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*Original*

Past, present and future of the thin film CdTe/CdS solar cells / Bosio, A.; Rosa, G.; Romeo, N.. - In: SOLAR ENERGY. - ISSN 0038-092X. - 175:(2018), pp. 31-43. [10.1016/j.solener.2018.01.018]

*Availability:*

This version is available at: 11381/2838566 since: 2021-03-18T16:40:39Z

*Publisher:*

Elsevier Ltd

*Published*

DOI:10.1016/j.solener.2018.01.018

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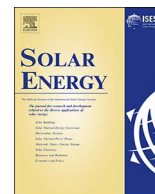
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25 April 2024



Contents lists available at ScienceDirect

## Solar Energy

journal homepage: [www.elsevier.com/locate/solener](http://www.elsevier.com/locate/solener)

## Past, present and future of the thin film CdTe/CdS solar cells

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## ARTICLE INFO

## Keywords:

Thin film  
Solar cell  
CdTe  
Chlorine treatment  
Energy conversion efficiency

## ABSTRACT

Recently, the CdTe solar cell technology reached a high-tech level able to realize devices showing efficiencies close to 22%. Nowadays, this technology acquires more and more market share, becoming the most promising among the thin film technologies. These important achievements are the result of more than 40 years of studies and researches that have synergically group together the photovoltaic module manufacturing technology with semiconductor and interfaces physics, modeling, characterization and measurements on electronic devices.

This paper shows the main steps of the production process of the thin film CdTe/CdS-based solar cells both from a technological and from a physical point of view.

In particular, the main differences between cells fabricated in superstrate and in substrate configuration will be highlighted. For each of these two structures the fundamental layers, their main alternatives, chemical and thermal treatments, interfaces, the won challenges and the still open-problems will be presented and discussed.

## 1. Introduction

Global annual Photovoltaic (PV) power production is expected to reach 500 GW by 2020 (75 GW in 2016) making this one the fastest growing markets. As a consequence, the PV market is a billion dollar sector in which China is the leader both for solar cells production and for yearly installed capacity. Concerning the installed PV plant Germany, USA, India, Japan and Italy follow in this order. At the same time, research has taken giant steps in this field by developing easier manufacturing processes to market cheaper, more efficient and customer-friendly modules.

In addition to classical monocrystalline and multicrystalline solar cells novel techniques such as nanocrystalline, metamorphic multi-junction, organic processing, thin film and others will pay an important role in the future development of a more and more innovative material and efficient solar cell. Thin-film (TF) photovoltaic has proven its low-cost potential since many years and large area modules, based on cadmium telluride (CdTe) and copper indium-gallium diselenide (CIGS) technologies, are on the market with efficiencies up to 17% providing output power well above 125 W and 175 W respectively (<http://www.firstsolar.com/Modules/Series-4>; <https://www.solar-frontier.eu/en/download/products/>) when measured in Standard Conditions (STC). Nowadays, these modules are sold at a price that makes them competitive with the fossil energy sources. In fact, the so-called Grid-parity has been achieved in many countries, and not just for the solar heavily-irradiated countries such as the Mediterranean area.

CdTe, the most commercial successful TF technology, puts its

fortune into some particular physico-chemical peculiarities: (1) direct energy band gap of 1.45 eV close to the maximum of the solar spectrum, (2) absorption coefficient in the visible part of the solar spectrum in the range of  $(10^4 \div 10^5) \text{ cm}^{-1}$ , which means that 1  $\mu\text{m}$  thick layer is enough to capture all the visible light, (3) it exhibits a high formation enthalpy ( $100 \text{ kJ mol}^{-1}$ ), which means a great thermodynamic stability, (4) it sublimes and evaporates congruently by means of the equilibrium reaction  $\text{CdTe} \rightleftharpoons \text{Cd} + \frac{1}{2} \text{Te}_2$ . The high stability and the congruent evaporation allow the growth by means of very different preparation methods. (5) it naturally grows with intrinsic stoichiometry defects that make it moderately p-type, (6) post-growth treatment reduces defects, increases crystalline quality making grain boundaries electrically inactive.

All these remarkable qualities were well-known since the '50s, when CdTe was deeply studied as absorber material in solar cells (Loferski, 1956). It took at least another 20 years to make the first all thin film solar cell exhibiting a modest 6% efficiency (Bonnet and Rabenhorst, 1972). Step by step thin film technology was refined and in 1982, an efficiency of 10% was exceeded (Tyan and Perez-Alburne, 1982), which was considered a threshold value for the large-scale development of this technology. After about another 10 years the efficiency rises up to 15% (Britt and Ferekides, 1993) and only in the last decade the efficiency passes from a 16% (Wu et al., 2001) to 22.1% (<http://investor.firstsolar.com/releasedetail.cfm?ReleaseID=956479>) as reported in NREL's most recent "Best Research Cell Efficiencies" reference chart ([www.nrel.gov/ncpv/images/efficiency\\_chart.jpg](http://www.nrel.gov/ncpv/images/efficiency_chart.jpg)).

From the beginning, the high efficiency solar cell was based on CdS

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<https://doi.org/10.1016/j.solener.2018.01.018>

Received 8 October 2017; Accepted 8 January 2018  
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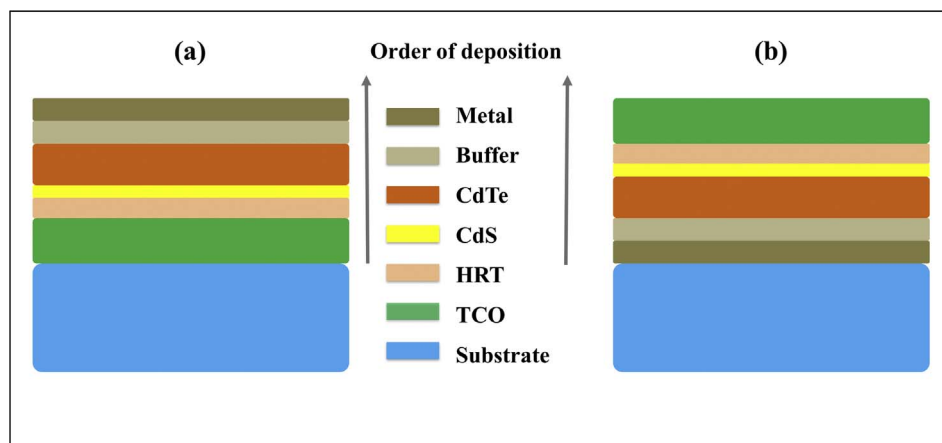


Fig. 1. Not in scale view of the sequence layers in a CdTe thin-film solar cell with highlighted the order of deposition: (a) superstrate configuration, (b) substrate configuration.

as *n*-type partner for the junction formation with the *p*-type CdTe absorber. A lot of the early work on the solar cell was concentrated on the growth of the layers and on the formation of the junction, but it became immediately clear that the technique used for the deposition of the absorber and for the formation of the junction was not of primary importance. Post-deposition process had to be applied to the as-deposited CdTe/CdS layer stacks. An high temperature (about 670 K) heat treatment in Chlorine ambient was discovered to be necessary in order to reach a material crystalline quality good enough to obtain high efficiency devices. Previous work, during the 1970s, on the II-VI single crystals growth in halogen ambient (Paorici et al., 1972, 1973) was crucial for understanding the consequence of the CdTe/CdS stack treatment in chlorine atmosphere.

After that, the attention of the researchers focused on the other layers: first was improved the front-contact, both from transparency and from chemical stability point of view. Indium tin oxide (ITO), aluminum doped zinc oxide (ZAO) and fluorine doped tin oxide (FTO) were replaced by cadmium stannate (CTO), which is a very high conductive and transparent material (Wu, 2004). Moreover, a second low-conductive and high-transparent layer was added in order to improve the stability of the front-contact. CTO was coupled with a thin layer of zinc stannate (ZTO), while ITO, ZAO and FTO are commonly used with a pure ZnO or alternatively a pure SnO<sub>2</sub> thin layer. The use of these (100 ÷ 200) nm-thick high-resistivity transparent (HRT) layers can hinder the diffusion of impurities from the underneath transparent conducting oxide (TCO) and/or from the substrate. Furthermore, due to their relatively high resistivity, HRT layers reduce the shunt effect, which could come from pinholes in the very thin CdS film.

Secondly, due to the high electron affinity exhibited by *p*-type CdTe, a low-resistance and ohmic electrical contact on the surface of the CdTe film is very difficult to obtain. Different methods are performed but all of these are based on the Te-rich preparation of the surface of the CdTe layer and consequent doping with copper or mercury. Despite this was considered the best way for solving the back-contact problem, some drawbacks were immediately highlighted; copper is a very fast diffuser into the grain boundaries of the CdTe film causing, in the worst case, the short circuit of the junction.

Only with a very fine optimization of the back-contact formation (surface preparation of CdTe layer, copper thickness, annealing temperature and time), the stability over-time issue was settled and in 1990s solar cells, with the impressive efficiency of 15.8% (Britt and Ferekides, 1993), were realized.

In the following 10 years, the efficiency of the devices progressed slightly reaching, however, a good 16.7% (Wu et al., 2001). In the last decade, thanks to the deep modeling on the solar cell structure and an engineered CdTe<sub>x</sub>Se<sub>1-x</sub> graded band gap absorber layer, an efficiency of 22.1% was finally obtained. This is an efficiency comparable with those exhibited by the best devices based on poly-Si.

In the meantime, CdTe technology has become mature enough for an industrial development as it has been demonstrated by several production plant born in the 2000s; nowadays, the CdTe production capacity covers about 6% of the total PV production.

Thin film PV is competitive with the more traditional crystalline Si-based modules because TF technology facilitates the construction of a monolithic module exploiting on-line, fully automated production machine suitable for high productivity. In other words, a large glass substrate is introduced in a production line and another one goes out at the end line in the form of a finished module. For this reason, one module per minute is realized and its cost is comparable with the traditional energy supply. With the development of CdTe PV modules, recycling has also been carried out at the end of life in such a way to ensure an environmentally sustainable cycle.

PV producers, driven by the environmental sustainability of their large-scale production, formed a recycling network with the aim to recover all the module constituent materials at its end of life, establishing therefore, a virtuous circle. Worldwide, if a PV system is no longer sufficiently efficient, it will be recycled appropriately and the purchase of a new system can be nearly automatic.

We will analyze in detail the most famous process and the unknown tricks with which the best cells were and are still realized in the research laboratories. We will report on materials, interfaces, junctions and electrical contacts for making a clear picture of the state of the art of this technology on which a lot has been done and on which we still have to investigate to push the conversion efficiency closer to the theoretical Shockley-Queisser limit of 33% (Shockley and Queisser, 1961; Polman et al., 2016).

## 2. Solar cell structure

Thin-film design is completely different compared to the first generation of solar cells (monocrystalline and polycrystalline silicon). TF solar cells are characterized by two typical configurations: the substrate and the superstrate configurations (Fig. 1). The main difference between these two concepts, consists in the sequence of individual thin layers. In superstrate configuration, thin films are deposited on the substrate in the light-exposed to shaded side direction; as a consequence, only transparent substrates can be used since the light have to pass through the substrate. In case of the substrate configuration, the layers are deposited in opposite sequence, i.e. in the direction from shaded to light-exposed side. For this reason, opaque substrates are commonly used, including flexible thin metallic foil, polymers and commercial ceramics.

The sequence of the layers is crucial, since the final behavior of the CdTe-based solar cell depends on the interaction between the constituent layers, which varies by changing the film stack and the deposition order. Historically, the best cells have been fabricated in

superstrate configuration, while only in recent years, under the impulse of architectural integration in low energy buildings, together with the chance to implementing the very low-cost roll-to-roll technique, substrate configuration has also been studied. This structure has enabled cells with photovoltaic energy conversion efficiency, on laboratory scale, up to 13.6% on glass substrates and up to 11.5% (Kranz et al., 2013) on metal foils. The great difference between the world record efficiencies exhibited by solar cells fabricated with superstrate or substrate configuration depends mainly from the bad behavior of the back-contact that metal foils form with *p*-type CdTe. In fact, the choice of substrate materials is limited by matching the expansion coefficient and the work function. Moreover, during the activation thermal treatment, diffusion of impurities, coming from substrate, changes the electrical properties of the contact. Devices in substrate configuration are younger as compared with the superstrate ones and a lot of work on the layers interaction, diffusion, interfaces, back-contact and doping issue should be done.

### 2.1. Superstrate configuration

In this work, since the most developed architecture is the superstrate configuration and devices showing the best efficiencies have been made following this layer sequence, we will primarily discuss this type of configuration. Fig. 1a shown a typical solar cell superstrate structure.

#### 2.1.1. The substrate

From the beginning, high-efficiency CdTe-based solar cells and commercial modules are made on rigid glass; in this case, glass has to exhibit an optical transmission as high as possible, since solar light passes through the substrate and then it penetrates into the active layers of the cell. Several commercial glasses are “oxide glasses” with similar chemical composition. The main components are quartz (SiO<sub>2</sub>), sodium oxide (Na<sub>2</sub>O) and calcium oxide (CaO). All these compound are naturally present in sandstone and limestone. This glass, universally known as “soda-lime glass” (SLG), is characterized by a softening point of (790 ÷ 800) K. If sodium oxide is not used, an alkali-free (AF) glass is obtained, which exhibit a softening point well above 950 K.

Commercial glass contains iron impurities in the form of iron salts within the silicon oxide that reduce the transmission of light through the material. Low iron sand and limestone are natural sources for low iron glass. To produce low iron glass, furnaces must be designed to handle higher melting and refining temperatures. For this reason, low iron glass is on the market with a price 10% higher respect to the price of standard glass. The price increment is justified by the greater energy content and by the need of an accurate choice of the starting materials. Transmittance of low iron and alkali-free glasses are similar and, for both, depends on the thickness of the glass sheet.

Some attempts were made in order to obtain a flexible CdTe solar cell by using a high temperature resistant polymer. Best results were achieved by using Kapton polyimide, a Dupont polymer that remains stable up to 720 K. Flexible substrates are particularly appealing because they combine the ability to produce large-area extremely light photovoltaic devices with the high-rate roll-to-roll technology at reasonably low costs. Flexible CdTe superstrate cell processed on a polyimide foil exhibited an efficiency of 13.8% (not certified) (Salavei et al., 2015; Perrenoud, 2012). In this device the photocurrent was limited to 22.3 mA/cm<sup>2</sup>, due to polymer absorption (Fig. 2). Polyimide substrate limits also the processing temperature below 720 K, while maximum practical temperatures for roll-to-roll processing tend to be much lower (450 K) (Gessert, 2007). By the contrast, typical high-efficiency CdTe solar cells require processing temperatures well above 770 K (Wu et al., 2001).

Polyimide and standard SLG transmission is comparatively similar at long wavelengths but below 530 nm polyimide transmittance is not enough for PV application, although thin foils are used. In order to increase the photocurrent very thin window layer is commonly used

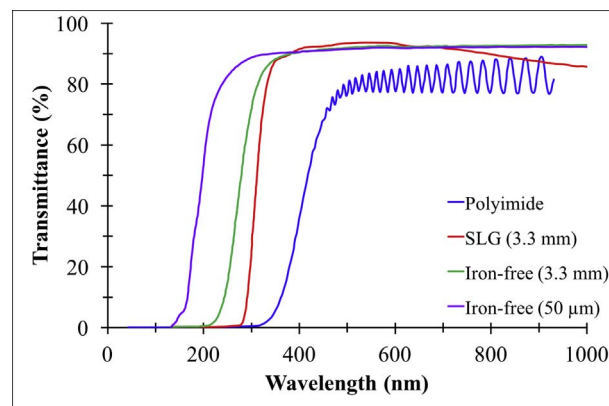


Fig. 2. Transmittance spectra covering the uv–vis–nir part of the light spectrum; standard SLG is compared with thin (50 μm) and thick (3,3 mm) iron-free SLG and with 7 μm thick Kapton polyimide. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

minimizing the loss due to CdS absorption, which starts close to 520 nm. The advantage of thin CdS disappears by using yellow polyimides because they also absorb in the same region of the light spectrum.

#### 2.1.2. The front-contact

In thin film technology crucial elements are certainly transparent electrodes, which constitute the front-contact both in superstrate or substrate solar devices. The main role for a transparent electrode is to let the light pass through the device active layers (which requires visible transparency) and to let the photo-generated carriers exit the device for reaching an external load (which requires a good electrical conductivity). A great improvement of performing transparent conductors has been achieved over the last decades, mainly focusing the development of Transparent Conducting Oxides (TCOs) thin films. The study of these materials has unequivocally established that wide bandgap ( $\geq 3$  eV) metal oxides are particularly suitable, considering their transparency and conductivity upon degenerate doping (commonly *n*-type), to solve the typical problem of the front-contact layer in TF-based solar cell.

Requirements for optical transparency in the visible region of the solar light and electrical conductivity appear to be contradictory: in fact, these properties lead to opposite conditions in terms of bandgap, which must be large in order to avoid the absorption of visible light and must be small to allow the filling of the conduction band by near-free electron. On the other hand, the low-energy (high-wavelength) limit for optical transparency is set by the fundamental energy band gap and the degenerate condition results in an additional increasing of the effective band gap. The last is the well-known Burstein-Moss (B-M) effect (Moss, 1954), which happened when the Fermi level, due to the heavy doping, lies into the conduction band. In this case, the energy levels at the bottom of the conduction band are occupied by electrons coming from the donor states and the electron originating from the valence band, as a consequence of the absorption of light, can only occupy the higher empty energy levels. As a result, the effective energy gap appears greater if compared with the fundamental one. In other words, the higher the Fermi level is, the more conductive the TCOs are, but transmittance is affected by two opposite effects:

- (i). When the B-M effect is effective the transparency is higher;
- (ii). When the TCO is characterized by a degenerate doping level, free carrier absorption will shift the associated plasma frequency from the infrared into the visible range, decreasing the optical transparency.

The first large scale use of TCO occurred during the world war II,

involving transparent heaters for de-icing applications in aircraft windshields but it was principally in '90 that the research on transparent contacts for optoelectronic and energy conversion devices found a great boost due to the pushing demand for flat panel display production (Ginley and Bright, 2000). The development of these materials has been significantly influenced by the discovery and optimization of the remarkable optical and electrical properties of what is still now the most widely used TCO, namely Indium-Tin Oxide (ITO) (Fortunato et al., 2007; Granqvist, 2007). In this material, in order to obtain an electrical resistivity lower than  $10^{-4} \Omega\text{-cm}$  a solid solution of  $\text{SnO}_2$  in  $\text{In}_2\text{O}_3$  was optimized. The use of ITO in the production of flat panel displays, coupled with the shortage of indium made its prices higher and more unstable (Kumar and Zhou, 2010); hence the need to develop alternative, indium-free materials (Minami, 2005). This stimulates the research to develop several other TCOs, based on doped  $\text{SnO}_2$ , ZnO and ternary or quaternary mixture of metal oxides (Gordon, 2000; Minami, 2000; Exarhos and Zhou, 2007).

During the last two decades, CdTe technology made extensive use of ITO, fluorine doped  $\text{SnO}_2$  (FTO), aluminum doped ZnO (AZO) and  $\text{Cd}_2\text{SnO}_4$  (CTO). These TCOs were coupled with buffer layers of the same family such as: pure  $\text{SnO}_2$ , ZnO and  $\text{Zn}_2\text{SnO}_4$ . The most investigated couples are summarized in Table 1. ITO is coupled with different HRT layers (un-doped  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$  and ZnO) while FTO is normally combined with pure  $\text{SnO}_2$  and CTO is paired with ZTO. Besides the role of the HRT film (it reduces the shunt effect coming from pinholes in CdS film and hinders the diffusion of impurities from the TCO or from the substrate) the bi-layer structure could change the chemical and physical stability of the front-contact. For example,  $\text{SnO}_2$  doesn't interact with CdS, while ZnO could mix with CdS during the high-temperature treatment of the front-contact/CdS/CdTe stack in chlorine atmosphere. In order to control the stability of the front-contact, this interaction must be taken into account.

Moreover, in order to obtain a conductivity of  $10^{-4} \Omega\text{-cm}$ , a density of the charge carriers of the order of  $10^{21} \text{cm}^{-3}$  is needed, being the mobility between 10 and  $50 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$  for a wide range of TCOs. In other words, these TCOs are degenerate semiconductor with a typical free-carrier absorption in the near-infrared (NIR) region of the solar spectrum. This is particularly true for ITO films, as it is clearly seen in Fig. 3, where a transparency below 70% for wavelength greater 825 nm is shown.

This behavior is less important for high-gap absorber (such as CdTe) but it is crucial for materials showing energy gap  $E_g \leq 1.4 \text{eV}$  (such as CIGS). This aspect could become important also for CdTe technology if graded band gap profile into the absorber layer is taken into account in advanced high efficiency ( $\geq 20\%$ ) solar cell. In order to increase the

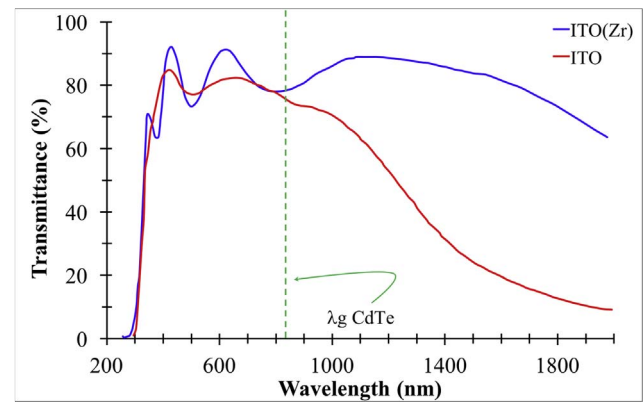


Fig. 3. Transmittance spectra of ITO films. In green color the wavelength corresponding to CdTe energy gap is also showed. The red curve corresponds to the transmission spectrum of a standard ITO  $[(\text{In}_2\text{O}_3)_{0.9}(\text{SnO}_2)_{0.1}]$  film. The blue curve is related to the transmission spectrum of a Zr-doped ITO (ITO(Zr)) film with the following composition  $[(\text{In}_2\text{O}_3)_{0.9}(\text{SnO}_2)_{0.09}(\text{ZrO}_2)_{0.01}]$ . Both films, deposited on soda-lime glass by pulsed d.c. sputtering at a temperature of  $400^\circ\text{C}$ , have a thickness of about 300 nm. ITO film exhibited a charge carrier density  $N = 1.3 \cdot 10^{21} \text{cm}^{-3}$  and a mobility  $\mu = 27 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  corresponding to a resistivity  $\rho = 1.8 \Omega\text{cm}$ . ITO(Zr) film exhibited a charge carrier density  $N = 7.6 \cdot 10^{20} \text{cm}^{-3}$  and a mobility  $\mu = 39 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  corresponding to a resistivity  $\rho = 2.1 \Omega\text{cm}$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

photocurrent a low-gap material ( $\text{CdTe}_x\text{Se}_{1-x}$  with  $X < 0.5$ ) could be used in the middle region of the absorber layer, while at the junction a very thin layer of a high-gap material is preferred for preserving the photovoltage.

To overcome this limit a little quantity of a high-permittivity oxides (such as  $\text{ZrO}_2$  or  $\text{HfO}_2$ ) is added to the ITO film during the deposition. The arising permittivity ( $\epsilon_\infty$ ) increase can shift the plasma resonance wavelength ( $\lambda_p$ ) to a longer wavelength. As a result, an appreciable improvement in the NIR transmission is obtained without any considerable change in the charge carrier concentration or mobility (Fig. 3) (Gessert et al., 2009).

However, it should be said that at industrial level the preferred front-contact is FTO, which includes in itself a good transparency, stability over time and good economy. On the contrary, ITO is becoming more and more expensive due to the fact that indium is considered a rare element on the Earth crust and to its huge use in flat panel displays.

When ZnO is used as HRT layer a little part of the ultraviolet spectrum is lost (Fig. 4) because the optical gap of ZnO is lower than

Table 1

The most popular TCOs and buffer layers used as bi-layer front-contact in high efficiency CdTe-based solar cells. The considered deposition techniques are related to research laboratories and not to the commercial conductive glasses.

TCO	Dep. process	Resistivity range ( $10^{-4} \Omega\text{cm}$ )	Buffer layer	Dep. process	Resistivity range ( $\Omega\text{cm}$ )
ITO ( $E_g = 3.7 \text{eV}$ ) (Sn-doped $\text{In}_2\text{O}_3$ )	sputt./PLD ( $T = 300^\circ\text{C}$ )	$1\text{--}3^{\S}$	$\text{SnO}_2$ ( $E_g = 3.6 \text{eV}$ ) (O-vacancies)	React. Sputt. of Sn in Ar/ $\text{O}_2$	$10^2\text{--}10^4$
			$\text{In}_2\text{O}_3$ ( $E_g = 3.7 \text{eV}$ )	React. Sputt. of In in Ar/ $\text{O}_2$	$10\text{--}10^{2\text{§§}}$
			ZnO ( $E_g = 3.3 \text{eV}$ )	React. Sputt. of Zn in Ar/ $\text{O}_2$	$10\text{--}10^5$
FTO ( $E_g = 3.6 \text{eV}$ ) (F-doped $\text{SnO}_2$ )	APCVD/SP ( $T = 480^\circ\text{C}$ )	$3\text{--}8^{\text{§§§}}$	ZnO ( $E_g = 3.3 \text{eV}$ )	React. Sputt. of Zn in Ar/ $\text{O}_2$	$10\text{--}10^5$
CTO ( $E_g = 3.1 \text{eV}$ ) (self-doped)	rf-co-sputt. CdO/ $\text{SnO}_2$	$1.2\text{--}10^{\text{§§§}}$	$\text{SnO}_2$ ( $E_g = 3.9 \text{eV}$ ) (Optical gap)	React. Sputt. of Sn in Ar/ $\text{O}_2$	$10\text{--}10^{4\text{§§§}}$
			ZTO ( $E_g = 3.4 \text{eV}$ )	rf-co-sputt. of ZnO and $\text{SnO}_2$	$10^{-1}\text{--}10^{2\text{§§§§}}$

<sup>§</sup> Mamazza et al. (2005).

<sup>§§</sup> Li et al. (1999).

<sup>§§§</sup> Bosio et al. (2005).

<sup>§§§§</sup> Sato et al. (2009).

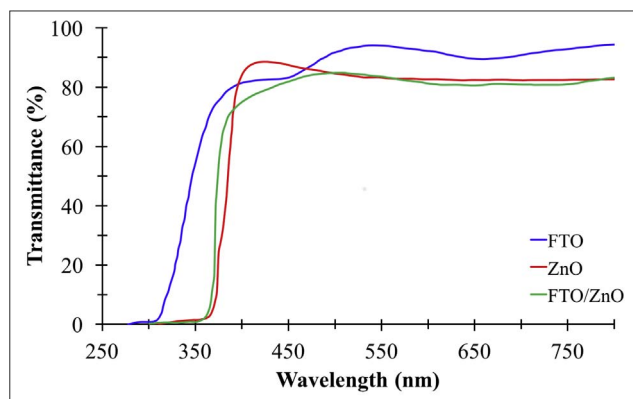


Fig. 4. Transmittance spectra of FTO, ZnO and FTO covered by ZnO films. Commercially available FTO film deposited on iron-free SLG is used. ZnO films are deposited by R. F. reactive sputtering at 570 K substrate temperature. The thickness of the FTO films are around 300 nm while ZnO films are 100 nm thick. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that of  $\text{SnO}_2$  but an unexpected gain on the side of the interaction between the window (generally CdS) and the front-contact is reached. In fact, ZnO and CdS being II-VI compound could interact better together during the high-temperature treatment typical of the CdTe process, as a result the sticking coefficient improves and denser, pinholes-free CdS films are easier obtained.

### 2.1.3. The window layer

The so-called window layer, coupled with CdTe is normally a sulphide material; up to now, high efficiency solar cells are made by using CdS as window layer. CdS naturally grows *n*-type making it a good candidate as a partner for the formation of the junction with *p*-type CdTe film. Moreover, it exhibits an energy gap of 2.42 eV, which allows the visible part of the solar light to pass through in order to reach the absorber layer. CdS role is crucial for obtaining high-efficiency solar cells, even though it is more difficult to understand why, given the lattice mismatch between CdS and CdTe over 10%. During the high-temperature step of the solar cell production a helpful inter-diffusion at the interface between the two material takes place, minimizing the interface states due to structural defects. In particular, the heat-treatment in chlorine ambient at about 670 K of the CdS/CdTe stack is fundamental to promote the intermixing between CdS and CdTe following the phase diagram of the Cd-S-Te-Cl system. In order to use a more transparent material some attempts were made by using ZnS instead of CdS or making use of a ZnS/CdS bilayer with a thin CdS film (Grice et al., 2016). Since an inter-diffusion between the two sulphides occurs, some investigations took the direction to study the ZnCdS system, widening directly the window layer band gap in the range 2.42 eV (CdS) up to 3.6 eV (ZnS) (Kartopu et al., 2014). The final result of these researches were not encouraging because the expected increase in both photovoltage and photocurrent didn't happen probably due to an increase in the number of defects at the ZnCdS/CdTe interface respect to the CdS/CdTe junction, in both cases after optimized chlorine heat treatment. Evidently, the Zn-Cd-S-Te-Cl system is not favorable as the Cd-S-Te-Cl system is in reducing the structural defects between ZnCdS and CdTe. Summarizing, it was speculated that the intermixing between the sulphides and CdTe promotes the reduction of the interface carrier recombination but, up to now, there isn't any experimental evidence about this important issue.

However, the strong dependence of the quality of the device on the correct interaction between the active layers, CdS and CdTe, is evident. As a consequence, the techniques used for the deposition of these layers play a fundamental role. For CdS the more popular deposition techniques can be distinguished in high- (H-T) and low-temperature (L-T) techniques depending on the substrate temperature during deposition,

which could be below or above 470 K respectively. Chemical bath deposition (CBD), high-vacuum thermal evaporation (HVTE) and R. F. sputtering are part of the L-T methods, while close-spaced sublimation (CSS) is a H-T deposition procedure. On laboratory scale, solar cells exhibiting a very good photovoltaic energy conversion efficiency was obtained by using CdS film deposited by CBD, but in industrial production, sputtering and CSS are normally preferred since the CBD process is not fast enough and moreover, gives a large amount of waste, which has to be recycled.

In CBD, by exploiting the thiourea decomposition in an alkaline solution of cadmium salts, CdS films can be easily deposited, following the chemical process suggested by (Ortega-Borges and Lincot, 1993; Dona and Herrero, 1997). These CdS layers show very high density, compactness and are pinhole-free but the as-deposited films are not suitable for the junction formation. An annealing of the film at a temperature well above 670 K is needed in order to remove some stoichiometric defects such as sulphur and cadmium excess. Moreover, the heat treatment promotes some beneficial changes in the crystalline structure of the as-deposited films, which are characterized by an hexagonal-cubic mixed phase, while the post-treated films present the only wurzite phase. This structural change is made possible because, at high-temperature, wurzite form is more stable than zincblende. As a drawback, the high-temperature annealing promotes also an oxidation of the film surface since  $\text{Cd}(\text{OH})_2$  precipitates into the CdS film during the CBD deposition process. Cadmium hydroxide could separate into cadmium oxide and water vapor during the heat treatment of the CdS films giving rise to a CdS + CdO mixture. It was observed that up to 30% of CdO is not detrimental for the formation of a high efficiency *p-n* junction with CdTe.

CdS could be also evaporated from graphite crucibles at a temperatures well above 970 K in a high-vacuum evaporation chamber and deposited in a range of substrate temperature between (320 ÷ 470) K. Also in this case, an annealing of the as-deposited films performed both in vacuum or in a hydrogen atmosphere at a temperature of (670 ÷ 720) K is necessary, in order to obtain an essential chemical stability of the evaporated films. The heat treatment benefits are well known in terms of re-crystallization, promoting the coalescence of small grains and restoring the correct stoichiometry by evaporating the Cd and S excesses that are inevitably embedded during the low-temperature deposition of the CdS film. Nevertheless, HVTE-CdS films do not have the same compactness of the films obtained by CBD and it is not difficult to find pinholes if the film thickness is less than 200 nm. For this reason, the average thickness of CdS, when coupled with CdTe for the solar cell preparation, is never less than 300 nm. Such a high thickness of the window material actually contributes to a photocurrent loss, which is only marginally compensated by the photo-conversion, still considering that this material exhibit an energy gap of 2.42 eV. HVTE will become a winning technique if used in all those processes where deposition temperatures below 720 K are required. For this reason, this deposition method is used for the production of flexible PV modules where the substrate is a polymeric material. Moreover, the implementation of the roll-to-roll technology, typical of flexible substrates, can push the industrial production into the BIPV direction.

Even the sputtering deposition of polycrystalline CdS thin film is to be counted among the L-T techniques. By introducing a little more detail into this technique, it is known (Romeo et al., 2003) that CdS films prepared by R. F. sputtering at a substrate temperature of about 470 K in a pure Ar atmosphere have neither crystalline quality nor chemical stability to promote the proper interaction with the CdTe layer essential to produce high efficiency devices. Normally, the situation does not even improve by performing a heat treatment above 770 K in a vacuum chamber for thirty minutes.

This negative result is clearly seen through a very high diode reverse current. One possible explanation is that the grain boundaries of the CdS film are active and can channel the CdS/CdTe junction reverse current. To get over this problem, a partial pressure of a reactive gas,

such as oxygen or fluorine-based gas, are introduced into the sputtering chamber during the deposition. For example, Ar containing 3% of  $\text{CHF}_3$  could be used. The sputtering discharge ionizes the decomposed elements of this gas, making free negative fluorine ions which, being electronegative, hit the substrate that is the positive electrode for a great part of the R. F. period (Romeo et al., 2003). Moreover, these ions have enough energy to sputter back the more weakly bonded Cd or S atoms leaving a more stoichiometric and better crystallized film, which means a great gain in optical and structural quality. Furthermore, it was demonstrated that the presence of fluorine into the sputtering chamber doesn't contribute as an effective dopant to the CdS charge carrier density. Despite this, solar cells prepared by using 60 nm CdS thick films deposited by sputtering in fluorine presence showed efficiency in the range of (15 ÷ 16)%. Energetic fluorine ions, impinging the film surface, favor the formation of a fluorine compound such as  $\text{CdF}_2$  during the growth of the CdS film. This insulating material, mainly segregated into the grain boundaries of the CdS polycrystalline film, can passivate them, while the  $\text{CdF}_2$  layer, which grows on the CdS surface during the deposition may adjust the proper interaction with CdTe. Due to the small amount and the amorphous nature of this material, it is very difficult to have an unquestionable measure of its presence, although the change in interaction with CdTe remains clearly observable.

Exploiting the structural and optical superior qualities of the deposited CdS films, CSS is the most used technique among the H-T deposition processes. This deposition method is based on the CdS dissociation at high temperature ( $\geq 870$  K) in an inert or reactive gas atmosphere under a pressure in the range ( $10 \div 10^4$ ) Pa. As an effect of the high temperature, the CdS solid source separates its elements, which could recombine on the surface of the growing film if the substrate temperature and gas pressure are suitable for the CdS deposition. If the deposition occurs in pure Argon, it is not infrequently to observe the formation of pinholes disabling the normal operation of the *p-n* junction.

Conversely, if oxygen is used as reactive gas into the deposition chamber, substantial changes in film structure are seen. Oxygen atoms may act as transport agent affecting the sublimation-deposition equilibrium and could be also incorporated into the growing film.

Moreover, oxygen influences the nucleation process of the incoming Cd and S atoms on the surface of the substrate since it increases the number of nucleation sites. As a result, a denser CdS film is obtained. X-ray diffraction spectra performed on these films typically show the hexagonal phase, which is the stable structure of CdS when deposited at high temperature ( $\geq 770$  K) in form of thin film and a second phase associated to monoclinic  $\text{CdSO}_3$  (see Fig. 5). This secondary phase is segregated into the grain boundaries and on the surface of the CdS film.

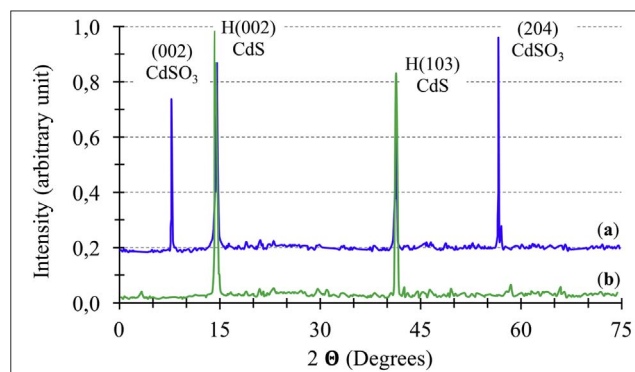


Fig. 5. X-ray spectra of CSS-deposited CdS films. (a) CdS grown with and (b) without  $\text{O}_2$  in the CSS deposition chamber. In particular, CdS shows the  $\text{H}(0\ 0\ 2)$  and  $\text{H}(1\ 0\ 3)$  reflections, typical of the hexagonal (wurtzite) structure, while  $\text{CdSO}_3$  exhibits the  $(0\ 0\ 2)$  and the  $(2\ 0\ 4)$  reflections characteristic of the monoclinic crystallization. In order to make the spectra more readable, the reflections belonging to the TCO layer were removed. (redrawn from A. Bosio et al., 2011).

For this reason, the best results are obtained when these films are annealed in a controlled atmosphere containing Ar + 20% $\text{H}_2$  (forming gas) at a temperature of 690 K for 15 min.

When coupled with CdTe, these CdS films have demonstrated their great potential as window layer in high-efficiency ( $> 15\%$ ) solar cells. The beneficial effect of  $\text{O}_2$  in preparing CdS by CSS has been also reported by Ferekides et al., 1996.

In the H-T processes, Atomic Layer Deposition (ALD) technique should be mentioned. Despite this technique offers very high uniformity over large areas, a good crystalline quality of the deposited thin films and a low pin-hole density, it is not used in an industrial production of CdS/CdTe-based solar modules. A low-pressure ALD reactor requires the transport of reagents and a shuttering action by using a computer-controlled inert gas flow in order to reach a layer-by-layer deposition. Different reagents allow the deposition of diverse materials with special stoichiometry by means of a sequential chemical reaction on the surface of the growing film.

In case of CdS, as a reactants elemental Cd and S are normally used and the deposition is carried out at a substrate temperature in the range of (620 ÷ 770) K. Also CdTe could be deposited by using elemental Cd and Te at a deposition temperature in the range of (620 ÷ 720) K. Generally, if a graded layer between CdS and CdTe layers is processed by gradually changing the Cd-S-Te proportions from pure CdS to pure CdTe, a good-efficiency ( $< 14\%$ ) solar cells are obtained.

#### 2.1.4. The CdTe layer

Homojunction, heterojunction, *p-i-n* and Schottky barrier configurations have been historically investigated for CdTe-based solar cells (Anthony et al., 1985; Chu et al., 1988; Fahrenbruch and Bube, 1983). After the first attempt, heterojunction was the most successful structure becoming early the widely used. Many wide-gap semiconductors can be used as *n*-type partner with CdTe, which is natively *p*-type doped when deposited at a substrate temperature above 570 K. Nevertheless, several studies and experiments demonstrated that CdS is the most suitable material to associate with CdTe for obtaining high efficiency solar cells. This is due to the favorable intermixing between the two semiconductors, which removes native defects making the CdTe/CdS interface very near to a homojunction structure.

CdTe thin films are normally deposited with a great number of L-T and H-T techniques. Among the first one we mention ALD, Spray Pyrolysis (SP), HVTE, Sputtering (S) and ED, while CSS and Vapor Transport Deposition (VTD) are certainly the main representative between the second ones. Despite important differences between these techniques, the performance reached by the CdTe-based solar cells is quite independent from the deposition method as a consequence of the great versatility and of the thermal-chemical post-deposition treatments. The most efficient devices are produced with the H-T processes, while L-T technologies have acquired a major place in the production of flexible cells where high temperatures are avoided. In particular, CSS and VTD are the production methods that have been implemented at an industrial level for producing high efficiency CdTe-based modules; nowadays, these modules, with an efficiency above 17%, are commercially available on the PV market.

One of the main advantages of CSS technique relates to the high quality of the as-deposited CdTe film, characterized by large crystalline grain, which could mean a small defect density.

The grain size of these CSS-deposited films is in the range of (5 ÷ 10)  $\mu\text{m}$  for film thickness of about (7 ÷ 8)  $\mu\text{m}$ . Large and columnar grains are desirable in order to reduce transverse grain boundaries, which decrease the mean free path and the lifetime of the charge carriers. But unfortunately, increasing the grain size, also the dimension of voids between the grains increases and the film has to be thicker for containing the formation of pinholes.

The great thickness of CSS-deposited films is one of the major problems encountered by researchers. In fact, the CdTe absorption coefficient, corresponding to wavelengths in the range of sunlight spectrum,

is higher than  $10^4 \text{ cm}^{-1}$ , which means that a film thickness of only  $1 \mu\text{m}$  is enough for converting completely all the visible light. Such a thickness would be optimal for both optical and electrical purposes, but in practice it is very hard to achieve if CSS-deposition is performed.

At high temperature ( $> 1120 \text{ K}$ ) CdTe single crystals are easy to dope *p*-type with P, As, N typical acceptor dopants, but it is very hard to obtain an extrinsic doping when CdTe is in thin film form. This is due to the polycrystalline nature of the CdTe layers, which allows the dopant atoms to segregate into the grain boundaries of the film when the temperature is not high enough, making not effective the doping action. As a result, in case of H-T deposition techniques, CdTe is a typical electrically quite-compensated semiconducting material and its conductivity is principally due to intrinsic native defects. Hopefully, native-donor defects density is at least two or three order of magnitude below the acceptor density, giving rise to a clear *p*-type electrical conductivity. In dark conditions, a  $10 \mu\text{m}$  thick CSS-deposited CdTe film, exhibits a typical resistivity of about  $(10^4 \div 10^5) \Omega\text{-cm}$  and just under light the resistivity goes down to  $(10^2 \div 10^3) \Omega\text{-cm}$ . Since only  $1 \mu\text{m}$  of the film close to the junction is involved in the photo-conversion of the solar light, only this material has the proper resistivity required for an absorber material in solar cells. This means that nine tenth of the CdTe film, remaining in the dark, introduce a series resistance ranging about  $(10 \div 100) \Omega$  for a device area of  $1 \text{ cm}^2$ . This series resistance is too high for obtaining a high efficiency solar cell and several ingenious solutions were proposed and some of them were transferred to the industrial production. It is simple to suggest of decreasing the thickness of the absorber layer in such a way to have a proper resistance for the CdTe layer, but as said before,  $(1 \div 2) \mu\text{m}$  thick films exhibit unavoidable pinholes. To overcome this unpleasant drawback, oxygen is normally added to the process chamber when CdTe film is deposited by CSS or by VTD. Oxygen influences very strongly the CdTe growth. The main effect is evident on the dimension of the crystalline grains; in particular, a fast Fourier analysis has indicated that the average grain size of the CdTe films changes from  $10 \mu\text{m}$  for films grown in pure Ar, to  $(2 \div 3) \mu\text{m}$  for films grown in Ar + O<sub>2</sub> atmosphere (Bosio et al., 2011). By varying the oxygen partial pressure from 0 to 100% respect to the Ar + O<sub>2</sub> total pressure, it is possible to change the interaction between the CdS surface and the incoming Cd and Te atoms at the very first stage of the CdTe deposition. Evidently, in presence of oxygen the equilibrium between the CdTe sticking coefficient and the surface diffusion coefficient changes. This is probably due to the presence of CdO and TeO<sub>2</sub> species, which play an important role on the surface diffusion of the impinging atoms. In presence of oxygen, Cd and Te may have a reduced reactivity and, as a consequence, they stay for more time on the surface of the substrate before recombining and a less defective CdTe could be formed. Since the first stage of the growth is very important for the quality of the whole film, we have to consider that the oxygen partial pressure affects the nucleation process, increases the number of nucleation sites, being effective in promoting a denser growth of the CdTe film. The quantity of oxygen embedded into the CdTe film strongly depend on the O<sub>2</sub> partial pressure and on the substrate temperature. Anyway, a small amount of CdTeO<sub>3</sub> is normally segregated at the grain boundaries of the CdTe film performing a welcome passivation function. This dual effect can also be achieved by exploiting sputtering coupled with CSS deposition of the CdTe film. The main difference between a thick ( $\approx 10 \mu\text{m}$ ) and a thin ( $\approx 2 \mu\text{m}$ ) CSS-deposited CdTe layer consists in a reduction of the crystalline grain size, widened grain boundaries and some voids very clearly seen in the thinner one (Fig. 6(a)). In this conditions, weak *p-n* junctions are formed and lower photovoltages and fill factors are obtained. From depth profiling analysis made by secondary ions mass spectroscopy (SIMS), both these films exhibit the same Te-rich stoichiometry of the crystalline grain surface (Fig. 6(b)). At this stage, if cadmium is not added to the system, for example making a heat treatment in presence of CdCl<sub>2</sub> or similar chlorine salts, the surface of CdTe film remains Te-rich.

On the contrary, sputtered CdTe (S-CdTe) thin films, deposited at

substrate temperature below  $620 \text{ K}$ , are very dense with an optimum coverage and are pinhole-free also at a thickness of about  $100 \text{ nm}$  (Fig. 7(a)). These films show a Cd-rich stoichiometry (Fig. 7(b)), which means Te-vacancies leading a *n*-type conductivity of about  $1 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ , even if the Cd/Te ratio of the starting material is  $R_{\text{Cd/Te}} = 1$ . After a CdCl<sub>2</sub> treatment, the thin S-CdTe layer deposited on top of a  $2 \mu\text{m}$  thick CSS-CdTe is mainly segregated into the grain boundaries of the CSS-deposited one, filling in all the pin-holes. As a result, starting from the back-contact side of the CdTe film, a *p-n* junction is formed between the grain boundaries and the bulk, giving rise to a new passivation concept. This active passivation acts as a mirror for the minority carriers, extending their lifetime and it is effective in preventing the formations of shunt paths in the junction region. This behavior is confirmed by the STEM-EDX analysis performed on a CdTe bilayer immediately after the chlorine-treatment as it is showed in Fig. 8.

Among the L-T techniques S-P represents one of the first investigated deposition process for low cost fabrication of CdTe-based solar cells (Serreze et al., 1981; Boone et al., 1982; Nikale et al., 2011). Unfortunately, this technique makes use of very thick layers both for window and for absorber layers. The losses due to the absorption of the solar light into the window layer and the internal resistances of materials have prevented this technique to succeed, giving rise to moderate photovoltaic conversion efficiencies almost never exceeding 10%.

In the low temperature deposition techniques, worthy of note is certainly HVTE. CdTe films deposited by HVTE are characterized by a thickness of about  $(2 \div 3) \mu\text{m}$ , very good compactness and an average grain size of about  $(0.1 \div 0.5) \mu\text{m}$  (Romeo et al., 2001). In general, the grain dimension of these films implies mobility and life time of the charge carriers too low for the formation of a good *p-n* junction and a proper collection of the photo-generated carriers. The grain growth is enhanced by a post-deposition annealing (the “chlorine treatment”) reducing, also in this case, the density of stacking faults and misfit dislocations and the number and dimensions of the grain boundaries (Moutinho et al., 1997). As a result, CdTe with grain size larger enough for using as an absorber layer in high efficiency solar cell is obtained. All HVTE-deposited CdTe/CdS solar cells exhibit so far efficiency in the range  $(13 \div 15)\%$  on rigid substrate and  $(11 \div 12)\%$  on flexible (polyimide) one (Tiwari et al., 2001; Perrenoud et al., 2009).

Maybe, electrodeposition is one of the more exploited large area L-T technique, since the 90’s when PV modules based on ED-CdTe was fabricated in BP Solar’s laboratories (Turner et al., 1994; Cunningham et al., 2002). However, electrodeposition of semiconducting materials was firstly introduced in the 70’s (Danaher and Lyons 1978; Kröger, 1978; Panicker et al., 1978) and in the early 1980’s (Fulop and Taylor, 1985; Ortega and Herrero, 1989) a thin film ED-CdTe-based solar cell with a remarkable efficiency above 8% was successfully obtained (Basol, 1984). In the last two decades further research and development was slowed down until recently, another breakthrough was found in ED-CdS/CdTe reaching a record efficiency of 15.3%. This device was fabricated taking into account a different architecture of the solar cell: was firstly considered that ED-deposited CdTe shows a typical *n*-type conductivity and secondly the innovative glass/FTO/*n*-CdS/*n*-CdTe/*p*-CdTe/Au sequence was applied for producing the solar cell. In this case the main improvement is related to the presence of a *p-n* homojunction close to the back-contact instead of the more classical Schottky barrier (Ojo and Dharmadasa, 2016).

Also R. F. magnetron sputtering is one of the most used L-T deposition process (Soliman et al., 1996) and it has been proven for industrial application. This technique is particularly suitable every time the adhesion of the growing film to the substrate is a fundamental issue. Effectively, one of the main advantage of S-deposition is that a higher film density is easily obtained. Moreover, a controlled change in stoichiometry can be achieved by adding reactive species to the process atmosphere and/or using a negative bias applied to the substrate exploiting the back-sputtering effect on the surface of the growing film. The use of low energy particle bombardment for achieving lower



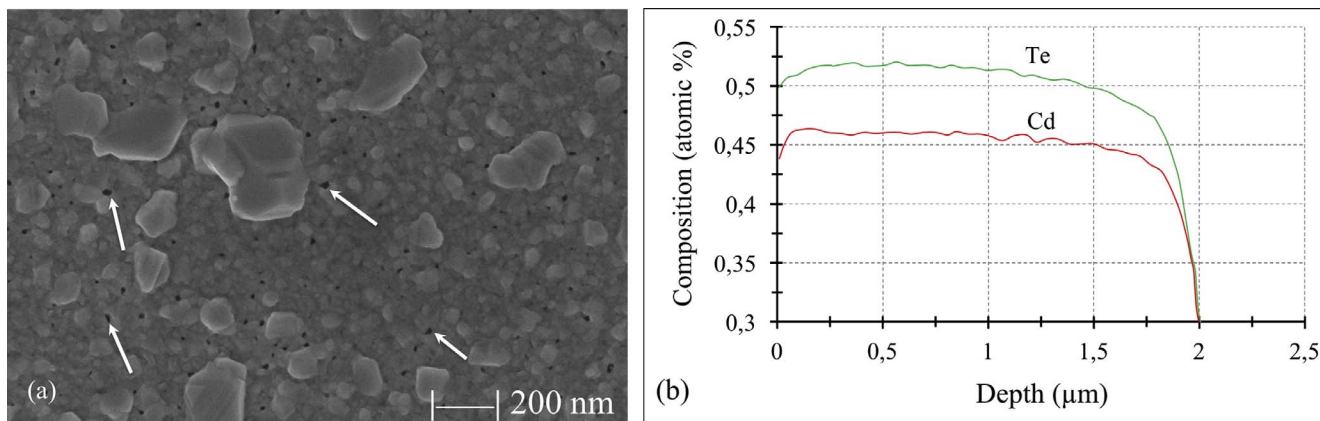


Fig. 6. (a) SEM image of the surface morphology of a 2  $\mu\text{m}$  thick CdTe layer deposited by CSS; the black points in the picture, highlighted by white arrows, correspond to holes probably due to an incomplete coalescence of the CdTe crystalline grains. (b) SIMS measurement carried out on the film showed in (a). (redrawn from Bosio et al. (2016)).

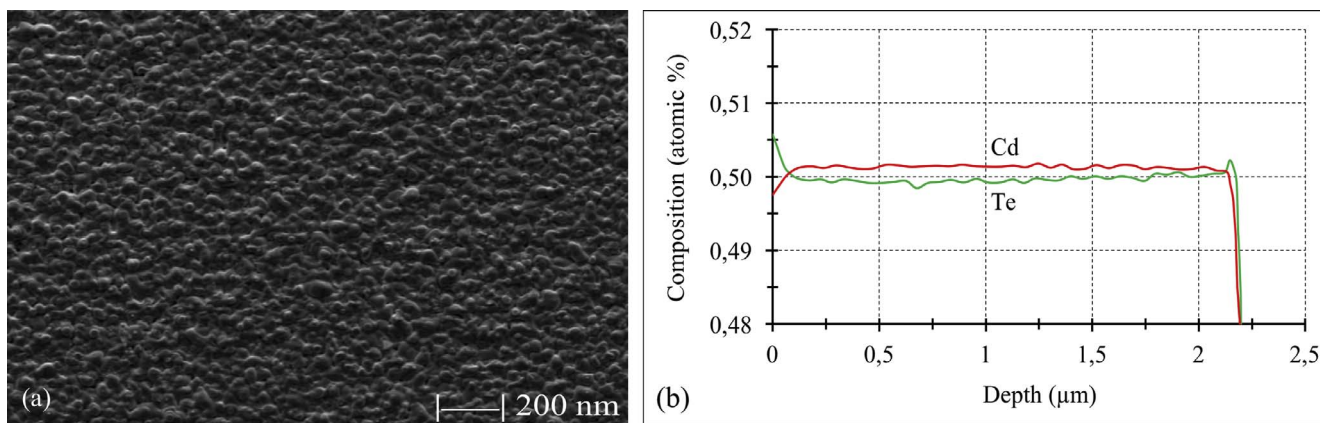


Fig. 7. (a) SEM image of the surface of a S-CdTe film with a thickness of 200 nm before the typical Cl-treatment; (b) SIMS measurement put in evidence the Cd-rich nature of a 2,2  $\mu\text{m}$  thick S-CdTe film also after the Cl-treatment. (redrawn from Bosio et al. (2016)).

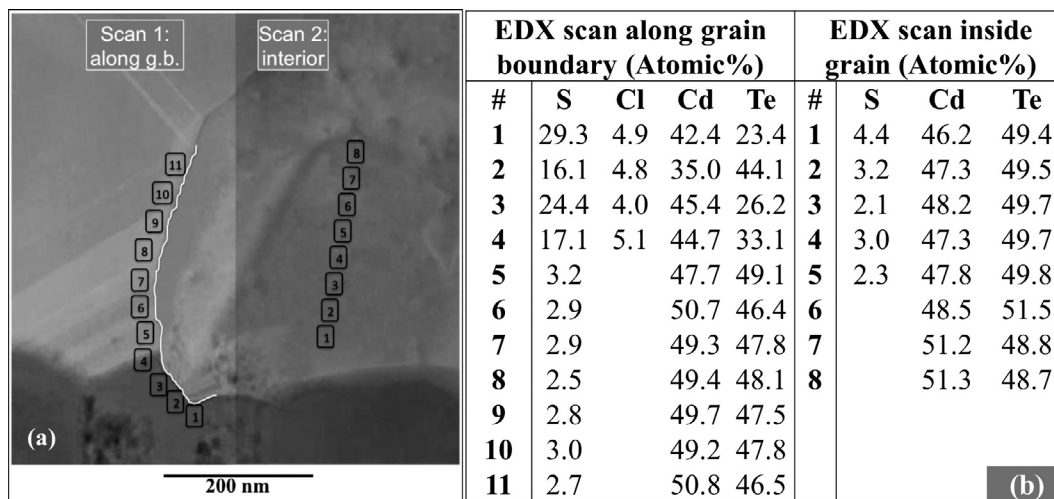
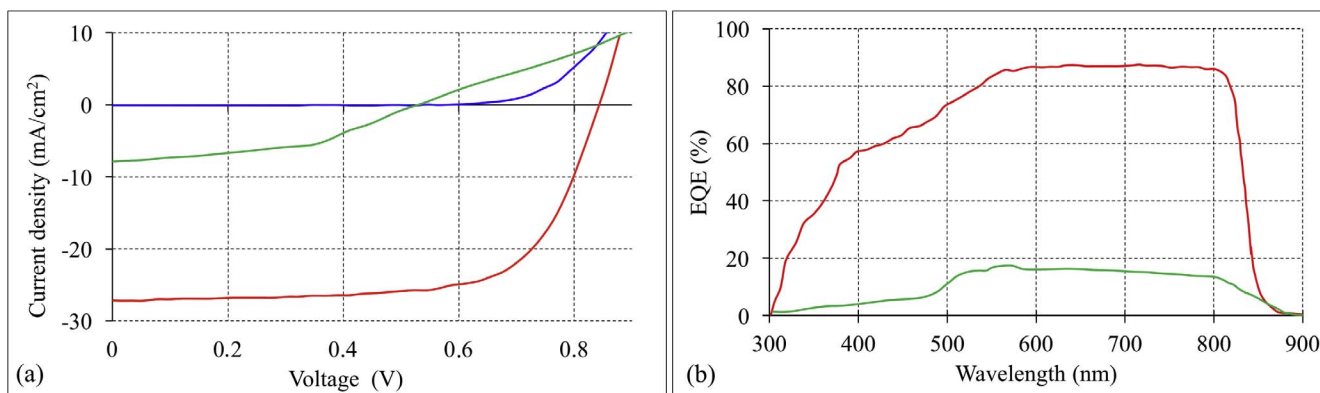


Fig. 8. (a) The stoichiometry of the grain-boundary (left sequence) and of the grain-surface (right sequence) was measured by Energy-Dispersive X-ray Analysis (EDX) using a scanning transmission electron microscope (STEM). The values of this measurement are listed in Table (b). (redrawn from Bosio et al. (2016)).

growth temperatures along with the use of excited species for improving the stoichiometry control during the film growth, makes S-deposition one of the most versatile technique able to obtain both *n*- and *p*-type CdTe polycrystalline film. The optical and electrical properties of S-CdTe and S-CdS deposited films are strongly dependent on process parameters as well as sputtering power, argon and reactive gas pressure, bias voltage, substrate temperature, target-substrate distance,

etc., allowing a very fine-tuning of the desired physical characteristics of the active layer.

Thickness of these films is finely controlled and exploiting the excellent coverage, which means no-pinholes, it is possible to work with thicknesses of only (2 ÷ 3)  $\mu\text{m}$  (Paudel et al., 2012). By appropriately adjusting the chlorine treatment parameters, CdTe films with sufficiently large crystalline grains can be obtained and solar cells with



**Fig. 9.** Behavior of a CdTe-based solar cell with and without the chlorine treatment of the CdS/CdTe stack. (a-red and blue color) under light and dark J-V characteristic respectively of a Cl-treated cell taken at STC showing photovoltaic conversion efficiency (PCE) of 15,8%; (a-green color) under light J-V characteristic of an un-treated cell taken at STC exhibiting a PCE of 1,96%. (b-red color) External quantum efficiency of the same cell characterized in (a-red color) corresponding to a Cl-treated device; (b-green color) External quantum efficiency of the same cell characterized in (a-green color) corresponding to an un-treated device. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

efficiency over 14% have been produced (Compaan et al., 2004).

### 2.1.5. The chlorine treatment

A post-deposition treatment in chlorine-containing atmosphere at temperatures in the range (640 ÷ 700) K of the CdS/CdTe stacked layers is routinely carried out in order to increase the grain size and to improve the quality of the grain boundaries of the absorber film. Moreover, the Cl-treatment is also effective in removing the native structural defects, promoting the intermixing between CdS and CdTe at their interface letting the realization of a high efficiency solar cell.

In Fig. 9 it is clearly seen the beneficial effect of the heat treatment of the CdS/CdTe system in a Cl-containing atmosphere. The poor spectral response highlighted in the EQE curve, reaffirmed in the under light J-V characteristic of the untreated sample is probably explained by means of a great number of structural defects, which prevent the charge carriers to move inside the absorber layer promoting recombination of the photo-generated electron-hole pairs. On the contrary, the treated samples exhibit a very good response mostly in the long wavelength region, since longer wavelength means greater absorption length. These photons generate electron-hole pairs fairly far from the junction region. Only if recombination is negligible the lifetime is good enough to allow these carriers to reach external contacts.

As Cl-supplier chlorine salts are typically used in form of thin films, which are deposited, with various techniques, on top of the CdTe layer. Among them the most popular are NH<sub>4</sub>Cl, NaCl, MgCl<sub>2</sub>, CdCl<sub>2</sub> (Bayhan, 2004; Hiie, 2003; Niles et al., 1998; Romeo et al., 1999; Williams et al., 2015; Potlog et al., 2003; Potter et al., 2000), which are deposited either by vapor deposition or by drop-casting of a Cl-salt/methanol solution followed by an air-anneal. Cadmium-free salts offer the great advantage to be more environmentally sustainable than CdCl<sub>2</sub>, which was historically the first and the most used one. As an alternative, a halogen carrier gas able to release chlorine or chlorine radicals at the treatment temperature could be used. In this case, chlorine-based Freons or gases of the chlorine family itself (HCl, Cl<sub>2</sub>...) can accomplish this basic task. Normally, chlorine containing gases are very aggressive and the heat treatment of the CdTe films in presence of these gases becomes extremely critical (Zhou et al., 1994; Qu et al., 1996). In order to ensure a good control of the system, fluorinated hydrocarbons are added to chlorine or to the chlorinated species in the process gas (Romeo et al., 2006). Why the fluorine presence helps to stabilize the reaction between CdTe and chlorine making the system more reproducible? Normally, only the CdTe-Cl<sub>2</sub> reaction is considered since a lot of systematic studies and experiments consider CdCl<sub>2</sub> as chlorine supplier, but in presence of F<sub>2</sub> or F-based species also a fluorine compound could be formed. At the treatment temperature, these are stable

materials, while in presence of chlorine they present a metastable behavior. Among the fluorine-based compound, CdF<sub>2</sub> is the most probable to form at the treatment temperature and its presence is effective in lowering the growth rate of the chlorine containing counterparts (CdCl<sub>2</sub>). In this way the chlorine aggressiveness decreases making the system under control by simply adjust the chlorine/fluorine ratio.

From the CdTe module industrial production point of view, use of water-soluble CdCl<sub>2</sub> sets environmental risks. Recent studies have been demonstrated that the replacement of toxic and expensive CdCl<sub>2</sub> is made possible by using nontoxic and cheaper MgCl<sub>2</sub> without any performance loss of the solar cell (Major et al., 2014).

All studies concerning chlorine treatment show that the efficiency of the devices is closely dependent on how extent is the re-crystallization of the crystalline grains of CdTe film. This in turn depends on the dissociation energy of the molecule salt and in particular on the cation Cl bond. As a general rule lower energies promote greater re-crystallization and consequently higher efficiency. This finding can help in choosing chlorine salt as a substitute for CdCl<sub>2</sub> and highlights that chlorine containing gases with the addition of fluorinated gases can be a winning choice.

### 2.1.6. The back-contact

Currently, most contacting processes include three main steps:

- (1) CdTe surface is submitted to a wet-chemical treatment (Nitric-Phosphoric – N-P etching or Bromine-methanol – Br-MeOH etching) to produce a surface with reproducible stoichiometry, free of unwanted compounds (e.g., Cl or CdCl<sub>2</sub>, oxides, etc.). The N-P etching results beneficial also for the formation of a Te-rich layer on top of the CdTe film, while the Br-MeOH etching leaves the CdTe surface Cd-rich.
- (2) The Te-rich surface plays an important role in the formation of a contact interface layer, which promotes the proper equilibrium between the valence band of CdTe with the work function of the true metal contact through the formation of a low-resistance tunneling barrier. Only semimetals or degenerate semiconductor could achieve this function and often the degenerate condition is reached by adding a little quantity (few nm) of copper to the interface layer (e.g. ZnTe (Meyers, 1987; Gessert et al., 1996), PbTe (Mitchell, 1988), HgTe (Janik and Triboulet, 1983), Te (Niles et al., 1996), Cu<sub>x</sub>Te (Wu et al., 2007; Romeo et al., 2010), M<sub>2</sub>Te<sub>3</sub> where M = As, Bi, Sb (Bosio et al., 2013)).
- (3) On top of the interface and/or the buffer layers an outer metallization is deposited. This metallic film provides the true electrical electrode which reduces the sheet-resistance losses.

As suggested in literature cited at point 2, all the materials taken into consideration are metal-based tellurides or a telluride compound is requested to be formed as in the case of  $\text{Cu}_x\text{Te}$ , when copper is deposited on top of the Te-rich surface of CdTe films. Since metal atoms and in particular Cu, are very fast diffusors inside CdTe crystalline grains and grain-boundaries, the use of Cu-doped metal-based buffer material makes this contact hypercritical. The diffusion of metal atoms inside the CdTe film generates shunt paths between the two external electrodes, which destroy the junction, getting the device unusable. In literature, this is universally recognized to be the origin of an instability overtime of the device. To overcome this serious problem different approaches were undertaken and one of the most adopted is to finely control the amount of copper deposited on the Te-rich surface of the CdTe layer immediately after the chemical etching. In other cases the CdTe surface is naturally grown Te-rich, as described in the previous paragraph and any chemical etching is not needed. A very good over time stability is obtained if a buffer layer (such as  $\text{M}_2\text{Te}_3$ ) between the Cu very thin layer and the CdTe film surface is interposed. The buffer layer, binding Cu atoms, acts as a filter for their diffusion and a better control on the formation of the degenerate interface layer is obtained.

Despite the chemical etching is part of the industrial production process of CdTe-based modules, a more environmental sustainable method is desirable especially for not handling and disposing large quantities of acids and great amount of deionized water. As described before, CSS technique naturally gives a Te-rich surface, which could be lost if CdTe film is treated with  $\text{CdCl}_2$ , since cadmium contained in the salt compensates the excess of tellurium, making the surface of the CdTe film close to stoichiometry. On the contrary, if the Te-rich surface is treated in chlorine atmosphere with the only presence of the cation (chlorine or fluorine) it remains with its own excess and it doesn't need any chemical etching before the contact deposition. At this stage, if a buffer layer of the  $\text{M}_2\text{Te}_3$  family with a thin Cu film is used, coupled with an air-annealing at 470 K for 10 min, a low-resistance ohmic contact is routinely obtained. Since this system tends to release Cu, Sb, As or Bi atoms, which diffuse into the grain boundaries of the polycrystalline CdTe film, it may simultaneously cause two different phenomena (Du, 2009; Durose et al., 2002): (1) they can bind to tellurium excess, forming a p-type  $\text{M}_2\text{Te}_3$  or  $\text{Cu}_x\text{Te}$  degenerate interface layer. Te-rich surface layer has the fundamental function to stop the diffusion of metal atoms released from the back-contact. (2) The chemical affinity between M and Oxygen atoms promotes the formation of an oxide, such as  $\text{M}_2\text{O}_5$ , into the grain boundaries of the CdTe film which, being an insulating material, contributes to the passivation of grain boundaries eliminating their ability to recombine the charge carriers.

In both these cases, there would be an increase in the performance of the solar cell. In addition to a low resistance, a good back-contact must ensure the device to have an excellent over time stability. As-described back-contacts making use of buffer layers easily exceed the accelerated lifetime test showing a good behavior when left for 1300 h under  $1000 \text{ W/m}^2$  at a temperature of 350 K. Normally the test says that these cells lose less than 20% of their performance, which means a very good durability of these devices corresponding to a PCE equal to 80% of the initial value after 25 years of work in their natural ambient.

Summarizing, the stability of this device depends heavily on the back-contact stability. A good back-contact assumes that:

- The surface of the CdTe film is Te-rich;
- The presence of a “filter” (buffer) coupled with a thin layer of Cu (2 ÷ 3 nm) promoting the formation of a heavily doped interface layer;
- The whole system is thermally air-treated at about 470 K for ten minutes.

If this receipt is respected, good over time stability of the devices is generally reached, allowing an industrial large-scale production of CdTe-based modules.

## 2.2. Substrate configuration

An alternative to the most used superstrate architecture is the TCO/CdS/CdTe/metal “substrate” configuration (Fig. 1b). In this case, also opaque substrates could be used and, among them, thin metal foil are the most requested, since they are flexible, light and cost effective. Moreover, metal sheets may enable the roll-to-roll technique allowing a wide variety of applications, including vehicle- and building-integrated photovoltaics (BIPV).

Despite the difficulty in implementing this type of device, several studies have gone in the direction of exceeding these problems, since this architecture could elegantly offers some advantages overtaking one of the biggest limitations suffered by the superstrate configuration; in this case, CdTe doping and CdTe/CdS junction formation become separated steps and could be individually optimized. On the other hands, substrate devices encountered not yet solved problems. For example an ohmic back-contact remains a challenging open issue partially overcome by the inclusion of a buffer layer between the Mo and the CdTe film. Solar cell produced on Mo/glass substrates gave efficiencies in the range of (13.6 ÷ 11.3)% by using Te/ $\text{MoO}_3$  and CuTe buffer layers respectively (Gretener et al., 2013; Dhere et al., 2012). While the best performance reported to date on a metal substrate CdTe solar cell fabricated on Mo foil is 11.5% (Kranz et al., 2013). Moreover, production of large area devices requires the implementation of the monolithic integration of all the module for making the electrical series interconnection of every cell. As a consequence, the metal substrate has to be electrically insulated from the back-contact of the solar cell, otherwise series interconnection would not be possible having the system a common electrode. This dielectric film is often deposited by R. F. sputtering making use of insulating target such as  $\text{Al}_2\text{O}_3$  and/or  $\text{SiO}_2$ , exploiting the technology developed for CIGS-based solar cell on flexible substrates (Herz et al., 2002).  $\text{Al}_2\text{O}_3$  layers could be effective as a diffusion barrier between the metal substrate and the back-contact in order to reduce metal ion diffusion from the substrate thus decreasing the number of defects inside the absorber layer. This is an important feature because the back-contact, being the first step of the process, must resist through the remaining high temperature processes, which make the system conditions very severe. In standard superstrate configuration back-contact is the final procedure of the cell fabrication and this doesn't represent an issue. The dielectric barrier fulfills a dual task by isolating the device electrically and chemically from the metal substrate.

As said before, another important issue in CdTe solar cell preparation is the chlorine heat-treatment. In this cell configuration it was shown (Williams et al., 2014) that an optimized double annealing process is needed in order to obtain the best performance: firstly the typical chlorine treatment of the CdTe layer acting on defects, doping, nano-grain, etc... is carried out, while the second step consists in a high-temperature (820 ÷ 870) K annealing following CdS and TCO deposition, which enhances sulphur-tellurium inter-diffusion improving the diode quality.

Despite these arrangements, the final performance of these devices is far from the normal operation of their superstrate configuration counterparts showing that several problems are still open.

## 2.3. Main results and future prospects

Durability over time is one of the main features of a solar cell. The time-stability must be maintained for all the lifetime of the photovoltaic modules (25 years) in hard operating environmental condition. On this side, CdTe technology has achieved excellent results only after the implementation of buffer layers (tellurides) between CdTe film and back-contact with the aim of keeping under control every unwanted diffusion from the contact material. This is a passive action made by the buffer material itself with its properties such as thickness of the film, diffusion coefficient of the migrant atoms at working temperature,

electronic affinity, carriers density, coverage, etc... Moreover, at all the interfaces there are inter-diffused phases and this is particularly evident in the grain-boundaries of the CdTe film within which there is a deep penetration of the back-contact. Recently, a new concept of passivation comes out, where the buffer layer is not only a barrier against diffusion fitting the energy band profile of CdTe with the back-contact, but it could become active part of an enhanced innovative device (Tuteja et al., 2016; Kanevce et al., 2017). n-type material, segregated into grain boundaries of CdTe layer, causes a type-inversion surface, which works as a mirror for the minority carriers extending their life-time.

Grain boundaries as source of shunt paths for the photo-generated carriers are neutralized with a net gain in junction quality and in device durability.

By considering the intrinsic difficulties encountered in doping p-type the CdTe polycrystalline films, thickness reduction of the absorber layer is mandatory in order to optimize the internal resistance of the device and minimize the electrical power loss. This is made possible by using a double layer strategy: over a 3  $\mu\text{m}$  thick CSS-CdTe layer, a second CdTe film, 0.2  $\mu\text{m}$  thick, deposited by sputtering exhibiting a n-type conductivity, completely eliminates pinholes always present in CSS-films with thickness less than 4  $\mu\text{m}$ . In this way, a very good coverage is obtained together with a smart passivation of the CdTe grain boundaries. Following this approach, 16% efficiency CdTe solar cells are routinely produced on laboratory scale.

In order to increase the efficiency other new concepts need to be developed. Recombinant processes have to be minimized not only on the surface of the grain but also within the crystalline grains especially in the interface region removing the structural defects (mismatch, dislocations, etc...), which still remain after chlorine treatment. The life-time of the charge carriers has to be three or four times greater than those measured in solar cells exhibiting 16% efficiency (Poplawsky, 2016; Poplawsky et al., 2016).

One of the main efficiency limitations is the low open circuit voltage, which is generally close to 0.85 V while it would be expected, according to the band gap, to be at least around 1 Volt.

With average values of 25/26 mA/cm<sup>2</sup> for current density and fill factor close to 75%, a 1 Volt open circuit voltage solar cell would deliver around 19.5% efficiency, which would go well beyond 20% by reducing optical losses and increasing the FF towards 80%. The old and new challenges are summarized in the following:

Open circuit voltage over 0.95 V, by managing the absorber energy gap and by improving carrier lifetime and CdTe doping level, could be reached.

In pure-CdTe solar cell, the maximum photo-voltage that can be obtained is limited by the difference between the Fermi's quasi-levels in the junction region, which in turn is limited by the doping density within the absorber layer. The impossibility of reaching doping density high enough for recovering all the voltage that the CdTe energy gap could give is well known. One possible solution is to use a larger gap material to form junction with CdS eg. adding a small amount of Zn to the CdTe. The thickness of this layer must be sufficiently thin (10 nm) to allow tunneling of electrons generated by light inside the absorber. On the contrary, in order to better absorb the solar light, an absorbing material with a smaller energy gap than that of CdTe would be desirable. In this way, near infrared photons produce electron-hole pairs which would otherwise be lost, increasing consequently the solar cell photocurrent. A suitable material for this purpose is CdTe<sub>x</sub>Se<sub>(1-x)</sub> with x between 0 and 0.5 (Menga and Yanb, 2016; Poplawsky, 2016; Poplawsky et al., 2016). Depending on the value of x, the best appropriate energy gap material for better absorbing the wide part of solar light spectrum is easy to find. Moreover, parasitic light absorption in CdS could be reduced by introducing materials with larger energy band gap and/or smaller absorption coefficient such as Cd(O,S) or Cd<sub>x</sub>Zn<sub>(1-x)</sub>S.

Fill factor could be improved from 75% towards 80% by engineering the p/n junction in a passivated polycrystalline thin CdTe

layer (2  $\mu\text{m}$  thick) putting together the new concepts described before concerning grain boundary smart passivation, minority carriers mirror preventing the recombination at back-contact and negligible internal resistance.

An important challenge for CdTe is the module final cost per Wp. Not surprisingly CdTe photovoltaics is one of the few thin-film top ten best-selling technologies. The high scalability and the low production cost have allowed very low-cost per watt, competitive with silicon crystalline production. Up to now, efficiencies around 16% are achieved in European laboratories but there is a strong potential to increase this value well above 20% (21% has already been obtained by the American company First Solar). If both high efficiency and low cost production will be obtained, the cost per watt of finished modules will be dramatically reduced (0.3 US\$/Wp) definitely reaching, everywhere, the so-called grid-parity.

### 3. Conclusion

This paper summarizes the main aspects faced over the years to solve the efficiency and time-stability problems in CdS/CdTe solar cells both in superstrate and substrate devices.

We have analyzed the research made in the last two decades to optimize every single layer of the solar cell and how these layers interact, with particular relevance to the study of interfaces and their influence on the final operation of the device. During this period, the main problems have been identified and the different applied solutions are described. Reduction of the absorber thickness, grain boundaries passivation, back-contact quality, CdTe doping, recombination/lifetime of the charge carriers and interface defects are only few of the addressed issues at which researchers tried to give a convincing solution. Some open problems still remain, such as interface defects and CdTe doping, although big steps have been made in this direction as well. Smart grain boundaries passivation coupled with enhanced back-contact and energy band gap engineering of the absorber are only two of the last innovations which can lead to device efficiency greater than 20%, which is, nowadays, the minimum goal to be considered as a promising device for industrial production.

Summarizing this analysis, the paper highlights the great potential of CdTe thin film technology, which proves to be closer and closer to produce device with efficiencies shown by silicon thus becoming a crucial candidate for global low-cost PV market in the near future.

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