth and transparent. Besides, we found out that 100 nm of this material are sufficient to passivate the diffusion of sodium atoms into the film from the soda-lime glass. For this reason and for its intrinsic stability, IFO is perhaps, the best-suited material for solar cell production.

Depositing in sequence 400 nm of IFO and 100 nm of CdS onto 1 inch² soda-lime glass, we were able to obtain a 14% efficient CdTe/CdS solar cell.

2.6. Fluorine doped zinc oxide (FZO)

ZnO thin films have been prepared by a variety of thin film deposition techniques, such as D.C. reactive and R.F. magnetron sputtering, chemical vapor deposition (CVD), reactive thermal evaporation and Chemical Bath Deposition (CBD) [36–38]. The sputtered films are normally polycrystalline with an average grain size of about 5–30 nm with a wurtzite-type structure with a strong *c*-axis preferred orientation perpendicular to the substrate.

Pure and stoichiometric zinc oxide films show a very high resistivity and a direct band gap of about 3.2 eV. Furthermore ZnO has one of the largest electromechanical coupling coefficients. Due to this property, zinc oxide is a well-known piezoelectric material, which has been used as a transducer for surface acoustic wave devices. In the last 10 years, ZnO has been intensively

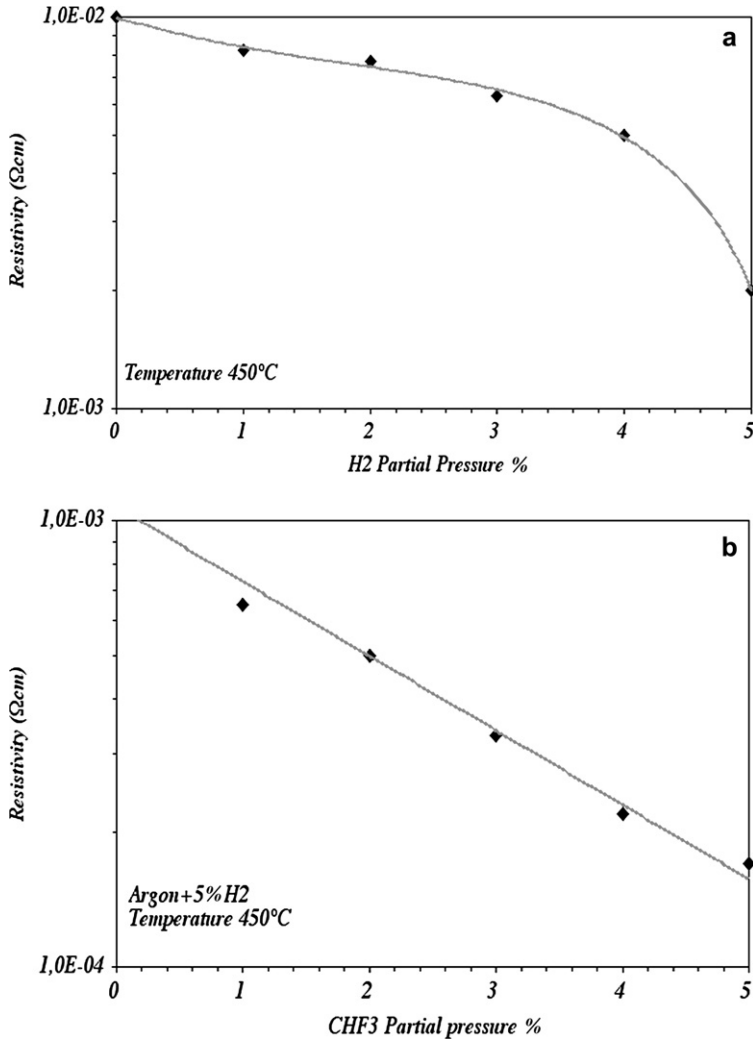


Fig. 3. (a) Variation of the INO film resistivity as a function of the percentage of H₂ with respect to the total Ar + H₂ pressure used in the sputtering chamber during film deposition. (b) Variation of the INO:F (IFO) film resistivity as a function of the percentage of CHF₃ with respect to the total Ar + CHF₃ + H₂ pressure used in the sputtering. The substrate temperature was kept at 450 °C for all the deposited films.

used as a TCO for photovoltaic applications and as a gas sensor device. The primary need is for a ZnO film with high transparency in the visible region and with a high conductivity.

In order to reach a good conductivity it is common practice to dope ZnO with trivalent cations such as indium and aluminum. In our laboratory we obtained ZnO:Al (AZO) thin films, deposited by R.F. sputtering, with a resistivity of the order of $8 \times 10^{-4} \Omega\text{cm}$ and with a very good transparency, over 90% in the range 450–850 nm of the visible spectrum.

The starting target was a hot-pressed powder mixture of 98 weight% ZnO and 2 weight% Al₂O₃ supplied by Cerac Inc. Since the ZnO:Al thin films are not stable at high temperature with respect to Al diffusion, as we observed by making use of these films in our CdTe/CdS solar

cell, we tried to dope ZnO films with fluorine. In order to do that we used reactive R.F. sputtering technique starting from a pure Cerac ZnO target and introducing into the sputtering chamber a gas mixture containing Ar, H₂ and CHF₃. The H₂ partial pressure was fixed at 5% with respect to the total Ar + H₂ pressure, while the CHF₃ pressure was varied in the range 1–10% of the total Ar + CHF₃ pressure in order to change the fluorine doping level in the ZnO:F film.

The presence of H₂ in the sputtering chamber causes the creation of some oxygen vacancies in the ZnO matrix giving more possibility for fluorine to substitute oxygen atoms and, as a consequence, to better dope the ZnO film during its deposition. We observed that the presence of hydrogen into the sputtering chamber made the deposition of ZnO films almost independent of substrate temperature in the range 200–350 °C.

In fact, low resistivity, of the order of $8 \times 10^{-4} \Omega \text{ cm}$ and high transparency has been achieved by making use of the maximum quantity of CHF₃, independent of the substrate temperature in the above mentioned range (Fig. 4).

It was also demonstrated that this doping level did not change with heat treatment of the ZnO film in air at a temperature higher than 500 °C. This means that fluorine substitutes for oxygen making a stable chemical bond with Zn suggesting that it is an effective dopant for ZnO.

2.7. Zinc and cadmium stannate (Zn₂SnO₄–Cd₂SnO₄)

Zn₂SnO₄ and Cd₂SnO₄ thin films were prepared by reactive R.F. sputtering in a mixture of Ar + 50%O₂. Both the materials are very transparent exhibiting a transparency larger than 90% in the wavelength range between 400 and 850 nm. Zn₂SnO₄ thin films showed a resistivity of the order of $10^{-2} \Omega \text{ cm}$. This resistivity is too high for Zn₂SnO₄ films to be used in solar cell production. We tried to dope Zn₂SnO₄ by reactive sputtering with CHF₃ but, unfortunately fluorine did not act as an effective dopant in this material; probably, the presence of oxygen during the sputtering deposition, inhibits fluorine atoms from entering the Zn₂SnO₄ matrix. The

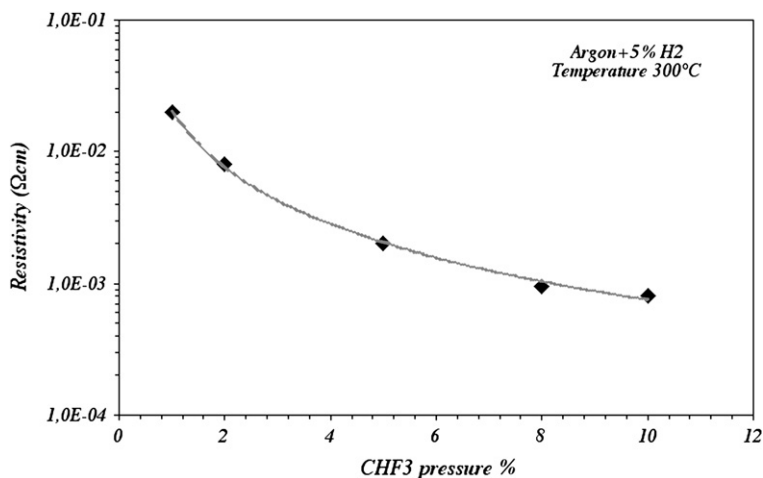


Fig. 4. Variation of the ZnO:F film resistivity as a function of the percentage of the trifluoromethane (CHF₃) with respect to the total Ar + CHF₃ pressure used in the sputtering chamber during the deposition. The hydrogen was fixed at 5% with respect to the total Ar + H₂ pressure and the substrate temperature was kept at 300 °C for all the deposited ZnO films.

preparation of Cd_2SnO_4 thin films was carried out with the same sputtering parameters as used with the Zn_2SnO_4 deposition and the resistivity of these films was on the order of $2 \times 10^{-4} \Omega \text{ cm}$ that is comparable with the resistivity of the best ITO and IGO films. Because of its high transparency and conductivity this material seems to be quite suitable for achieving high efficiency CdTe/CdS solar cells [39]. However, the sputtering target supplied by Cerac Inc., since it is made by hot pressing a mixture of CdO and SnO_2 powders, and since CdO is hygroscopic, it is difficult to handle. Due to this fact, the target is not sufficiently stable and in order to avoid some damage, the sputtering power density must be kept very low. As a consequence, the deposition rate was $\leq 2 \text{ \AA/s}$. Since this material is highly hygroscopic, we discovered some problems when the soda-lime glass covered by Cd_2SnO_4 was exposed to air. Despite this, we were able to obtain highly efficient solar cells.

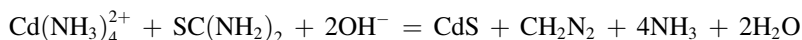
3. The CdS layer

The CdS film in the CdTe/CdS solar cell is the so-called window layer. Since it is n-type it enables the formation of a p–n junction with p-type CdTe. With an energy gap of 2.42 eV, CdS is transparent in the visible part of the solar light spectrum and therefore the solar light can penetrate into the CdTe layer thus giving rise to the photovoltaic effect. In order to have a highly efficient solar cell, an excellent p–n junction with a very good contact on the p-type CdTe is needed. Since the p–n junction formed between n-type CdS and p-type CdTe is strongly dependent on a proper interaction between these two layers, the deposition technique used to prepare these materials becomes very important. In particular for CdS the most suitable deposition techniques are the following: R.F. Sputtering [20], Close-Spaced Sublimation (CSS) [19], High-Vacuum Thermal Evaporation (HVTE) [40,41] and Chemical Bath Deposition (CBD) [18,42]. Although the highest energy conversion efficiency was obtained by using a CdS layer prepared by CBD, it is normally preferred to use the sputtering or CSS deposition method since CBD is not so suitable for large-scale production.

3.1. CdS by Chemical Bath Deposition (CBD)

Thin film semiconductors of metal chalcogenides, such as sulfides or selenides, may be deposited on metal foils, glass and polymer substrates. This happens when these substrates are dipped into a solution containing metal complex ions and sulfide or selenide ions. This technique is the so-called Chemical Bath Deposition (CBD) method [18,42] and it is often demonstrated that CBD is a low-cost simple technique to achieve good quality CdS films, suitable for obtaining high efficiency CdTe/CdS based solar cells.

In CBD, CdS films can be prepared by exploiting the decomposition of thiourea in an alkaline solution of cadmium salts, following the reaction:



According to this reaction a chemical bath for the deposition of CdS could contain an aqueous solution of cadmium acetate ($\text{Cd}(\text{CH}_3\text{CO}_2)_2$) as a cadmium ion source, thiourea ($\text{N}_2\text{H}_4\text{CS}$) as a sulfur ion source, ammonium hydroxide (NH_4OH) as a complexing agent and ammonium acetate ($\text{CH}_3\text{CO}_2\text{NH}_4$) as a stabilizing buffer agent for the reaction.

The previous reaction implies that the growth of CdS films can occur either by ion-by-ion condensation of Cd and S ions on the surface of the substrate or by adsorption of colloidal

particles of CdS. The behavior of the growth process is schematically summarized in these three remarkable points:

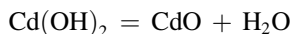
- *Nucleation period*: first of all the chemical reactions in the bath are completed and an initial monolayer of the metal chalcogenide is formed on the surface of the substrate (the CBD technique requires extremely careful substrate cleaning).
- *Growth phase*: when the surface of the substrate is entirely covered by the initial monolayer, this can act as a catalytic surface for the condensation of metal and of chalcogenide ions resulting in film growth.
- *Terminal phase*: during growth the chemical reactions change and, as a consequence, the deposition rate changes. In fact, the growth rate assumes a maximum value after a certain time depending on the solution parameters and finally, when the ions species diminish, it achieves a terminal phase at which the film stops growing.

Taking these considerations into account, it is possible to assert that, if the aim of the deposition is a high film thickness, it is necessary to combine a relatively high initial concentration of metal ions in the bath with a relatively low temperature. In contrast, if the objective is the deposition of a thin layer, typically ≤ 50 nm, it is more appropriate to use a very dilute concentration and a relatively high deposition temperature.

Since CdS exists in two crystalline forms, the hexagonal (wurtzite) and the cubic (zincblende) phase, with CBD technique it is possible to deposit CdS films in both these crystalline structures depending mainly on the chemical composition of the bath, the temperature and the pH of the solution. It was found out that the as-deposited CdS films contain both cubic and hexagonal structural forms as a mixture. It was also seen that the percentage of hexagonal structured grains increases by annealing the film at temperatures above 400 °C. This is explained by considering that the wurtzite form is more stable than zincblende at high temperatures in CdS films. Another confirmation of the transformation in the crystalline phase comes from the absorption spectrum; in fact, the energy gap of 2.42 eV is observed only for films annealed at a temperature above 400 °C for 1 h in a nitrogen atmosphere. As-deposited films exhibit a lower value of the energy gap typical of the cubic phase.

Although the CBD technique allows the deposition of CdS thin films which are very dense, compact, smooth and without pinholes, the as-deposited films are not suitable for photovoltaic device fabrication when used as an n-type partner with p-type CdTe. An annealing of the film at high temperature is needed for the reasons explained before. The annealing promotes some beneficial changes in the film such as the reorganization in the crystalline structure or the re-evaporation of excess sulfur atoms, but some detrimental effects, like the self-oxidation of the CdS film, were also observed.

Even though the annealing is always carried out in an inert atmosphere, one of the possible oxidation agents is the absorbed water in the film from the bath solution. Another possible mechanism able to explain the oxidation may be the following reaction:



Here some Cd(OH)₂ precipitates in the film during the CBD process and it can change to CdO at high temperature giving water vapor that can cause further oxidation.

When the oxidation produces more than 30% of CdO in the CdS film we see a sharp decrease in the energy gap value. In other words, in a mixture of CdS + CdO one measures always the energy gap of CdO.

In spite of this aspect it is important to notice that, by using a CBD CdS thin film in a CdTe based solar cell, an energy efficiency record was obtained, but an important step of this process consisted in the annealing of the CdS film in an atmosphere containing Ar + 20%H₂ (forming gas). Despite this remarkable result, it must be considered that CBD is not suitable for large-scale production since the deposition process is not fast and gives a waste that needs to be recycled.

3.2. CdS by Close-Spaced Sublimation (CSS)

In Close-Spaced Sublimation (CSS) CdS is sublimed from a solid source (see Fig. 5) [19,20]. The deposition of CdS films by CSS method is based on the reversible dissociation of CdS at high temperature in an inert gas ambient at a pressure in the range 1–100 mbar. The CdS source dissociates into its elements, which recombine on the substrate surface depositing a CdS film. Since the rate of sublimation depends strongly on the source temperature and the gas pressure in the reaction tube, the rate of CdS deposition varies similarly.

The most critical CSS process parameters for the deposition of the CdS film are the substrate/source temperature and the ambient conditions. For an inert gas such as Ar, it was found out that the films contained pinholes for temperatures as low as 400 °C and high deposition rates. Considerable changes in film structure were observed when the depositions were carried out in the presence of O₂. Oxygen may act as a transport agent as well as it can be incorporated in the film to form defect complexes. The use of oxygen was found out to be beneficial since it yields pinhole free films over a wide range of deposition conditions. The presence of O₂ in the deposition chamber, however, reduces the deposition rate and the mean grain size.

As an example, we describe the behavior of several CdS films prepared in our laboratory by CSS both, in pure Ar or in an Ar containing 50% of O₂ at a substrate temperature in the range of 480–530 °C. The CdS film deposition is carried out by putting in a graphite crucible a sintered sputtering-like CdS target. This target is disk shaped and manufactured with 99.999% pure CdS powder. Using a sintered target of CdS as a source any spitting of CdS powder is inhibited and the substrate can be placed directly in front of the source. During the CdS deposition the Ar + O₂ total gas pressure was 50 mbar and the distance between the source and the substrate was around 2–7 mm. The typical deposition rate was 50 nm/min and the time for film preparation was a few minutes for 10–150 nm thick CdS films.

Films prepared in pure Ar even though they exhibit high transparency and a good absorption spectrum were found not to be suitable for the preparation of efficiency CdTe/CdS solar cells.

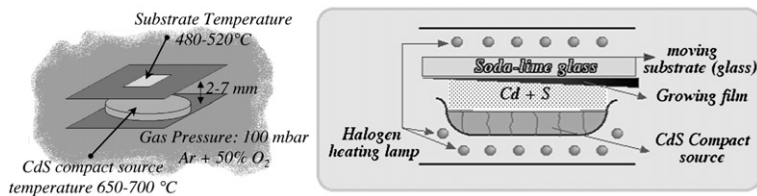


Fig. 5. Outline of the Close-Spaced Sublimation (CSS) system.

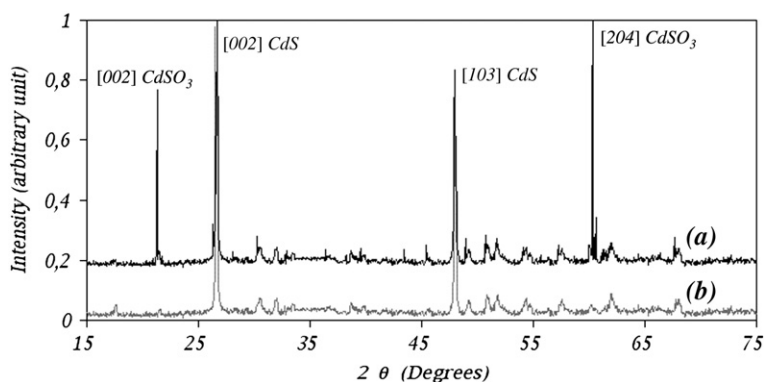


Fig. 6. X-Ray spectra of the CdS layers grown by a CSS technique. (a) CdS films grown with and (b) without O_2 in the deposition ambient. In this picture, in order to make the spectra more legible, we eliminated the reflections belonging to the TCO layers.

Films prepared in $Ar + O_2$ generally contain a large amount of O_2 , both on the surface and in the bulk as it has been seen by X-ray Diffraction (XRD). The XRD spectra were acquired with a diffractometer using $Cu K\alpha$ radiation and CdS, $CdSO_3$ and In_2O_3 standards were used to index the peaks. All the films were found to be of the hexagonal phase which is the stable structure of CdS films deposited at high temperatures (more than $500^\circ C$). Fig. 6 shows an XRD scan in the $15\text{--}75^\circ$ (2θ) range for films prepared in $Ar + O_2$ (top) and pure Ar (bottom). The spectrum of the CdS films prepared in an ambient containing more than 50% of oxygen indicated that a second phase was present, in fact the 21.2° and 60.1° peaks could be associated with monoclinic $CdSO_3$.

The presence of oxygen seems to affect the nucleation process, increasing the number of nucleation sites and promoting a denser growth of the CdS films. These results from the AFM analysis on the surface of a CdS film are shown in Fig. 7. In particular, a fast Fourier analysis has indicated that the average grain size of the CdS films changes from 80 nm for the film grown in pure Ar, to 10 nm for the film grown in $Ar + O_2$. The O_2 content reduces to less than 10% in the surface when the film is annealed for half an hour at $400\text{--}420^\circ C$ in 400 mbar of Ar containing 20% of H_2 . The annealed CdS film is more transparent than the as-deposited one. This can be clearly seen in Fig. 8.

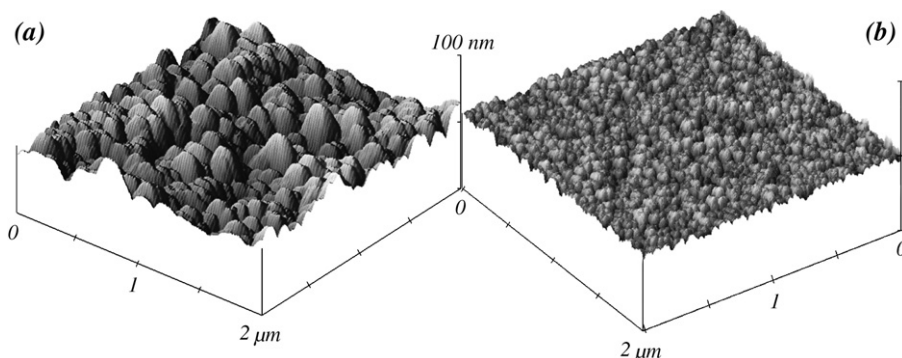


Fig. 7. Atomic force micrograph of the CdS film, deposited by CSS in (a) pure Ar and (b) $Ar + 50\% O_2$ atmosphere. Both the films were 100 nm thick.

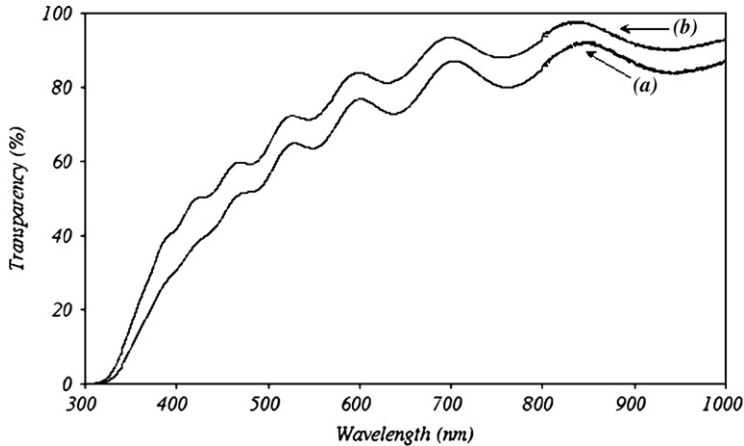


Fig. 8. Transparency spectrum of a 300 nm thick CdS film prepared by CSS in Ar + O₂: (a) As-deposited, (b) after annealing for 30 min at 400–420 °C in 400 mbar of Ar containing 20% of H₂.

Solar cells made with as-deposited CdS films exhibit low short-circuit currents indicating the presence of an insulating layer at the interface between the CdS and the CdTe which could be the CdSO₃ layer seen by X-rays. Solar cells made with CdS annealed in Ar + H₂ always exhibit a good performance with efficiency higher than 14% and a maximum efficiency approaching 15% (solar cell behavior is included in a later section). The beneficial effect of O₂ in preparing CdS by CSS has been also reported by Ferekides et al.

3.3. CdS by R.F. Sputtering

The CdS layers were grown by radio-frequency (R.F.) sputtering at a substrate temperature of about 220 °C, with a deposition rate up to 10 Å/s in an argon atmosphere of 10^{−3} mbar by using a 99.995% pure CdS vacuum cold-pressed target supplied by Cerac Inc. After the deposition, the soda-lime glass covered by the TCO–CdS bi-layer was heat treated in a vacuum chamber at 500 °C for 30 min. The efficiencies of solar cells prepared with this kind of CdS layer are quite poor, in the range of 8–10%. This result is due to the fact that these devices have too high a diode reverse saturation current. One possible explanation is that the interaction between CdS and CdTe is anomalous in that the grain boundaries in the CdS film are active and can channel the diode reverse current.

It is possible to get over this problem by introducing in the sputtering chamber during the CdS deposition argon containing 3% of CHF₃. This gas is decomposed and ionized in the sputtering discharge freeing F ions which, being strongly electronegative, are directed to the substrate that is the positive electrode; here two different events can happen:

- the presence of energetic F[−] ions near the substrate favors the formation of a fluorine compound such as CdF₂ during the growth of the CdS film [20].
- the F[−] ions, accelerated by the electric field present in the discharge, hit the film surface during the deposition with energy sufficient to sputter back the more weakly bonded Cd or S atoms. This effect leaves a CdS film with high quality optical and the structural

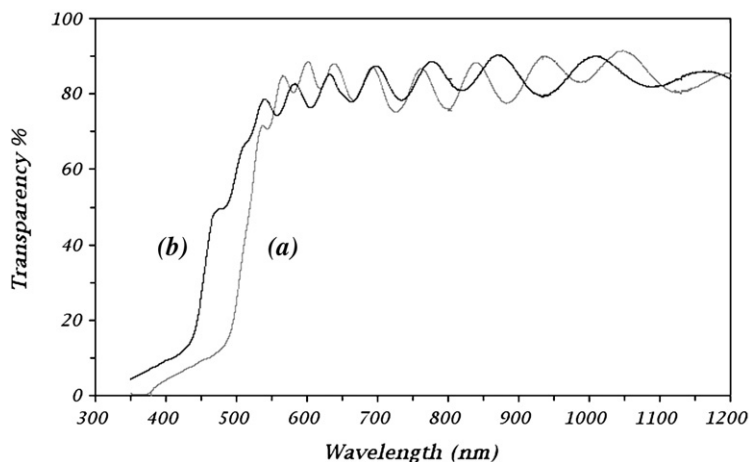


Fig. 9. Transmission spectrum of an 80 nm thick sputtered CdS film: (a) deposited in pure argon and (b) deposited in argon + CHF_3 . The shift toward shorter wavelengths of the absorption edge proves the beneficial effects of deposition in the presence of CHF_3 .

properties. We can see in Fig. 9 that the CdS films deposited in argon + CHF_3 have an energy gap greater than that of the films deposited in argon alone!

Despite the beneficial role of fluorine in the growth of sputtered CdS films, it was demonstrated that fluorine is not an effective dopant in CdS, since no change in the resistivity of the CdS layers was observed. However, solar cells fabricated using 80 nm CdS thick films deposited by sputtering in the presence of fluorine showed a very high efficiency of the order of 15–15.8%. We explain this fact by considering that CdS(F) may contain CdF_2 probably segregated in the grain boundaries. While the CdF_2 segregated in the grain boundaries can be useful to passivate them, the CdF_2 layer grown on the CdS surface may adjust the interaction between CdS and CdTe during the CdTe deposition by CSS.

These remarkable results are shown in Fig. 10 and demonstrate that CdS(F) can be used as-deposited without any other treatment. Probably this fact makes the CdS films deposited by sputtering in the presence of fluorine the best candidates for the industrial production of photovoltaic modules based on the CdTe/CdS thin film technology.

3.4. CdS by “High-Vacuum Thermal Evaporation” (HVTE)

Good photovoltaic devices are also obtained by using evaporated CdS layers. In fact it is possible to evaporate CdS thin films in a high vacuum evaporation chamber at a substrate temperature in the range of 150–200 °C. Graphite crucibles are normally used as evaporation sources in the range of temperatures between 700 and 900 °C. As-deposited, these CdS layers are not suitable for producing high efficiency CdTe/CdS solar cells, since they are not sufficiently stable. For this reason, before the growth of the CdTe layer, CdS films are annealed in vacuum or in a hydrogen atmosphere at 400–450 °C for 30 min. The beneficial effects of this thermal treatment are well known in terms of grain growth, re-crystallization and re-evaporation of stoichiometric excess such as not well bonded Cd and S atoms [40,41]. The as-deposited CdS films change their average grain size from 100–300 nm to 500 nm after the annealing and it appears that the heat treatment

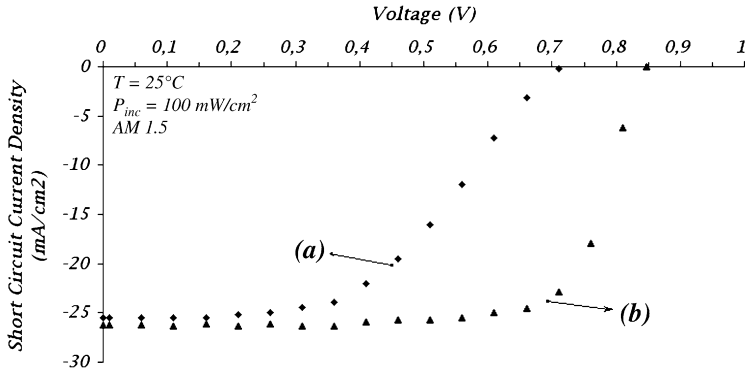


Fig. 10. J versus V characteristics of the CdTe/CdS solar cells taken in standard conditions in our laboratory: behavior of a device obtained by using a CdS layer deposited by sputtering (a) in pure argon and then annealed in vacuum at a 500 °C substrate temperature for 30 min. (b) in an argon + CHF₃ atmosphere.

re-crystallizes the CdS layers in such a way that some of the smaller grains can coalesce together to form bigger grains some 500 nm in width. Despite this, the resulting CdS layer is not so dense as the films obtained by sputtering or CBD and the average thickness of the CdS films used to prepare CdS/CdTe based solar cells is never below 300 nm. Actually, in HVTE CdS films, it is easy to find pinholes if their thickness is below 200 nm. Since it has been widely shown that the CdS layer contributes a negligible photocurrent, it constitutes a photocurrent loss for the wavelength range from 300 nm to 520 nm. This poor photo-response is probably due to the low lifetime of the holes and to a high recombination despite the high absorption coefficient of CdS in the wavelength range of interest ($>10^5 \text{ cm}^{-1}$). The parasitic optical absorption in CdS layer is the predominant loss in photocurrent, making it necessary to minimize the CdS thickness. The highest efficiency CdTe/CdS solar cells are distinguished by their high short-circuit current ($>25 \text{ mA/cm}^2$). This has been achieved using CdS film with a thickness below 100 nm deposited by CBD. It is possible to reduce the CdS film thickness only down to 100 nm whilst maintaining a uniform interface throughout processing in order to avoid the formation of parallel junctions between CdTe and the transparent conductive oxide (TCO), which have a much higher recombination current than CdTe/CdS. In practice, HVTE CdS films are suitable as n-type partners in high efficiency CdTe/CdS based solar cells only if their thickness is greater than 200–300 nm in order to avoid any complication due to pinholes. The use of thin CdS is also complicated by a further reduction in the thickness of the CdS film, which occurs during CdTe film growth or during post-deposition heat treatment. Anyway, devices prepared using HVTE CdS films, thermally treated as described above, with a thickness of about 300 nm show a fairly good performance, exhibiting efficiencies up to 12–13%.

The use of the HVTE technique could find a role in all the processes in which the temperature regimes do not exceed 450 °C. For this reason the HVTE deposition method is attractive for a very simple in-line production of large area CdTe/CdS based solar modules on polymer films [42], facilitating the roll-to-roll manufacturing of flexible solar modules.

4. The CdTe layer

CdTe exhibits a forbidden gap of 1.45 eV very close to the maximum for solar energy conversion. Also its gap is direct and its absorption coefficient is in the range of 10^4 – 10^5 cm^{-1} for

photon energies larger than the forbidden gap. This means that only a few micrometers of material are enough to absorb all the light. A theoretical maximum efficiency over 27% and a practical efficiency of 18.5% could be expected for this material with an open-circuit voltage of 880 mV and a short-circuit current density of 27 mA/cm² (with a negligible thin layer of CdS).

CdTe is one of the few II–VI compounds that can be prepared both p- and n-type, with typical doping like B, Al, In and Ga for n-type and Cu, Ag or group I and V elements for p-type. Doping is rather simple for single crystal samples. The main problem arising with polycrystalline thin films is that all metallic doping can very easily segregate in the grain boundaries giving rise to metallic, highly electrical conducting phases that can shunt the CdTe layer. This segregation problem is still present during preparation of the CdTe film and is present also during exposure to light of the CdTe/CdS based solar cell. Photo-induced diffusion is a very dangerous phenomenon for solar cells, because light gives rise to an enhanced electrical field, which is able to move ions within the lattice at relatively low temperatures. For these reasons, it is usually preferred not to dope these materials using external atomic species. Fortunately, in contrast, CdTe can be grown self-doped by both Cadmium and Tellurium vacancies. The first former (inducing an electrical p-type behavior) is the most favored during CdTe growth at high temperatures (≥ 500 °C). Thus, CdTe and CdS thin films employed in solar cells are usually grown undoped and it is necessary to take particular care with respect to the purity and stoichiometry of the starting materials.

Several methods have been used to deposit CdTe, namely vacuum evaporation and Atomic Layer Epitaxy (ALE) [43,44], Electro-deposition [18,21,45], Chemical Spray Pyrolysis [10], Screen Printing [46,47], Chemical Vapor Deposition or Metal-Organic Chemical Vapor Deposition (MOCVD) [21] and Close-Spaced Sublimation (CSS) [9,21–23,48,49].

High-Vacuum Evaporation: with this technique CdTe films are made by evaporation from a heated crucible and subsequent condensation of CdTe vapor on a heated substrate. Grain size enhancement and re-crystallization by thermal annealing in an ambient of chlorine salt have led to moderate device efficiencies of about 12–13%.

Atomic Layer Epitaxy (ALE): this is a thin film growth method, which is based on sequential chemical reaction on the surface. ALE offers the possibility to grow both CdS and CdTe in a single process. The main characteristics of thin film deposited by this method are the good crystalline quality, very high uniformity over a large area and very low pinhole density.

A low-pressure type ALE reactor involves reactant transport and shuttering using computer controlled inert gas flow. The reactors are typically equipped with four controlled sources for the solid reactants and a certain number of external sources for gas and liquid reactants. The reaction zone normally consists of a 1–3 mm space between 10×10 cm² substrates. Cadmium sulfide films are grown using elemental Cd and S as reactants. The process temperature for the CdS deposition is in the range of 300–500 °C. Using elemental Cd and Te atoms as reactants the process temperature is in the range 350–450 °C.

In order to obtain high efficiency devices a graded layer is processed between the CdS and the CdTe in which the Cd–S–Te proportion is gradually changed from pure CdS to pure CdTe. Solar cells entirely processed by means of the ALE technique have shown efficiencies up to 14%.

Electro-deposition: in electrodeposition, films of CdTe and CdS are formed from aqueous solutions of CdSO₄ and Te₂O₃ at temperatures of around 90 °C. The film deposition may be represented by two steps:

- tellurium reduction $\text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^- = \text{Te} + \text{H}_2\text{O}$
- reaction of deposited tellurium with Cd^{2+} ions in the solution $\text{Te} + \text{Cd}^{2+} + 2\text{e}^- = \text{CdTe}$

The critical variables of this deposition method are the type and the concentration of species present in the solution, the design of the deposition system, the solution temperature and the flow geometry. In order to produce high photoelectronic quality films, a thermal annealing at high temperature for several minutes is needed.

Even though electrodeposition uses relatively cheap equipment the low deposition rate and the health hazards of the toxic components used are aspects that do not correspond to the industrial criteria for large area production.

The best device on a laboratory scale (0.02 cm^2) exhibited an efficiency of 14.2%.

Chemical Spray Pyrolysis: in chemical spraying an aerosol of water droplets containing heat decomposable compounds of Cd, Te and S is sprayed onto a heated substrate forming CdTe or CdS films. The deposition temperature is about 480–520 °C. A CdS film of 6 μm thickness is deposited on top of a commercial conductive soda-lime glass and subsequently 6 μm of CdTe are deposited on top of CdS.

Due to the poor optoelectronic quality of the very small grains typical of the sprayed films device efficiencies produced with these layers are quite low. Since the CdS film thickness is rather high over 20% of the possible photocurrent is lost because 20% of the incident light is absorbed through the window layer. For this reason the maximum solar cell efficiencies obtained by spraying CdS and CdTe are in the range 8–10%.

Screen Printing: this process consists of an initial screen printing with subsequent drying and sintering of first a CdS film and then a CdTe film. In comparison with other technologies, screen printing normally leads to thick layers (10–20 μm instead to some micrometers) and requires very high temperatures for sintering. The sintering is carried out in a furnace in an inert gas atmosphere at a pressure of several bars and at a temperature in the range of 550–750 °C. The CdTe paste is obtained by mixing CdTe powders milled in water, CdCl_2 powder and propylene glycol. In a similar way the CdS paste is prepared. During the sintering process CdCl_2 is evaporated away from the film.

In CdS/CdTe solar cells prepared by this method, after the sintering step, a certain amount of intermixing between CdS and CdTe layers occur as a consequence of the high temperatures (up to 600–700 °C). This is strongly connected with the presence of liquid CdCl_2 , which is used as a sintering flux. Massive intermixing has to be avoided in order to obtain a good photo-response in the short wavelength region of the visible spectrum and then a high photovoltage and photocurrent. The morphology and the crystal structure of the screen printed-sintered solar cells benefit from the particular properties of sintering, such as the high temperature and the presence of liquid CdCl_2 . Despite the micrometers sized grains in contact in the junction region, the final efficiency of the device is quite low and, on a laboratory scale, scarcely reaches 12%. This is principally due to the high thickness of both the layers constituting the junction, which causes losses in photocurrent and a high series resistance inside the active layer.

Metal-Organic Chemical Vapor Deposition: in MOCVD, volatile, thermally decomposable organic compounds of Cd and Te are transported in gaseous form by a carrier gas, in general at ambient pressure (1 bar), toward the heated substrate where they decompose and react to form the CdTe film. In general MOCVD is a complicated process not easily scalable to large area production. Anyway on a laboratory scale a device efficiency of 11.9% was obtained.

All these techniques are able to produce cells with efficiencies larger than 10%. However, the highest efficiency solar cells have been prepared by close-spaced sublimation (CSS).

4.1. CdTe by “Close-Spaced Sublimation” (CSS)

The Close-Spaced Sublimation of CdTe is very similar to that of CdS (see Fig. 5). In our laboratory the deposition is carried out at high temperature in an inert or reactive gas at a pressure in the range 1–100 mbar. This type of deposition is possible because CdTe dissociates into its elements ($2\text{CdTe(s)} \leftrightarrow 2\text{Cd(g)} + \text{Te}_2\text{(g)}$), which can recombine on the substrate to form the CdTe film.

The CdTe deposition can be carried out with the use of a sintered sputtering-like target in a graphite crucible. This target is disk shaped 3.0 in diameter and is manufactured using 99.9999% purity CdTe powder (e.g. provided by Cerac Inc.) which is placed in a graphite crucible inside an oven. Then under a 10 bar N_2 pressure, the temperature is raised up to 1200 °C for few minutes and then slowly lowered to room temperature. As an encapsulant, B_2O_3 is used on top of the CdTe. The use of a sintered target as a CdTe source inhibits spitting of the CdTe so that the substrate can be directly faced to the source. Also, a 3 inch diameter dimension ensures a very uniform deposition because of its wider size with respect to the substrate (1 inch²). The distance between source and substrate is typically 2–7 mm and the temperature of source and substrate are 500 and 600 °C, respectively. With these parameters a 6 μm thick CdTe film can be deposited in 2 min.

As mentioned, a CdS/CdTe junction can never work as a photovoltaic device after deposition of both the layers without further treatment. The lattice mismatch between the two materials is 9.7% and the interface defects can capture the majority of free carriers crossing the junction. The only way to effect the formation of a good device is to create in the junction region a mixed compound, namely $\text{CdS}_x\text{Te}_{1-x}$, between the two active materials. In this way the lattice mismatch is gradually adapted, and the number of defects at the interface can be greatly reduced.

Some of the main advantages of the CSS method for junction formation with respect to the other mentioned techniques are related to the high quality of the as-deposited films, characterized by large crystalline grain size, which means a low defect density. During the CSS high temperature (500–600 °C) deposition of the CdTe layer on top of CdS film, the beneficial intermixing between these two layers begins to take place.

The absorption coefficient of CdTe, in the wavelength range corresponding to the sun light spectrum, is higher than 10^5 cm^{-1} thus a thickness of the film of 1–2 μm could be enough for converting all the visible light completely. Such a thickness would be optimal for both optical and electrical reasons, but in practice it is very hard to achieve without side problems. The grain size of CSS-deposited CdTe films is in the range of 5–10 μm (Fig. 11a). Large grain size and columnar morphology are desirable in order to reduce transverse grain boundaries causing, in part, the recombination of the charge carriers. On the other side with the increase of the grain size there is also an increase in the dimensions of voids between the grains, and the film has to be thicker in order to avoid the presence of pinholes.

The typical thickness of CdTe films deposited in a pure Ar atmosphere is around 8–10 μm and, in spite of the thickness, the problem of pinholes is present. The problem is partly solved by increasing the Ar pressure up to 100 mbar. The deposition rate can be kept at high levels, around 20–30 nm/s, by simply raising the temperature of the CdTe source. The higher pressure allows a more uniform heat distribution, a greater diffusion of the Cd and Te vapors and a smaller re-evaporation of the growing film from the substrate. The resulting CdTe films are flatter, denser, with smaller grain size and with less problems of shunting. Since the substrate temperature is fixed to a maximum value of 520 °C, if soda-lime

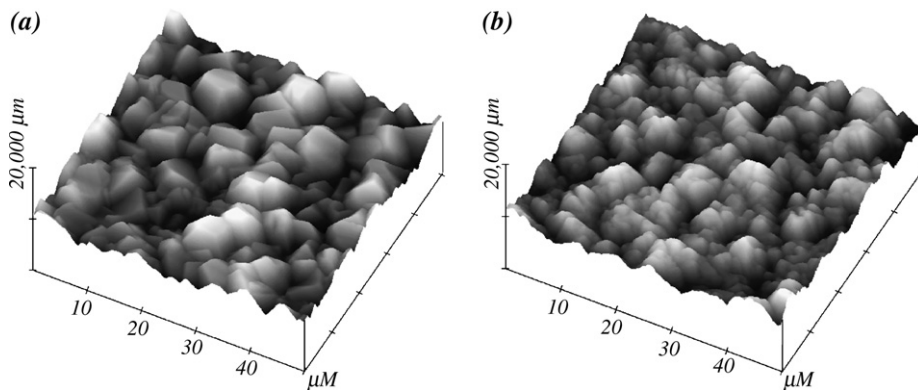


Fig. 11. AFM (Atomic Force Microscope) picture of two CdTe layers deposited at 500 °C substrate temperature by CSS technique with 650 °C source temperature. (a) Ambient: pure Ar; total pressure: 1 mbar; average grain size $\approx 10 \mu\text{m}$. (b) Ambient: Ar + O₂; total pressure: 1 mbar (Ar) + 1 mbar (O₂); average grain size $\approx 2\text{--}3 \mu\text{m}$.

glass is used, one of the most important parameters which can control the formation of the CdS_xTe_{1-x} layer, is the re-evaporation from the substrate at the beginning of the deposition. If the CdTe film grows on top of the CdS layer too quickly (very low re-evaporation) the intermixing between CdS and CdTe has not the time to be effective. For this reason the resulting devices show a poor performance, which are characterized by low photovoltages and fill factors with maximum efficiencies below 10%.

Many research groups have found that CdTe films grown by CSS enhanced their crystalline and electro-optical quality if the deposition is carried out in Ar + O₂ atmosphere. The effect of oxygen on the CdTe growth is very strong: it increases the CdTe conductivity and reduces the grain size making the film more compact allowing the use of thinner films about 4–6 μm thick. By varying the oxygen percentage from 1 to 100% with respect to the total Ar + O₂ atmosphere it is possible to adjust the interaction between the CdS surface and the arriving Cd and Te atoms at the beginning of the deposition. In other words, independent of the total pressure, in the presence of oxygen there is a change in the equilibrium between the CdTe sticking coefficient and the surface diffusion coefficient. Oxygen makes more stable the presence of Cd and Te atoms on the CdS surface due to its tendency to form compounds with both Cd and Te. These compounds, such as CdO and TeO₂, have chemical stability intermediate between that of CdTe and CdS and they play an important role on the surface diffusion of the impinging atoms. In fact, in the presence of O₂, the reaction between Cd and Te atoms is lowered and Cd and Te have more time to diffuse along the substrate before recombining to produce a less defective CdS_xTe_{1-x} intermixed layer. This starting point affects the nucleation process, increasing the number of nucleation sites and promotes a denser growth for the whole CdTe film. This can be seen also from the AFM analysis made on the surface of CdTe film as it is shown in Fig. 11b. In particular, a fast Fourier analysis has indicated that the average grain size of the CdTe films changes from 10 μm for the films grown in pure Ar, to 2–3 μm for the films grown with Ar + O₂. XRD spectra acquired with a diffractometer using Cu K α radiation, show that the as-deposited CdTe films (Fig. 12a and b) always exhibit the (002) hexagonal preferred orientation. CdTe films prepared in Ar + O₂ generally contain a very small amount of CdTeO₃ which crystallizes with a monoclinic structure, probably by segregating inside the CdTe grain boundaries (Fig. 12a).

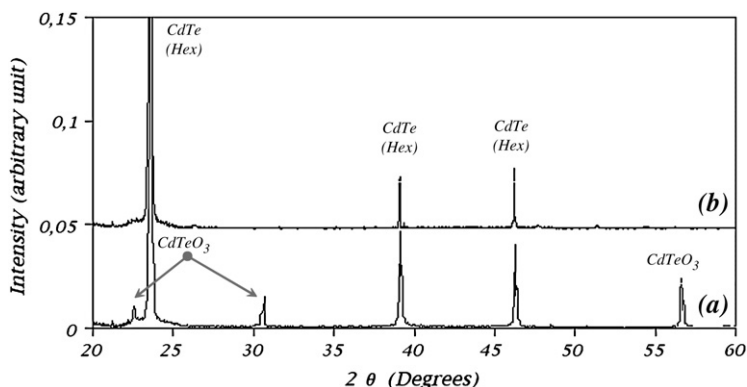
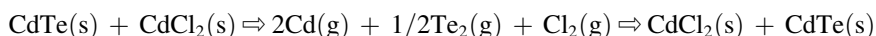


Fig. 12. X-Ray spectra of CdTe layers grown by the CSS technique. (a) CdTe films grown with and (b) without O₂ in the CSS deposition chamber. In this picture, in order to make the spectra more legible, the CdTe peaks belonging to the (002) orientation have been removed.

5. The heat treatment in a chlorine ambient

Treatment in the presence of Cl₂ is necessary, independently from the technique used to deposit CdTe, in order for the solar cell to exhibit high efficiency. If the CdCl₂ treatment is not performed, the short-circuit current of the solar cell is very low and also the efficiency is very low. This treatment is generally carried out by depositing a CdCl₂ film on top of CdTe by evaporation or by dipping the CdTe layer in a solution of CdCl₂–methanol and with a subsequent annealing at 400 °C in air or in an inert gas such as Ar [50,51]. One of the most serious problems encountered by using this material is that it is very hygroscopic (and toxic), thus it is better not to keep films in air at room temperature for a long time. During the annealing the small CdTe grains re-crystallize giving a better-organized CdTe matrix following possibly the process:



The presence of Cl₂ could favor the crystalline growth of CdTe by means of local vapor phase transport. In this way the small grains disappear and the CdS/CdTe interface is re-organized. This reaction seems to be strongly temperature dependent, with a marked sensitivity over some tens of degrees around 400 °C. It is independent of the thickness of the CdCl₂ layer (over 100 nm), from its uniformity and from the duration of the annealing (over 10 min). If the process is carried out in air, some oxides are formed on the CdTe surface. These oxides need to be removed before making the back contact by using an acid etch or by cleaning in a solution of Br–methanol. The introduction of oxygen, into the CSS chamber during the deposition of CdTe layers, enables one to carry out the CdCl₂ thermal treatment at the same temperature but in an inert gas atmosphere such as Ar or N₂. This fact is very important because the presence of oxygen during the CdTe deposition or during the CdCl₂ treatment can increase the number of p-type majority carriers. Generally, the presence of oxygen results in CdTe films having a lower resistivity compared with the films prepared under a pure Ar atmosphere, typically with a carrier density of the order of 10¹⁴–10¹⁵ cm^{−3}. Moreover, in case of annealing in Ar, the films do not show any oxide layer and thus no chemical etching is needed. Also the rinsing

in methanol can be avoided, because the CdCl_2 residues can be easily removed by evaporation by evacuating the annealing chamber. This is a very remarkable innovation for the CdTe/CdS based solar cells fabrication process since a wet stage is eliminated. In fact, in an in-line large area photovoltaic module production, any use of acids or liquid solutions is best avoided in order to not interrupt the process and also for safety considerations.

From an industrial production perspective we discovered another method for making the Cl_2 -treatment, which does not use any CdCl_2 [52]. The CdTe/CdS structure is put in an ampoule which is evacuated. A mixture of 100 mbar of Ar and 20 mbar of a non-toxic gas containing Cl_2 such as HCF_2Cl (difluorochloromethane) is introduced into the ampoule. The temperature of the ampoule is raised to 400 °C, an annealing of ≈ 5 –10 min is carried out and then the ampoule is evacuated again. After the treatment the CdTe morphology is completely changed due to an increase in the size of the small grains. Since HCF_2Cl decomposes at 400 °C and CdTe starts to decompose at around 400 °C, we suppose that the following process happens especially for the small grains that are the first ones to decompose:



By keeping a vacuum for a few minutes at a temperature of 400 °C the CdCl_2 formed on the CdTe surface by the above treatment re-evaporates leaving a clean CdTe surface ready for the back contact. The Cl_2 -treatment can be made with any gas of the Freon family. The only need is that the gas contains chlorine. This method is very effective in producing high efficiency cells. It avoids the use of CdCl_2 that could be dangerous and instead it uses a gas that is stable, inert and non-toxic at room temperature. Besides it eliminates the CdCl_2 evaporation step and, as a consequence, it is much more suitable for an industrial production. This process has been patented [53].

6. The back-contact problem

Most researchers make the contact on p-type CdTe films by using Cu-containing compounds, such as a Cu–Au alloy, Cu_2Te , ZnTe:Cu or Cu_2S [10–14]. It is believed that Cu is necessary to make an ohmic contact on p-type CdTe. In fact, copper, by diffusing into CdTe lowers its resistivity and for a while it gives a higher solar cell performance. Moreover CdS/CdTe solar cells made with contacts not containing Cu behave as if they have a high series resistance. A possible explanation of this behavior is that the series resistance does not come from the contact but from CdTe which possibly is more conducting at the interface than in the bulk. The higher conductivity close to the interface could come from the fact that CdTe mixes with CdS and lowers its gap. It must be considered that the highest efficiency solar cell so far reported has been made with some copper at the back contact.

Before depositing Cu, an etching in Br–methanol or in a mixture of $\text{HNO}_3/\text{HPO}_3$ acids is carried out in order to enrich the CdTe surface with Te. In this manner a Cu_2Te thin film can be formed, which could limit the copper diffusion into the CdTe film. The back contact is then completed with graphite paste. This type of back-contact works quite well but it introduces another drawback, that is, it provides the possibility for copper atoms to diffuse through the grain boundaries reaching the junction where they could create shunting paths. For this reason, if the solar cell has to live 20–30 years, copper must be avoided. This problem is completely solved at the University of Parma (Italy) where a new contact was developed, namely Sb_2Te_3 , which is a low gap (≈ 0.3 eV) compound, is p-type and exhibits a very low

resistivity ($2 \times 10^{-4} \Omega \text{ cm}$) when it is deposited by sputtering at a substrate temperature of 300°C [54]. Sb_2Te_3 can be deposited easily by sputtering, but it can also be deposited by vacuum evaporation. From the point of view of the process simplicity, it offers an important simplification by eliminating the need for etching of the film surface before making the contact. The Sb_2Te_3 as back contact does not require a Te-rich surface on top of the CdTe.

There are two reasons why the CdTe surface is etched before the deposition of the back contact. The first one is to remove the oxygen compounds that form on top of the CdTe film due to the fact that normally chlorine treatment is carried out in air. The second reason is to form a Te-rich surface that could be highly p-type conducting thus facilitating the formation of a good contact or to stop in some way the diffusion of the metal that is used as a contact since the metal can form a compound with Te. The first reason is removed when the chlorine treatment is performed in an Ar atmosphere. The second one is removed by using Sb_2Te_3 as a back contact since this semiconducting material contains Sb, a group V element, which if it dopes CdTe close to the surface, it dopes p-type.

In fact, it was verified that Sb_2Te_3 makes an ohmic contact with p-type CdTe thin films and was also found out that Sb_2Te_3 makes an ohmic contact on a p-type CdTe single crystal whose resistivity was of the order of $10^5 \Omega \text{ cm}$ [17]. Actually the back contact is completed by depositing, by D.C. sputtering, 100 nm of Mo or W. Furthermore the quality of the Sb_2Te_3 back contact has been investigated by studying the behavior of the current–voltage characteristics of the CdTe/CdS based solar cells over a period of 6 months by keeping the devices at 60°C in a dry ambient, under 10 suns under open-circuit conditions. Under these conditions no appreciable degradation of cells performance has been noticed apart from a slight increase in the open-circuit voltage (10–30 mV) while the fill factor suffered a decrease which after repeated tests was never greater than 1%. So we can conclude that it is possible to make very stable high efficiency CdS/CdTe polycrystalline thin film solar cells by using Sb_2Te_3 as back contact on p-type CdTe films.

7. The CdTe/CdS solar cell

The schematic structure of today's typical CdTe/CdS polycrystalline thin film solar cell is shown in Fig. 13. The cells are in the super-strate configuration, with light coming to the junction through the substrate [2,55,56].

Afterwards it is possible to draw up the list of all the layers that constitute the cell including the substrate:

- The substrate can be soda-lime glass (SLG, the common window glass) or special alkali-free glass. The choice of alkali-free glass assures no diffusion of pollutants species into the overhanging films and allows more freedom in cell processing, having a higher softening temperature. On the other side it is quite expensive, thus research oriented to large-scale production employs SLG, despite the problem of sodium or potassium diffusion and that of the lower softening temperature.
- The front-contact layer is commonly made of a TCO such as ITO (indium tin oxide), IFO (fluorine doped indium oxide) or FTO (fluorine doped tin oxide). On top of this electrical conductive layer are often deposited a few nanometers (50–200) of a buffer layer such as pure TO (tin oxide), ZnO (zinc oxide) or Ga_2O_3 (gallium oxide) which has the role of a shield against the probable diffusion of Na and K atoms. Generally, these layers are rather resistive showing electrical resistivity in the range of 10^2 – $10^5 \Omega \text{ cm}$; for this reason they

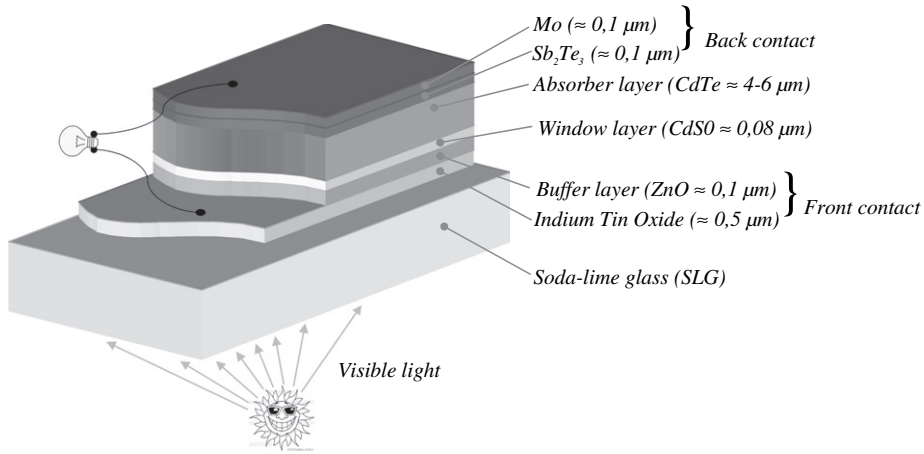


Fig. 13. Schematic of the CdTe/CdS solar cell structure.

are also effective in preventing an increase of the junction reverse saturation current (J_0) if some pinholes are present in the subsequent very thin CdS film [57].

- The window layer, that is the CdS film, represents the n-type part of the junction. In highly efficient CdTe based solar cells the CdS films are deposited either by CSS (CdS:O) or by sputtering (CdS:F). In order to maximize the solar cell photocurrent it is necessary to minimize the CdS film thickness and this is helped by the buffer layer presence between the CdS and the TCO films. Typical CdS layer thickness is in the range of 70–120 nm.
- In efficient CdTe/CdS solar cells, CSS (Close-Spaced Sublimation) is the most popular technique used to deposit 4–7 μm thick CdTe films. This deposition method is particularly suitable for large-scale application since it is very fast (only 1 or 2 min are needed). Best cell performance is obtained if the CdTe films are grown in an oxidizing atmosphere.
- A heat treatment is usually carried out for all the system, as described before, at 380–420 $^{\circ}\text{C}$ in a medium containing chlorine (typically Freon gas). The treatment involving Cl_2 is typical for CdTe/CdS based solar cells since it is needed in order to re-crystallize the nano-grains, if they are present, and to remove structural defects inside the CdTe film.
- If the goal to be reached is the long-term stability of the device and not the worldwide efficiency record, the best suited back-contact has so far been made by depositing 100 nm of Sb_2Te_3 by sputtering on top of the CdTe layer in order to obtain a stable and ohmic contact [54,58]. The contact is well finished by depositing a metallic electrode that is a 100 nm thick Mo or W film, in the same sputtering chamber in which the Sb_2Te_3 layer is deposited.

On average, the efficiency of the cells made under similar conditions, by using the layers described above, is in the range of 15–15.8%. At Parma's laboratories this efficiency has been measured with an OrielTM solar simulator under 100 mW/cm^2 incident power and AM 1.5 solar light spectrum. The measurement system has been calibrated with a 14% efficient CdTe/CdS thin film solar cell previously certified at the Renewable Energies Unit of the Joint Research Centre, Ispra, Italy. A J versus V characteristic of a CdTe/CdS polycrystalline thin film solar cell fabricated in our laboratory is depicted in Fig. 14. Typical parameters of this

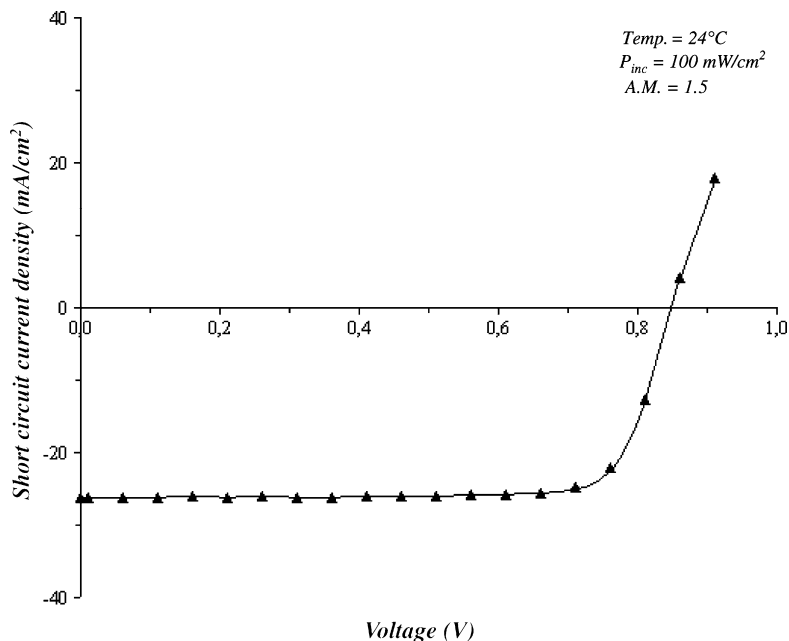


Fig. 14. J – V characteristic of the best all dry-processed CdTe/CdS based solar cell fabricated at Parma (Italy) University.

device are: an efficiency of 15.8% with a V_{oc} (open-circuit voltage) of 862 mV, a J_{sc} (short-circuit current density) of 25.5 mA/cm² and an ff (fill factor) of 0.72.

In order to obtain high efficiency solar cells with a high fill factor, as we have described in a previous section, it is necessary to deposit CdTe by CSS in the presence of O₂. Moreover the efficiency of the solar cell depends on the amount of O₂ in the CSS chamber, on the substrate temperature during the deposition and on the Cl₂ annealing temperature. A high content of O₂ or a high chlorine annealing temperature tends to give a higher fill factor and a lower open-circuit voltage. The short-circuit current is generally not affected except in the case in which a very large amount of O₂ and/or a high Cl₂ annealing temperature is used. In extreme cases the short-circuit current density could be much lower than 25 mA/cm². When a high substrate temperature, namely 520 °C, is used during the CdTe deposition, the fill factor tends to decrease since, at this temperature, less O₂ is incorporated in the film. In order to interpret these results, we made the hypothesis that O₂, mixing with CdS and CdTe reacts to form at the interface a mixed compound containing Cd, S, Te and O with a forbidden gap close to that of CdTe which is n-type. In this way a pseudo-homojunction is formed between this compound and p-type CdTe and this can explain the strong increase in the fill factor. This hypothesis is corroborated by several facts.

First the I – V characteristic in the dark exhibits an A diode factor close to 1 (where A is given in the diode formula $J = J_0 \exp[(eV/AkT) - 1]$). An A factor close to 1 is typical of a homojunction.

When a high content of O₂, namely more than 10%, and/or a high chlorine annealing temperature, namely more than 420 °C, are used, the short-circuit current density is much lower than 25 mA/cm² despite a high open-circuit voltage and principally a high obtained fill factor (0.74–0.75).

Probably due to a strong intermixing, favored by the oxygen presence, a thick n-type layer, larger than the absorption length of the visible light, is formed and a good fraction of the carriers created by the photon absorption, do not reach the junction region. As a consequence, the amount of O_2 used during the CdTe deposition is very important in order to control the formation and the thickness of this presumed n-type layer. The formation of an n-type thick layer has been confirmed by measurements of the photocurrent as a function of wavelength: when the solar cell exhibits a J_{sc} much lower than 25 mA/cm^2 the photocurrent response drops very quickly for wavelengths shorter than that corresponding to the gap of CdTe.

It has also been reported that oxygen in the presence of chlorine enhances the concentration of Cl_{Te} which is a donor for CdTe and can form an n-type CdTe(S,O) layer at the interface [59].

8. Manufacturing of CdTe/CdS based PV modules

The techniques, which are used to make CdTe/CdS based solar cells, are CSS and sputtering, both are fast and easily scalable. A possible in-line process is shown in Fig. 15 [60,61]. Modules of $0.6 \times 1.2 \text{ m}^2$ can be covered with a cycle time of a few minutes. The soda-lime glasses move on a rail, travel into nine process chambers and leave the production machine when they are completely transformed into photovoltaic modules. In fact, the soda-lime glasses enter in a washing and drying machine after which they are heated up to 400°C and go into a sputtering chamber, where the front contact films

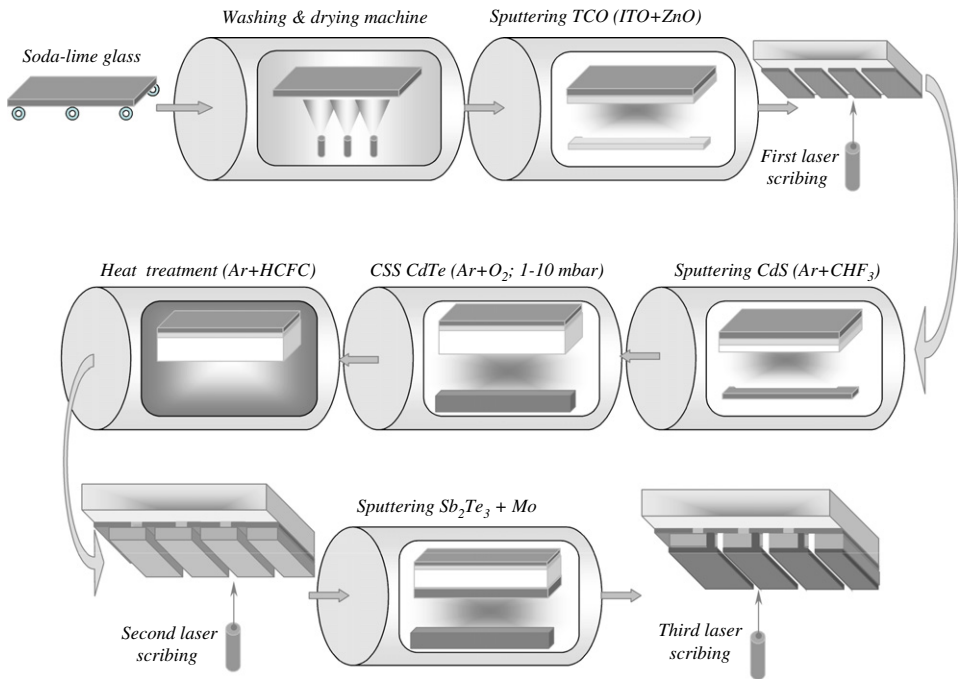


Fig. 15. Flow diagram of a possible in-line dry process for the production of CdTe/CdS based PV modules.

(TCO), 0.5–0.6 μm thick, are deposited. The temperature is decreased again to RT and a laser scribing is carried out in order to eliminate the TCO along parallel lines 1 cm distant one from each other and 40–60 μm large. The temperature is then raised up to 250 $^{\circ}\text{C}$ and 60–80 nm of CdS are deposited by reactive sputtering in an Ar + CHF_3 atmosphere. In sequence, the substrate temperature is raised up to 500 $^{\circ}\text{C}$ and 4–6 μm of CdTe are deposited by CSS. In a subsequent chamber, an HCF_2Cl treatment at 400 $^{\circ}\text{C}$ substrate temperature is carried out, for 1–2 min and then, at the same temperature, there is an annealing in vacuum for a few minutes. After decreasing the temperature to RT, a second laser scribing is done in order to remove CdS and CdTe in parallel lines as close as possible to the ones made before and equally large. Now the glasses enter in a sputtering chamber where 100 nm of Sb_2Te_3 are deposited at a substrate temperature of 300 $^{\circ}\text{C}$. In sequence 100 nm of Mo are sputtered on top of Sb_2Te_3 in order to increase the conductivity of the back contact. Finally a third laser scribing is carried out in parallel lines close to those made by the second laser scribing in order to have a module made up of solar cells 1 cm large and as long as the length of the glass all put in series (Fig. 16).

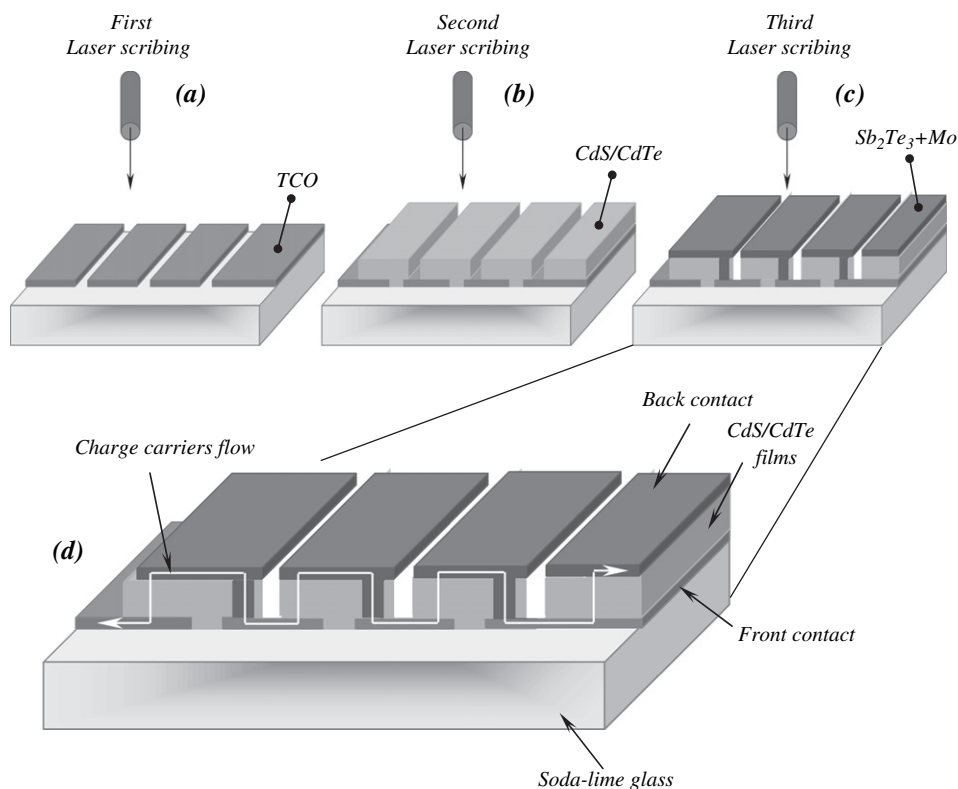


Fig. 16. Typical interconnects scheme for a CdTe/CdS based solar cell module. (a) Laser scribing of the TCO film. (b) Laser scribing of the active layers (CdS/CdTe). (c) Laser scribing of the back contact/active layers. (d) Enlargement of a schematic PV module in which the series electrical connections between all the solar cells constituting the module and the charge carrier path through the cell interconnections are visible.

The technology to fabricate CdTe/CdS thin film solar cells can be considered mature for a large-scale production of CdTe based modules. Several reasons contribute to demonstrate this assertion:

- 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 × 1.2 m² modules.
- Low cost soda-lime glass can be used as a substrate.
- 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.

The fabrication process can be completely automated and a production yield of one module every 2 min can be obtained, which implies a production cost substantially less than 1€/W_p (W_p = Peak Watt).

Nowadays, there are two companies producing CdTe/CdS modules namely First Solar in the United States and Antec Solar in Germany, but it is possible to simplify further their process in order to make it easier and more scalable for a larger scale. For planning a new production line it is essential to consider also the last process innovations that are principally developed at the University of Parma [62], such as:

- A new way of depositing CdS, namely sputtering in the presence of CHF₃.
- A gas such as CHF₂Cl instead of CdCl₂ for treating CdTe.
- A vacuum heat treatment of the CdTe film surface eliminating the etching step from the module fabrication process.
- A new ohmic and stable contact for p-CdTe films, that is, Sb₂Te₃.

9. Closing remarks

In this paper we explain that high-energy conversion efficiency of CdS/CdTe thin film solar cells cannot be achieved with hetero-junctions where the space charge is about equally distributed between the window and the absorber layer. In fact, in CdTe based solar cells the materials and processing have to be self-adjusting in a manner that the conductivity type is inverted into the absorber layer surface giving the possibility to make a homojunction. In this way the photocurrent becomes a majority carrier current before passing through the metallurgical interface [63]. The type-inversion is obtained by considering the inter-diffusion between the window and absorber layers that is greatly influenced by the heat treatment in chlorine ambient. Besides, the grain boundaries of the CdTe polycrystalline film are self-passivated since, during the CdTe growth, a segregation of an insulating material takes place and this prevents the recombination of the photo-generated carriers.

Taking into account these considerations we worked to make a simplified industrial in-line production of photovoltaic CdS/CdTe based modules and we discovered several process innovations regarding the solar cell fabrication.

These discoveries together with the intrinsic properties of the selected materials constituting the CdTe based PV module make possible the concept of a manufacturing plant as a single in-line thin film-processing unit.

The core of the deposition line can be fully automated with minimal human interference.

Only the module-finishing part components (lamination, external electrical contacting, support frames) will be manually handled.

Nowadays, considering these assets, CdTe/CdS based thin film technology is the only one that allows one to develop a mass production of PV modules so cheap ($<1\text{€}/\text{W}_\text{p}$) as to make PV's competitive on the energy market.

The last question that we want to point out is the environmental and health aspects linked to the cadmium presence in the CdS/CdTe based modules. Since CdTe PV's reached commercialization, some problems were raised about potential cadmium emission from CdTe PV modules. First of all cadmium telluride is not cadmium alone. The basis of the stability of CdTe is its extremely high binding energy of 6 eV per atom. For this reason the melting point of CdTe is at quite high temperature (around 1041 °C) and the material starts to evaporate at 1050 °C at atmospheric pressure. In case of fire, the covering glass melts sealing everything. This experiment has already been carried out and a great number of studies have shown that no environmental impact due to CdTe based PV is expected especially if proper life-cycle management system is provided by suppliers. In fact, recycling the modules at the end of their usual life would completely resolve any environmental concern [64–67].

From this point of view, we can conclude by asserting that during a useful life of 20–30 years, these modules do not produce any pollutant, and furthermore, by displacing fossil fuel and by the trapping of the Cd in a more stable form, they offer great environmental benefits!

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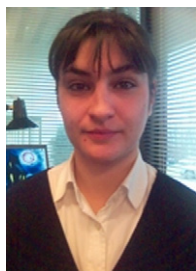


Dr. Alessio Bosio has been working on photovoltaics since 1984. Since then, he is co-author of more than 60 papers on CdTe/CdS and CuInGaSe₂/CdS thin film solar cells in international specialised journals and conference proceeding. He participated to almost all the European Joule Projects in the research group directed by Prof. Nicola Romeo. He is an expert in thin film deposition techniques, such as Electron Beam Gun (EBG), sputtering, Close-Spaced Sublimation (CSS) and vacuum thermal evaporation (VTE). He projected and optimised some deposition equipment like CSS and Selenization Chamber Reactor that are used to obtain high efficiency CuInSe₂/CdS and CdTe/CdS based thin film solar cells. He teaches “Thin Film Deposition Techniques” at the Science Faculty of the University of Parma since 1999.



Prof. Nicola Romeo has been working on photovoltaics since 1976. He made the first Cu-GaSe₂/CdS solar cell with a 5% efficiency. Since then, he has published more than 100 works on CdTe/CdS and CuInGaSe₂/CdS thin film solar cells. He participated for 8 years to the Energy Finalised Project and to almost all the European Joule Projects. He was able to obtain CdTe/CdS (2) and CuInSe₂/CdS thin film solar cells with efficiency around 15%. He is the director of a research group since 1976 and he teaches Physics at Science Faculty of the University of Parma since 1970. As an expert in CdTe/CdS thin film solar cells he delivered an invited talk to the European Material Science Conference held in Strasbourg (France) on the back contact in CdTe/CdS thin film solar cells. In 1981 he has worked for 9 months as a visiting professor at Stanford University.

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His activity is proved by more than 50 works published on national and international journal and conference proceedings in which he is co-author together with the other members of the research group.