

Thin film CdS/CdTe solar cells: Research perspectives

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Abstract

Polycrystalline thin film CdTe continues to be a leading material for the development of cost effective and reliable photovoltaics. The two key properties of this material are its band gap (1.5 eV), close to the ideal for photovoltaic conversion efficiency (1.45 eV), and its high optical absorption coefficient. Thin film CdTe solar cells are typically hetero-junctions with CdS being the n-type partner, or window layer. Efficiencies as high as 16.5% have been achieved, but still there is some potential for increasing them.

We make an analysis of the typical CdS/CdTe superstrate solar cell, and from it we establish critical issues and different lines of research in order to improve the current efficiencies. We also show that present record efficiencies are very close to the practical efficiency limit for a CdS/CdTe hetero-junction cell.

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1. Introduction

During 2002, large-scale production of solar cells worldwide stood above 500 MW_p, consisting ~40% of single crystal Si and ~51% multi-crystalline Si cells and about 8% based on thin film amorphous Si solar cells. About 2 GW_p of solar cells have been used worldwide in a variety of applications. The PV industry is already a billion dollar industry.

To provide a view of the current PV technologies it is useful to compare the manufacturing cost.

Fig. 1 shows the average module manufacturing cost per watt weighed by the production capacity, of thin-film modules in comparison with non thin-film modules based on data available in 2001 (Chopra et al., 2004; Mitchell et al., 2002). There has been a steady and rapid decline in the cost and one expects the cost comparison of thin-film cells to become even favorable. By 2007, thin-film solar cell technologies have the potential for producing cheaper devices on a large scale.

The best efficiency results reported for three of the more relevant thin-film solar cell technologies are summarized in Table 1 (Green et al., 2005). We see that CuInGaSe₂ and CdTe based solar cells have achieved efficiencies above those for a-Si cells.

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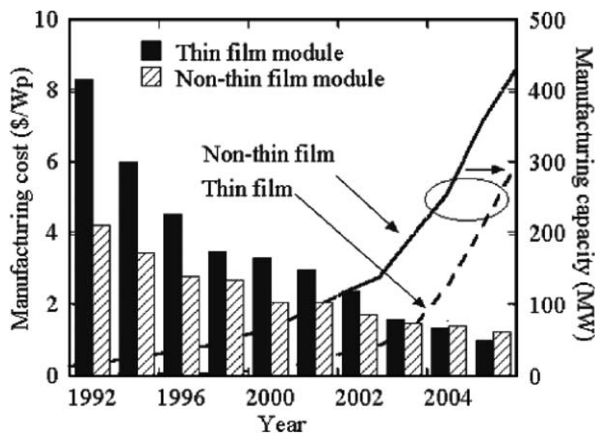


Fig. 1. Manufacturing cost and production capacity projections for thin-film and non-thin-film modules based on data available in year 2001 (Chopra et al., 2004; Mitchell et al., 2002).

Table 1

Selected record efficiencies of different thin-film solar cells confirmed by NREL

Cell type	Efficiency (%)	Area (cm ²)	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor (%)
a-Si	12.7	1	0.887	19.4	74.1
CuInSe ₂	15.4		0.515	41.2	72.6
CuInGaSe ₂	19.2	0.408	0.689	35.7	78.12
CuInAlSe ₂	16.9	0.470	0.621	36.0	75.5
CdTe	16.5	1.032	0.845	25.9	75.5

Other inexpensive solar cells are emerging with high potential such as those based on CuInAlSe₂. These chalcopyrite solar cells have achieved high efficiencies quickly, but very little is known about these materials, and such results are more empirical than based on a good knowledge of them. Hence, their development is always uncertain. On the other hand, multi-crystalline CdTe is a better known semiconductor, but still some problems remain to be solved, such as making good ohmic contacts on it, as we shall explain later.

In what follows we shall focus our attention to CdS/CdTe solar cells which, as shown in Table 1, have achieved record efficiencies of 16.5% since 2001. One of the main questions we shall try to answer is if this efficiency can be improved and how much.

2. State of the art for CdS/CdTe solar cells

As seen in Fig. 2, the typical superstrate structure of a CdTe/CdS solar cell is composed of 4 layers:

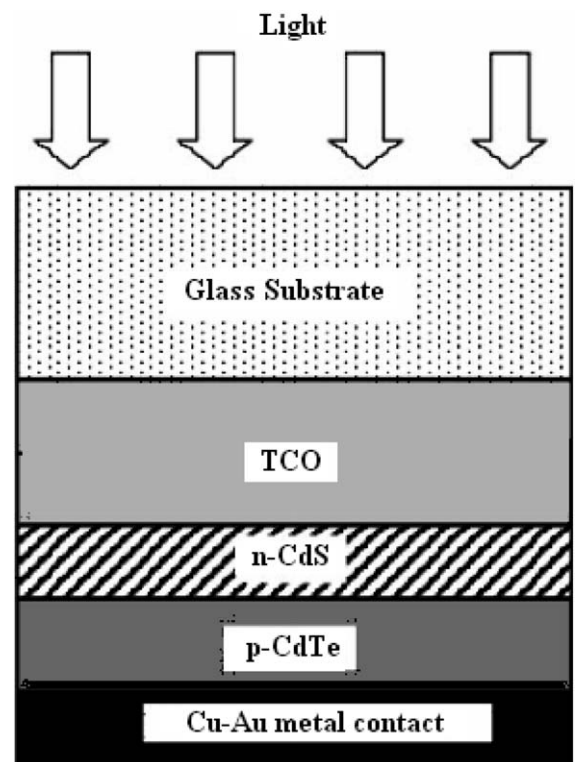


Fig. 2. Schematics of a typical superstrate CdS/CdTe solar cell structure.

1. a transparent and conducting oxide (TCO) which acts as a front contact;
2. a CdS film which is the so called window layer;
3. a CdTe film which is the absorber layer made on top of CdS;
4. the back contact on top of the CdTe layer.

The characteristics that are required in order for a TCO to be used as a front contact for CdTe/CdS thin-film solar cells are:

- high transparency, better than 85% in the wavelength region of interest (400–860 nm);
- low resistivity on the order of $2 \times 10^{-4} \Omega \text{ cm}$ or a sheet resistance less than $10 \Omega/\text{square}$;
- good stability at the maximum temperature at which other layers are prepared. This means that no diffusion from the TCO into the layers deposited subsequently must happen.

In Table 2 we show the properties of some of the most important materials used as TCO in solar cells (Chopra et al., 2004). Of particular interest is

Table 2

Properties of some of the most common transparent conducting oxides (TCO) and buffer layers

Material	Resistivity (Ω cm)	Transparency (%)
SnO ₂	8×10^{-4}	80
In ₂ O ₃ :Sn	2×10^{-4}	80
In ₂ O ₃ :Ga	2×10^{-4}	85
In ₂ O ₃ :F	2.5×10^{-4}	85
Cd ₂ SnO ₄	2×10^{-4}	85
Zn ₂ SnO ₄	10^{-2}	90
ZnO:In	8×10^{-4}	85

Cd₂SnO₄ (CTO) which has a transparency above 85% and resistivity as low as $2 \times 10^{-4} \Omega$ cm.

It is possible to take advantage of the different properties of two TCO films by forming a bi-layer. High-efficiency CIGS and CdTe devices are generally fabricated with such bi-layer structures, consisting of a highly conducting layer for low-resistance contact and lateral current collection and a much thinner high-resistivity layer (called buffer layer) of a suitable material, to minimize forward current through pinholes in the window layer. By incorporating a 50-nm-thick resistive SnO₂, In₂O₃, ZnO, or Zn₂SnO₄ layer, the CdS layer thickness can be reduced to <80 nm, which significantly improves the blue response of the CdTe devices. The presence of the smoother high-resistive layer also improves the CdS film morphology by providing large grains during chemical bath deposition.

A buffer layer may also act as an “etch-stop” layer during the back-contact formation process and greatly reduce shunting problems. For example, Zn₂SnO₄ (ZTO) films resists the etchant (e.g., a nitric/phosphoric-based acid etchant) used for back-contact formation (Wu, 2004). There is almost no etch for ZTO film in the NP etchant for more than 30 min, but ~ 1000 Å-thick chemical-bath-deposited (CBD) CdS film can be completely etched in the NP etchant within 20 min.

The CdS layer is prepared by several methods like evaporation, chemical bath deposition (CBD) and closed space sublimation (CSS). All these methods are suitable to prepare a CdS layer that, when used in CdTe/CdS solar cells, can give efficiencies larger than 10% even though the highest efficiency was obtained by using a CdS prepared by CBD. The choice of the CBD method was probably due to the fact that CBD makes a very compact film that covers perfectly the TCO layer.

A very important treatment independently of the deposition technique for both CdS and CdTe layers

is thermal annealing after deposition of CdCl₂ on top of the CdTe layer. If the CdCl₂ treatment is not performed, the short circuit current and the efficiency of the solar cell are very low. The treatment consists in depositing 300–400 nm of CdCl₂ on top of CdTe with a subsequent annealing at 400 °C for 15–20 min in air, or in an inert gas like Ar. During this process the small CdTe grains are put in vapour phase and re-crystallize giving a better-organized CdTe matrix. The presence of Cl₂ could favour the crystalline growth of CdTe by means of a local vapour phase transport. In this way the small grains disappear and the CdS/CdTe interface is reorganized.

Owing to its optoelectronic and chemical properties, CdTe is an ideal absorber material for high-efficiency low cost thin film polycrystalline solar cells. CdTe is a direct bandgap material with an energy gap of 1.5 eV, and an absorption coefficient $\sim 10^4$ cm⁻¹ in the visible region, which means that a layer thickness of a few micrometers is sufficient to absorb 90% of the incident photons. Owing to the high temperature of deposition in most cases, the films are deposited with Cd deficiency, giving rise to p-type conductivity. Because of the high ionicity (72%) of CdTe, the crystallites formed are well-passivated and strong chemical bonding (5.75 eV) results in high chemical and thermal stability. CdTe solar cell devices have proven to be remarkably tolerant to the deposition method and devices with efficiency >10% have been fabricated by several deposition techniques. Some of these techniques, close-spaced sublimation (CSS), electro-deposition and screen-printing have been scaled to yield large area modules. Solar cells based on CdS/CdTe junction have achieved an efficiency of 16.5% in small areas compared with the “theoretical maximum efficiency” of 29%. However, for the past 10 years the efficiency has changed only from 15.8% to 16.5%.

There are no low-cost metals available with appropriate higher work function (>4.5 eV) to form ohmic contact on CdTe and Au has been used in most cases. Ni-based contacts have also shown promising results. In an alternative approach, a pseudo-ohmic contact was developed for CdTe devices. Here, a highly doped semiconductor is first deposited, or formed on the CdTe surface, followed by the application of a metal film contact. With this purpose, semiconductors such as HgTe, ZnTe:Cu, Cu_xTe, and Te can be deposited between CdTe and the contact metal to achieve a good ohmic contact. Cu-doped graphite paste and antimony

telluride have also been tried, with mixed success. Etching of CdTe films using Br–methanol, NP solution, etc., creates a Te-rich p+ region, which can be useful in making a pseudo-ohmic contact with Cu/Au layer, since the use of elemental Cu leads to p++ Cu₂Te formation. Wet contacting methods and all-vapor contacting methods are actively being investigated for commercial development.

Despite the great effort for developing a good, reliable and stable ohmic contact, the results are not satisfactory yet, and this is still one of the main problems for high volume industrialization of CdS/CdTe solar cell modules.

Some of the above ideas have been developed in order to obtain high efficiency CdS/CdTe solar cells. In this way, the team led by Wu in the NREL in USA has achieved the highest efficiency for this kind of solar cells (Wu et al., 2001). In Fig. 3 we show the structure and approximate thickness for each layer with which they have attained conversion efficiency of 16.5%. Notice the presence of the mentioned CTO and ZTO bilayer for the TCO. Notice also that they have used a 10 μm CdTe layer, but with a very thin CdS layer below 0.1 μm . The graphite contact at the back of the CdTe layer usually contains Cu as seems to be needed in order to make good ohmic contacts on p-type CdTe. For the highest efficiency solar cell shown here:

$$V_{oc} = 845 \text{ mV}$$

$$J_{sc} = 25.88 \text{ mA/cm}^2, \quad \eta = 16.5\%$$

$$\text{FF} = 75.5\%$$

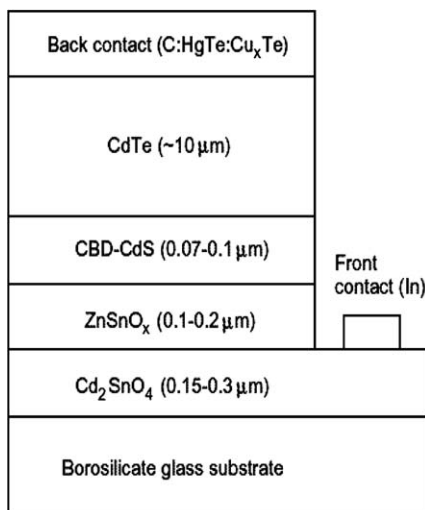


Fig. 3. Cd₂SnO₄/Zn₂SnO₄/CdS/CdTe record efficiency solar cell device structure.

3. How can we improve the record efficiency of CdS/CdTe solar cells?

In order to answer the above question, we must notice that the diverse preparation techniques for CdS and CdTe layers cause also a variety of properties such as carrier lifetimes, mobilities, and absorption coefficients. Unfortunately, much of the work is done empirically and no design or optimization methodology is followed since these characteristics should be known, but usually they are not when making solar cells.

In Table 3 some of the properties of CdS, as has been used by people doing simulation of CdS/CdTe solar cells, are shown. As we shall see, these values allow us to draw the ideal band-diagram at the hetero-junction of CdS with CdTe for a solar cell. The donor concentration will depend strongly on the deposition method, but a desirable value of 10^{17} cm^{-3} is given here. If this value could be increased to $1 \times 10^{18} \text{ cm}^{-3}$ by some doping process we could expect better results for the solar cell open circuit voltage.

In Table 4, similar properties for CdTe thin films are shown. Notice that with these values the electron diffusion length would be around 3–4 μm . However, due to the diverse quality of the CdTe deposited in different laboratories with different deposition techniques we can expect values between 1 and 8 μm . The majority carrier concentration is

Table 3

Typical electrical parameters for CdS films, according to different published reports

Parameter	Value	Parameter	Value
ϵ_s	9.0	N_A	0.0
μ_n	$350 \text{ cm}^2/\text{V s}$	N_D	$1 \times 10^{17} \text{ cm}^{-3}$
μ_p	$50 \text{ cm}^2/\text{V s}$	E_g	2.42 eV
N_C	$1.8 \times 10^{19} \text{ cm}^{-3}$	χ	4.5 eV
N_V	$2.4 \times 10^{18} \text{ cm}^{-3}$	Thickness	0.1 μm
τ	$1 \times 10^{-10} \text{ s}$		

Table 4

Similar typical electrical parameters for CdTe films

Parameter	Value	Parameter	Value
ϵ_s	9.4	N_A	$1 \times 10^{15} \text{ cm}^{-3}$
μ_n	$500 \text{ cm}^2/\text{V s}$	N_D	0.0
μ_p	$60 \text{ cm}^2/\text{V s}$	E_g	1.5 eV
N_C	$7.5 \times 10^{17} \text{ cm}^{-3}$	χ	4.28 eV
N_V	$1.8 \times 10^{18} \text{ cm}^{-3}$	Thickness	1–10 μm
τ	$1 \times 10^{-8} \text{ s}$		

also very low, about $1 \times 10^{15} \text{ cm}^{-3}$. Increasing this value to 10^{16} cm^{-3} should also cause a higher built-in voltage.

From the preceding data we can now draw the ideal band diagram for the CdS/CdTe hetero-junction as shown in Fig. 4. A built-in voltage of 0.95 V is expected. The conduction band discontinuity does not limit the electron photocurrent from CdTe to CdS. The hole photocurrent from CdS to CdTe is not limited either by the valence band discontinuity. In this diagram, we have indicated the possible presence of a CdSTe alloy film due to the diffusion of S into CdTe and Te into CdS. It has been speculated that this interlayer helps to improve the efficiency of the solar cell, for example by reducing the interface carrier recombination, but there is not any specific experimental result confirming this hypothesis. It is very likely that there is influence of this layer on the behavior of the solar cells but further study is needed.

As explained before, we have found a variety of data for the absorption coefficient of CdTe. This property and how it varies as a function of wavelength is very important and determines the CdTe layer thickness required for absorbing the sunlight radiation. The data shown in Fig. 5 corresponds to values reported for crystalline CdTe (Dubrovskii, 1961). It can be seen that the absorption length for photons with wavelength between 300 and 720 nm is less than 1 μm . Notice, however that for photons

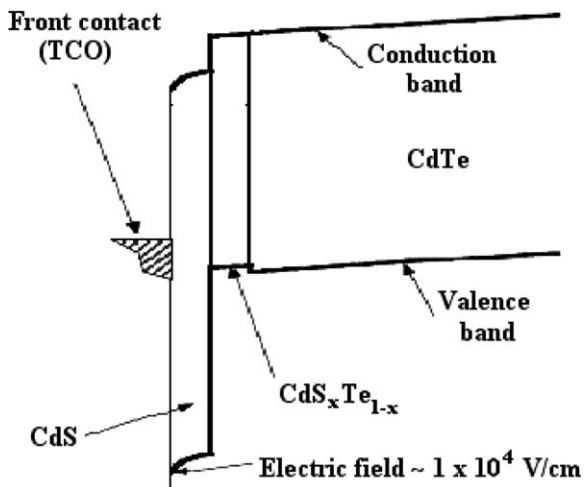


Fig. 4. Ideal band diagram at the CdS/CdTe interface. $\Delta E_C = 0.22 \text{ eV}$ and $\Delta E_V = 0.7 \text{ eV}$. The total built-in voltage is around 0.95 V when the doping at each side of the hetero-junction is assumed to be $N_D = 1 \times 10^{17} \text{ cm}^{-3}$ and $N_A = 1 \times 10^{15} \text{ cm}^{-3}$, respectively.

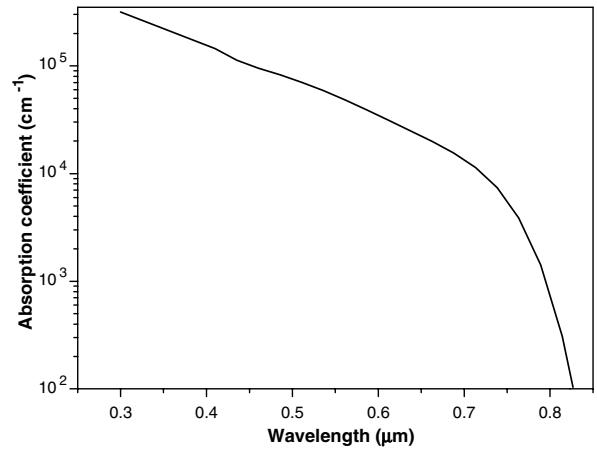


Fig. 5. CdTe absorption coefficient at room temperature.

with wavelength above 750 nm the absorption length becomes larger than several micrometers.

In order to establish an estimate of the appropriate CdTe thickness, in Fig. 6 we show the relative cumulative carrier generation rate, i.e. the total amount of carriers generated per unit area in the CdTe layer taking into account the absorbed photons from the surface up to position x inside this layer. The assumed spectrum was the AM1.5 global normalized to 100 mW/cm^2 . The graph shows the cumulative generation rate normalized to the total photon content in this spectrum. For CdTe thickness sufficiently large, the total generated carriers will be approximately 100% of what can be obtained from the solar spectrum assuming that only one

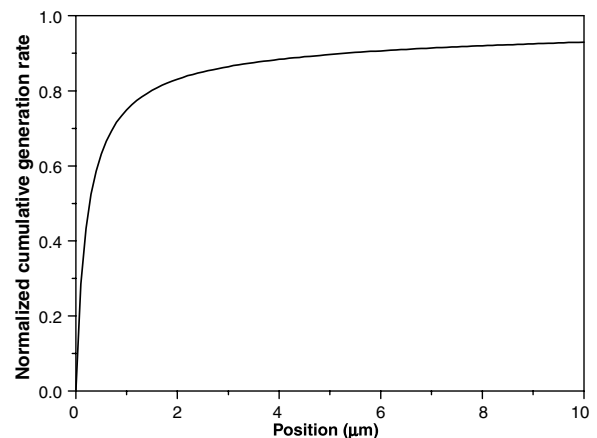


Fig. 6. Cumulative generation rate (total number of electron-hole pairs generated per unit area per unit time) as a function of position in the volume of the CdTe film. The global solar spectrum AM1.5 was assumed (normalized to 100 mW/cm^2).

electron–hole pair is generated for each photon absorbed.

This graph indicates that an estimated optimum value for the CdTe thickness is between 2 and 6 μm , since little gain is expected for the photocurrent if the thickness is increased above 6 μm , and degradation of the series resistance may cause a reduction of the filling factor. Below 2 μm the photocurrent would degrade quickly as the thickness becomes smaller.

A more detailed calculation has been made using well known expressions for the photocurrent in solar cells (Hovel, 1975). The expected photocurrent density (J_L) as a function of the CdTe layer thickness, taking into account the volume recombination and the surface recombination at the back contact, while neglecting the absorption losses in CdS, is shown in Fig. 7.

Two limiting cases were considered. The first was the case for zero recombination velocity at the back, and the second one was for very high recombination velocity there. We have also included the experimental results reported by Wu et al. (2001) and Compaan et al. (2004) for high efficiency solar cells. Notice that we have assumed 4 μm for the electron diffusion length, but the results do not vary very much when this parameter changes from 1 to 10 μm . Notice also that NREL results imply good quality (CSVT) material with an intermediate recombination velocity at the back contact. However, the results reported by

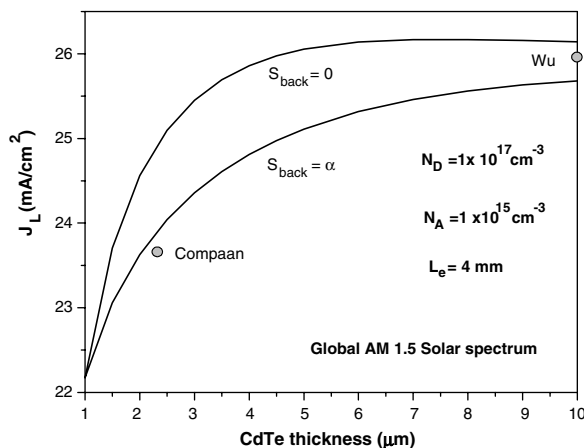


Fig. 7. Illumination current density (J_L) for CdS/CdTe solar cells as a function of the CdTe film thickness. Absorption and current generated in the CdS layer has been neglected. Two limiting cases were considered: no back surface recombination and very high recombination velocity at the back contact. In addition, two experimental points were included for reported high efficiency solar cells by Wu et al. (2001) and Compaan et al. (2004).

Compaan et al. (2004) and the results in this graph show that their material has not as good quality (smaller diffusion length) as Wu's since Compaan's group grow their CdTe films by sputtering.

From this graph, we can establish a better estimate for the optimum CdTe layer thickness. In this case, it seems that the smaller the back recombination velocity the smaller the required thickness for the CdTe layer. For high back recombination velocity, the optimum thickness becomes between 4 and 6 μm . However, the formation of a p++ region at the back for making the ohmic contact may help reducing the surface recombination velocity there, so that the optimum thickness for the CdTe layer becomes around 4 μm .

Let us remember the experimental results for the highest efficiency CdTe solar cells reported by Wu et al. (2001) and compare with some of our calculations. We may see that a short circuit current density (J_{sc}) of 25.88 mA/cm^2 is around 94% of what ideally can be obtained from a 10 μm CdTe solar cell (see Fig. 6). Hence, it will be very difficult to improve this value. A maximum J_{sc} of 26 mA/cm^2 is expected, particularly if the thickness is reduced slightly in order to improve the filling factor.

The measured open-circuit voltage of 845 mV is about 89% of the above calculated built-in voltage. In order to improve this value we should dope both the CdS and CdTe layers for increasing majority carrier concentrations at least one order of magnitude in each layer. By doing this we can expect that the open-circuit voltage increases to 960 mV, around 100 mV more than the current values.

The present record experimental filling factor (0.755) is around 87% of the ideal one for the measured open circuit voltage. When this voltage is increased, the filling factor should become close to 0.79, which is around 90% of the ideal one for the new voltage.

In other words, our realistic estimate for the maximum efficiency of CdS/CdTe cells is 17.6%, around 1% more than the present reported record efficiency, but this can be achieved only by improving the open-circuit voltage and the filling factor of these solar cells. In order to do this we need to have more control on doping CdS and CdTe and making better ohmic contacts to CdTe.

4. Some future research lines

From the above discussion we can propose some research directions for further improvement of CdS/

CdTe solar cells efficiency. For the TCO and buffer layers we have to look for a better combination such as ZnO:Al as TCO and Zn_2SnO_4 as a buffer layer, avoiding the use of Cd compounds such as Cd_2SnO_4 . This should also be combined with low temperature deposition of CdS and CdTe because these Zn compounds are not stable at high temperatures. Until today, nobody has experimented such a structure, i.e. ZnO:Al/ Zn_2SnO_4 /CdS/CdTe/ohmic contact. The diffusion of Zn and O into CdS should cause a larger bandgap and a decrease of the absorption losses in this material.

It will be difficult to substitute CdS as the window layer in this kind of solar cells since this material has shown that it forms an excellent hetero-junction with CdTe. Therefore, we can improve this material only by making it nano-crystalline when oxygen is introduced so that the bandgap becomes larger and a reduction of the absorption losses in the CdS layer is achieved. We still have some questions to answer regarding the effect of annealing in CdCl_2 . How much does Cl dope CdS? Can oxygen dope CdS in addition to the mentioned above crystallite size reduction? Can we control these phenomena?

It is well known that it is difficult to dope p-type CdTe to make it less resistive. It seems that Cu affects its behavior, but until now nobody has done a full study on the effect due to Cu. Oxygen also influence the electrical properties of CdTe. Higher acceptor doping levels would cause the required increase of built-in voltage in this structure. And related with this issue is the investigation for making better ohmic contacts on CdTe.

Only metals with very high work function would allow the formation of ideal ohmic contacts on p-type CdTe. These metals such as Au would be expensive and therefore are impractical. Hence, only the formation of a p^{++} CdTe surface would make contacts with low contact specific resistivity. In this regard, it seems that Cu has some influence on this phenomenon, and it is why graphite with copper seems to form good contacts on CdTe. However, still nobody would answer clearly if Cu dopes CdTe or if it reacts at the surface either. Understanding the effect of Cu on CdTe would allow control of the CdTe electrical properties for achieving better ohmic contacts on it.

Due to the CdS/CdTe solar cell research maturity which has achieved record conversion efficiencies very close to the expected limit efficiency, according to our above calculations, it is now important to

accelerate the development of this kind of solar cell at the manufacturing level. Some of the research lines mentioned above would contribute in this sense, like the understanding of Cu and Oxygen on both CdS and CdTe, the formation of ohmic contacts to CdTe, and the compatibility of film deposition for all the layers for these solar cells. When these problems are solved, CdS/CdTe solar cell market growth can be expected.

5. Conclusions

In summary, we have shown that the present record conversion efficiencies of CdS/CdTe solar cells are very close to the efficiency limit that can be achieved from this kind of hetero-junction cell. A much higher short circuit current density is not expected, but open-circuit voltage and filling factor can be improved achieving a maximum efficiency around 17.5%, i.e. 1% up from the current record. Our calculations explain also why the record efficiency has increased from 15.8% to only 16.5% during the last 10 years.

Finally, we have pointed out that before massive production competitive with other technologies is achieved, the problems related to contact resistivity, stability and reliability of ohmic contacts on CdTe must be solved.

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