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# Innovative Elastic Thin-Film Solar Cell Structures

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## 1. Introduction

The idea of thin films dates back to the inception of photovoltaics in the early sixties. It is an idea based on achieving truly low-cost photovoltaics appropriate for mass production, where usage of inexpensive active materials is essential. Since the photovoltaic (PV) modules deliver relatively little electric power in comparison with combustion-based energy sources, solar cells must be cheap to produce energy that can be competitive. Thin films are considered to be the answer to that low-cost requirement [1].

Replacement of single crystalline silicon with poly and amorphous films, caused the decline of material requirements, which has led to lower final prices [2]. Furthermore, the thickness of cell layers was reduced several times throughout the usage of materials with higher optical absorption coefficients. Unique, thin film and lightweight, devices of low manufacturing costs and high flexibility, were obtained by applying special materials and production techniques, e.g. CIS, CIGS or CdTe/CdS technologies and organic elements. Taking advantage of those properties, there is a great potential of new, useful applications, such as building integrated photovoltaics (BIPV), portable elastic systems or clothing and smart textiles as well [3].

Low material utilization, mass production and integrated module fabrication are basic advantages of thin film solar cells over their monocrystalline counterparts [4]. Figure 1 (by NREL) shows the development of thin film photovoltaic cells since 1975.

The development of cadmium telluride (CdTe) based thin film solar cells started in 1972 with 6% efficient CdS/CdTe [5] to reach the present peak efficiency of 16.5% obtained by NREL researchers in 2002 [6]. Chalcopyrite based laboratory cells (CIS, CIGS) have recently achieved a record efficiency of 20% [7], which is the highest among thin film PV cells (see Table 1). Solar modules based on chalcopyrites, uniquely combines advantages of thin film technology with the efficiency and stability of conventional crystalline silicon cells [4].

Thin film solar cell type	CIGS	CdTe/CdS	a-Si
Cell area [cm <sup>2</sup> ]	0.5	1.0	0.25
Highest efficiency [%]	20.0	16.5	13.3
Typical efficiency range [%]	12.0 – 20.0	10.0 – 16.5	8.0 – 13.3

Table 1. Efficiencies of CIGS, CdTe and a-Si thin film solar cells [8].

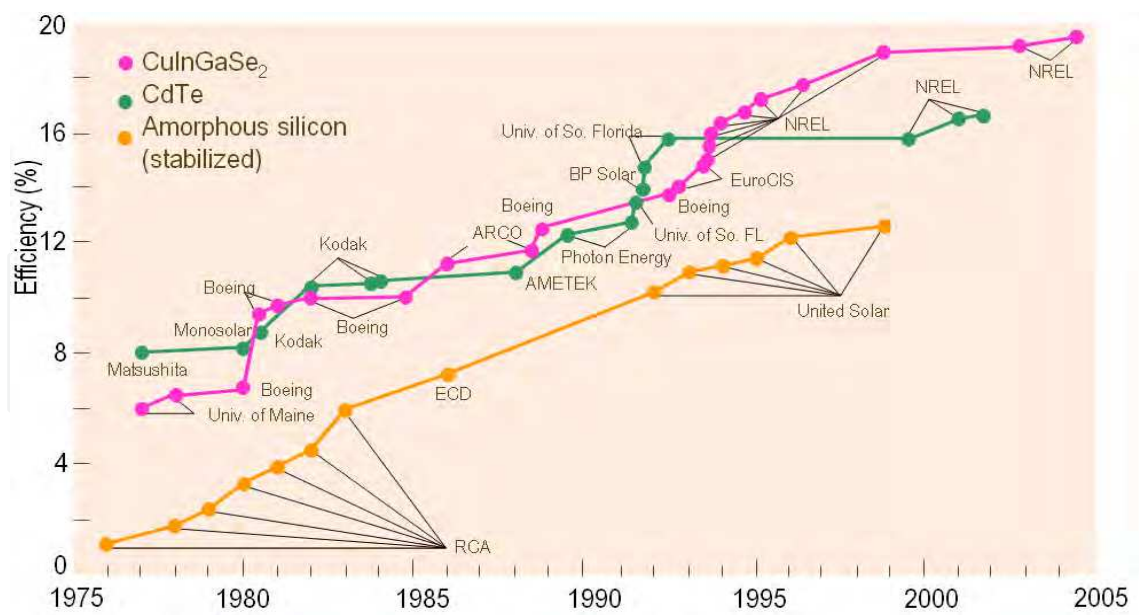


Fig. 1. Best laboratory PV cell efficiencies for thin films [source: [www.nrel.gov](http://www.nrel.gov)]

To comprehend the developmental issues of thin films, it is important to examine each individually. Each has a unique set of advantages and shortcomings in terms of their potential to reach the needed performance, reliability and cost goals [1].

1.1 CdTe cells and modules

Cadmium telluride based solar cells are one of the most promising in thin film photovoltaics. With a bandgap of 1.45 eV the material well suited to match the AM 1.5 solar spectrum. Furthermore, its high absorption coefficient causes that only a few microns absorber film is required for solar cell operation. The typical thin film CdTe/CdS structure is shown on Figure 2. Figure 3 presents the total life-cycle Cd emissions to prove that CdTe based PV cell are environment friendly and health safe.

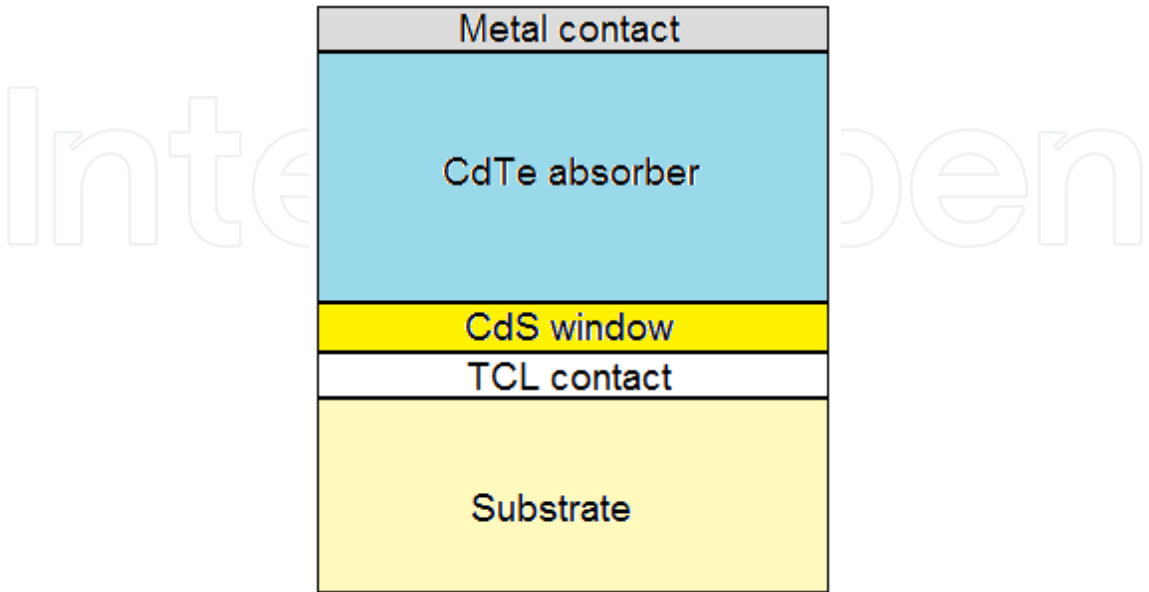


Fig. 2. Typical structure of CdTe thin film solar cell.

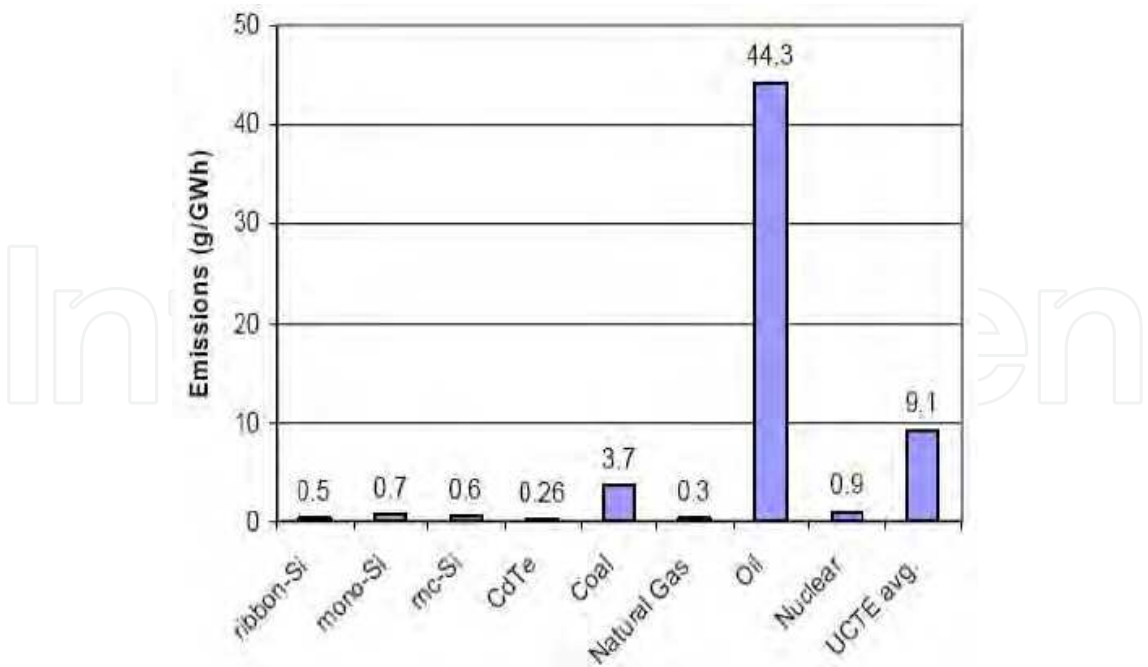


Fig. 3. Total life-cycle Cd emissions by Brookhaven National Laboratory [9].

Low-cost soda-lime glass, foil or polymer film can be used as the substrate of CdTe/CdS solar cell. The best results of 16.5% efficiency are achieved with glass substrate (Table 1). However, Laboratory for Thin Films and Photovoltaics at EMPA, Switzerland obtained 12.7% efficiency of single CdTe solar cell on polymer foil and 7.5% of monolithically interconnected flexible CdTe solar module of 32 cm<sup>2</sup> total area [10]. Transparent conductive layers (TCL) are usually thin conductive metal oxides, such as ITO (*Indium Tin Oxide*), Zn<sub>2</sub>O<sub>4</sub>, Cd<sub>2</sub>SnO<sub>4</sub>, ZnO:Al, CdO, ZnO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub> or RuSiO<sub>4</sub>. However, lastly in flexible solar cells, transparent conductive oxides (TCO) are being replaced by carbon nanotube (CNT) composites [11] or graphene. The CdS film is grown either by chemical bath deposition (CBD), close space sublimation (CSS), chemical vapor deposition (CVD), sputtering or vapor transport deposition (VTD). For the growth of CdTe, three leading methods are used for module fabrication: CSS, electro-deposition (ED) and VTD. Wide variety of metals can be used as back contact for thin film CdTe solar cells, e.g. Cu, Au, Cu/Au, Ni, Ni/Al, Sb/Al, Sb/Au [12].

Several thin-film PV companies are actively involved in commercializing thin-film PV technologies. In the area of CdTe technology major players are or were in the past: First Solar (USA), Primestar Solar (USA), BP Solar (USA), Antec Solar (Germany), Calyxo (Germany), CTF Solar (Germany), Arendi (Italy), Abound Solar (USA), Matsushita Battery (Japan) [8, 12, 13]. This effort lead to 18% share of CdTe cells in global PV marked in 2009 [14].

1.2 CIS/ CIGS/ CIGSS structures

Other promising material for thin film solar cell absorber layer is copper indium diselenide CuInSe<sub>2</sub>. CIS has a direct bandgap of 0.95 eV which can be increased by the addition of gallium to the absorber film. About 30% of Ga added to CIS layer (CIGS cell), changes the bandgap from 0.95 eV to almost 1.2 eV, which improves its match with the AM 1.5 solar spectrum. Higher gallium content (of 40%) has a detrimental effect on the device performance, because of its negative impact on the charge transport properties. The best

gallium to indium ratio is 3:7 for high efficiency PV devices. The role of sulfur in CIGSS is to increase the bandgap of the absorber film [12], which can boost the AM 1.5 spectrum fitting even more. The typical thin film CIGS solar cell structure is shown on Figure 4. Figure 5 presents an example CIGS cell structure manufactured in the Laboratory for Thin Films and Photovoltaics at EMPA, Switzerland.

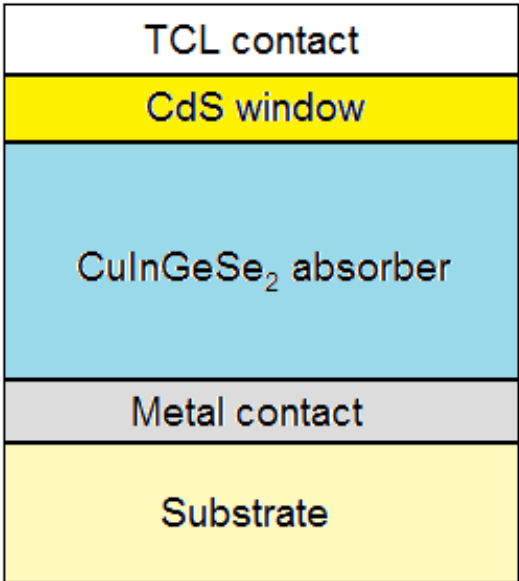


Fig. 4. Typical structure of CIGS thin film solar cell.

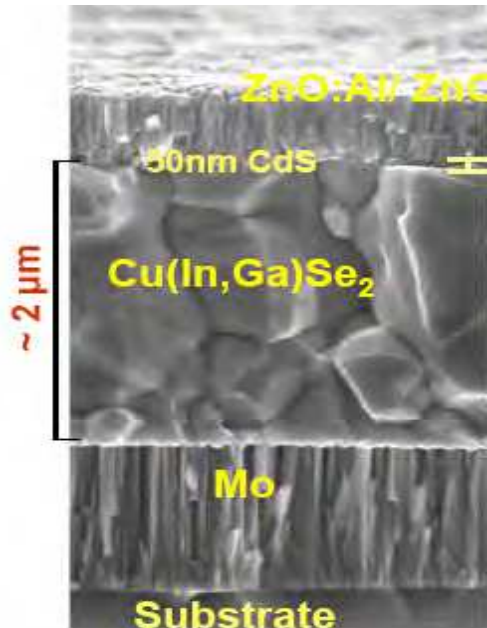


Fig. 5. CIGS cell structure manufactured at EMPA, Switzerland [8].

Worldwide, several companies are presently offering commercial thin-film PV CIGS products: Würth Solar, (Germany), Global Solar, (USA), Honda, (Japan), Showa Shell, (Japan), Sulfurcell, (Germany), Solibro (Germany), Avancis (Germany), Solyndra (USA), Centrotherm (Germany). Also, worldwide, about 34 companies are actively developing thin-

film CIGS PV technologies. These companies are using different deposition methods for growing the thin CIGS absorber layers, as is shown in Table 2 [13].

Company	Substrate	Back contact	Process	Front contact
Shell Solar	Glass	Mo	Sputter/ Selenization	ZnO
Global Solar	Steel	Mo	Co-evaporation	ITO
Miasole	Glass	Mo	Sputter	ZnO
Wurt Solar	Glass	Mo	Co-evaporation	ZnO
Avancis	Glass	Mo	Sputter/ RTP	ZnO
Daystar Tech.	Glass	Mo	Sputter	ZnO
EPV	Glass	Mo	Sputter/ Evaporation	ZnO
Ascent Solar	Polymer	Mo	Co-evaporation	ZnO
ISET	Glass/Flexible	Mo	Ink/ Selenization	ZnO
Nanosolar	Flexible	Mo	Print/ RTP	ZnO
Solo Power	Steel	Mo	ED/ RTP	ZnO

Table 2. Thin film CIGS technology.

The absorber layer for commercial products uses either co-evaporation or the two-stage process such as the deposition of the precursors (Cu, Ga, In) by sputtering followed by selenization. Absorber layer can be made out of three chalcopyrite chemical compounds: Cu(In,Ga)Se<sub>2</sub>, Cu(In,Ga)(S,Se)<sub>2</sub>, CuInS<sub>2</sub> which are respectively CIGS, CIGSS and CIS. As a back, metal contact Mo deposited by sputtering is most commonly used. Majority of companies (Table 2) use ZnO as the front transparent conductive layer. Zinc oxide is deposited either by sputtering or chemical vapor deposition [13]. Window layer of CdS (or alternatives, such as ZnS [8]) can be grown by analogous methods as in CdTe solar structure (CBD, CSS, CVD etc.).

As a substrate of thin film CIGS solar cell, either glass, metal (steel) sheet or polymer might be chosen. Highest efficiencies, as noted in Table 1, were achieved for modules on glass substrate. However, such solution have several inconveniences, which are for example: bulkiness, fragility and heaviness. Flexible substrates, on the other hand, offer both manufacturing and application related advantages, such as: large active area, roll-to-roll high speed (throughput) deposition, high material utilization, low thermal budget, monolithic interconnection, lower costs, light-weight and flexibility. Table 3 presents the comparison of thin film CIGS solar cell on steel and polymer substrate.

To conclude this subsection, we should ask a question: “why thin film CIGS and CdTe solar cells are worth attention?”. The answer was given and it can be summarized in several points:

1. they are highly efficient,
2. active layers can be deposited on various substrates including flexible ones,
3. they have extremely stable performance,
4. they cause no environmental or health hazards,
5. they are low cost,
6. these cells are attractive for both terrestrial and space applications [8].



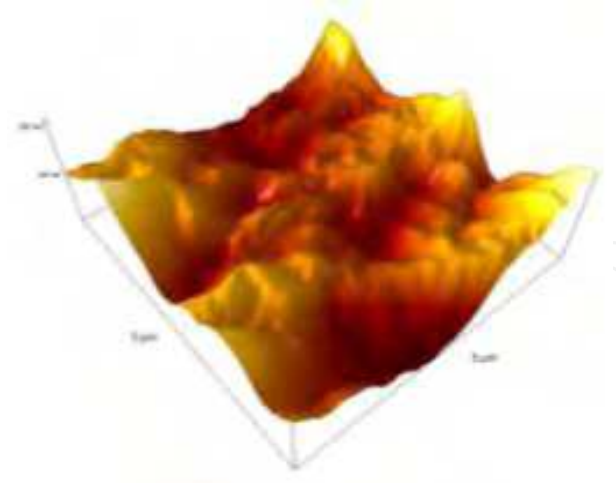
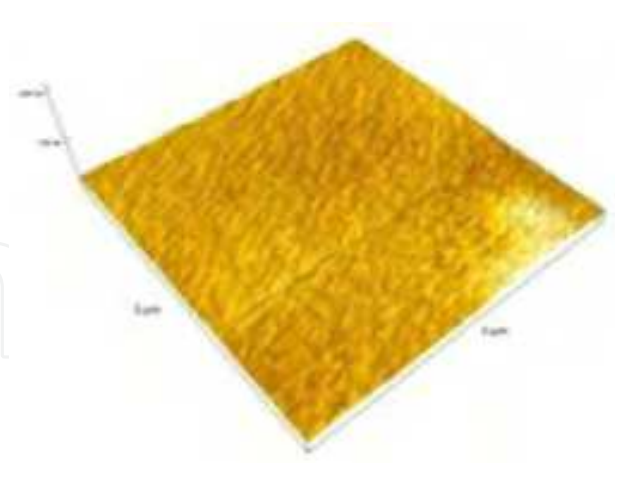
Metal (steel)	Polymer
	
Rough surface, kinks	Smooth surface
Conducting surface	Insulating surface
Metal impurities	No metal impurities
Barrier coatings needed for monolithic interconnection	No need of barrier coatings for monolithic interconnection
High temperature: 550- 650 °C	Low temperature: 450 °C
Highest efficiency: 18% on Ti foil	Highest efficiency: 16%

Table 3. Substrates for flexible CIGS solar modules [8].

Thin-film photovoltaic cells and modules are already widely popularized, mainly because of their small production costs and relatively high efficiency [15]. Moreover, some other, significant advantages, such as small weight and flexibility may be offered. That is the reason why large number of applications is being pursued using thin-film PV technologies, including building-integrated photovoltaics (BIPV), roof-top applications and utility-scale applications [13].

2. Manufacturing technologies of elastic thin – film CdS/CdTe solar cells

Cadmium telluride solar cells are placed among thin-film polycrystalline structures of high optical absorption and relatively low material consumption, with long development history [16]. Numerous virtues of each semiconductor compound as well as good cooperation within p-n heterojunction give the opportunity of efficient and cheap monolithic solar modules construction. Additionally, elastic structure of polycrystalline layers enables the flexibility of the manufactured modules and gives possibility of new implementations. The experiments leading to this goal were undertaken by various manufacturing technologies, however to maintain high optoelectronic parameters of the manufactured cells, independently on employed technology, proper polycrystalline structure must be preserved.

Standard technology of CdTe solar cells manufacturing is based of column grain structure. This specific material organization occurs owing to vertical growth of hexagonal CdTe and CdS grains and gives the opportunity of high optical generation, smooth vertical charge carrier transport and thus high conversion efficiency. Both semiconductors are predestined

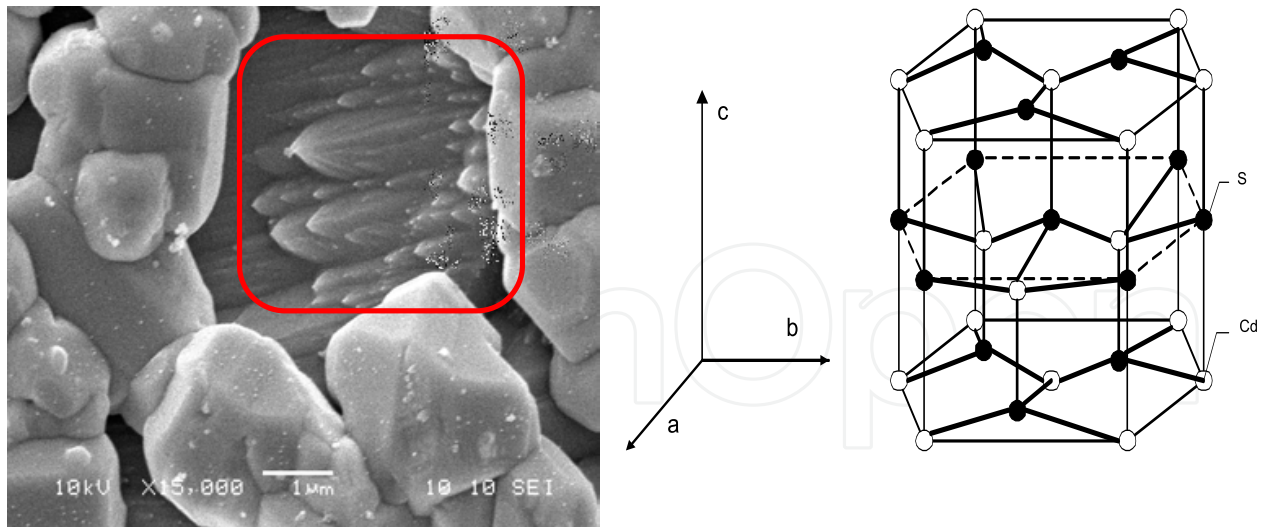


Fig. 6. SEM picture and the diagram of CdS wurtzite grains with vertical growth orientation and CdS hexagonal grain model.

to achieving of this structure under some technology circumstances [17] and may be matched with crystal constant differences not higher than 9,7% [18]. Structure of model CdS layer, obtained by authors, organized in wurtzite phase is presented in Figure 6.

The most popular manufacturing technologies of CdS/CdTe solar cells are nowadays CVD (*Chemical Vapour Deposition*) and the variants like PECVD (*ang: Plasma Enhanced CVD, or MOCVD (Metall Organic Chemical Vapour Deposition)* [19], CBD (*Chemical Bath Deposition*) and physical methods like PVD (*Physical Vapour Deposition*), CSS (*Close Space Sublimation*) [20], and variants of CSVT (*Close Space Vapour Transport*) [21, 22]. Alternatively screen-printing technology was also successfully employed for production of relatively thick CdTe base [23]. Morphology of the last mentioned layers was verified by authors with the help of SEM analysis indicating dense compact structure of hexagonal grains (Figure 7).

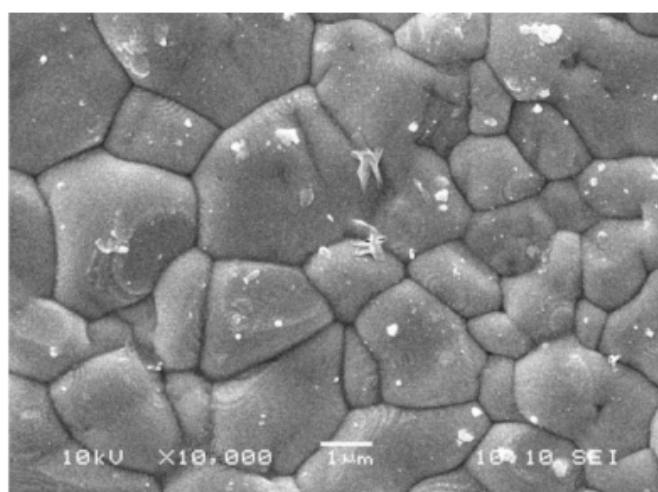


Fig. 7. SEM picture of dense, compact CdTe grain layer up to 8µm, manufactured by ICSVT technology on glass substrate.

As the additional experiments AFM profile of this layer, presented in Figure 8 was prepared.



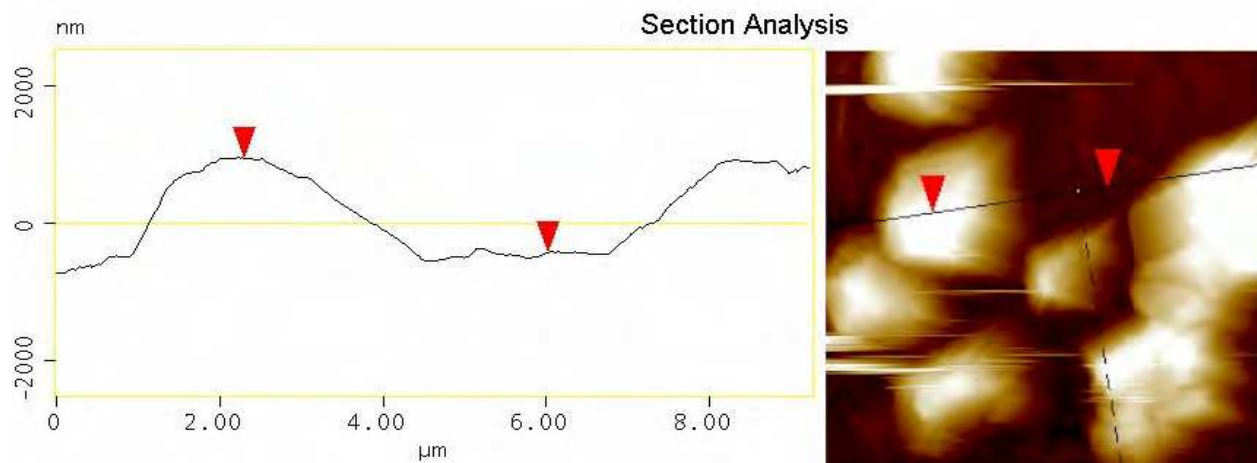


Fig. 8. AFM profiling of CdTe polycrystalline layer, made by ICSVT technology.

This measurement gives some important information about grains structure and inter-crystal surfaces. By means of polycrystalline CdS/CdTe layers profiling one may easily detect the diameter and grain shape but also the inter-grain valleys depth and possible structure fluctuations and layer discontinuities. These structure disorders may result in serious parameter losses by producing of shunt interconnections or other charge flow parasitic effects. Taking into account cadmium dichloride dissolvent presence, frequently caused by recrystallization demands morphology defects may cause a real and serious threat for CdS/CdTe structure functioning. No such phenomenon was confirmed by presented results.

All new production techniques of thin -film polycrystalline solar cells and particularly CdS/CdTe structure, designed for new application field, should be verified according to obtained layers profile to eliminate structure disorder. Since AFM spectroscopy gives the profiling results for some strictly limited area for wider statistical examination mechanical profiling of high accuracy may be applied. These experiments were also conducted for test CdS/CdTe structure. The experiment for each sample was conducted by the help of mechanical profilometer Dektak 3 VEECO Instruments. The measurements were performed for representative 100  $\mu\text{m}$  scan range with 50nm resolution.

As the first analysis ICSVT CdTe layer morphology was checked (Figure 9). By this investigation the average grain diameter of 6-8 $\mu\text{m}$  was confirmed and the typical roughness of 1200 Å. Series of measurements confirmed dense, compact structure of absorber grains with no interlayer shunts. Obtained average roughness and the CdTe grain surface profile suggests that inter-grain trenches are insufficient for significant degradation of shunt resistance value. The total layer level fluctuations are smaller than 4  $\mu\text{m}$ , which taking into consideration typical glass thickness accuracy confirms homogenous thickness of the whole base layer.

Alternative technology, used for CdS/CdTe cell layers deposition is a standard PVD method. Under some circumstances it offers a possibility of semiconductor material deposition even on profiled, elastic and untypical substrates. Evaporation of examined materials caused serious technology problems connected with proper thickness of obtained layers and homogeneous structure of deposited material. Some serious parasitic effect like boiling, splitting and granulation of the material were solved by proper temperature profile and optimized one-directional tantalum evaporation source adopted by authors [24].

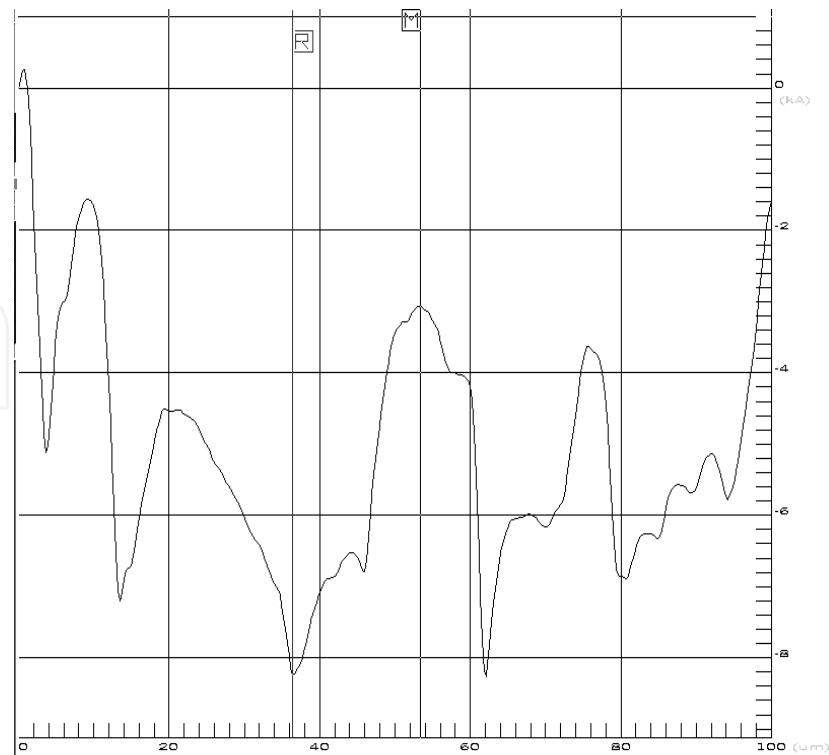


Fig. 9. Morphology of CdTe solar cell base absorber manufactured by ICSVT technology on glass substrate.

The investigation of CdTe base manufactured by evaporation and subsequent recrystallization is presented in Figure 10.

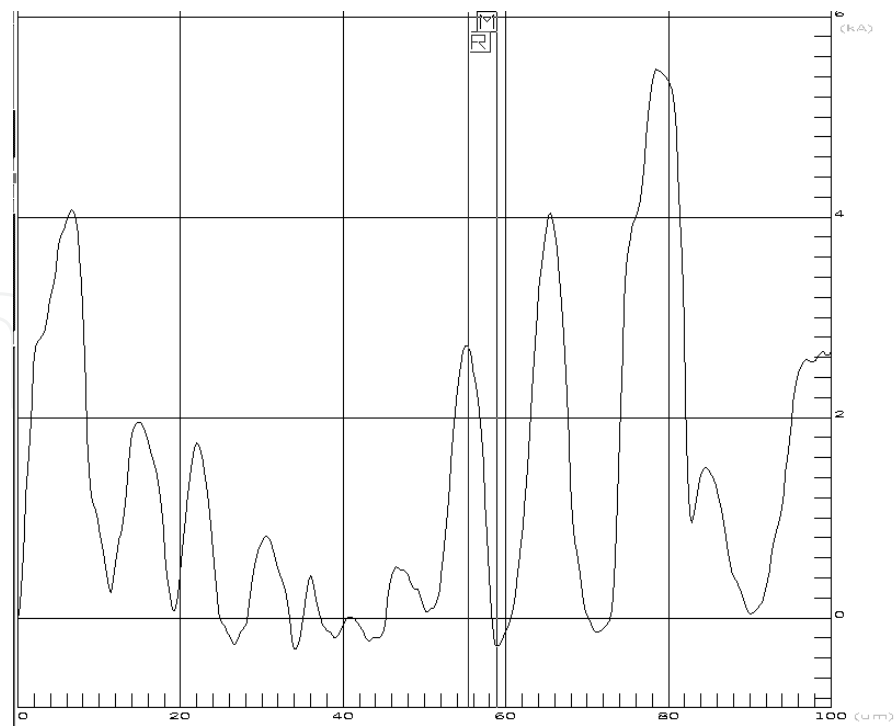


Fig. 10. Morphology of CdTe solar cell base absorber manufactured by evaporation and subsequent high-temp. recrystallization.

The measurements indicated homogenous grains of the average dimension 2-4 $\mu\text{m}$ . Typical roughness of 1230  $\mu\text{m}$  is similar layers obtained by ICSVT, however one may observe higher peak values of grain top-trench profile. This may result in some interlayer parasitic connections. Additionally in this case, total layer thickness fluctuation is similar to the layer thickness ( $\pm 2 \mu\text{m}$ ), what may cause some absorber discontinuities.

Third investigated technology (Figure 11) is based on adaptation of screen-printing technique for semiconductor layers manufacturing. Printing paste is produced by milling of cadmium and tellurium in stoichiometric proportion and mixing with special binder. After printing, leveling and drying process CdTe layer is recrystallized in high-temperature process similarly to the previously described way.

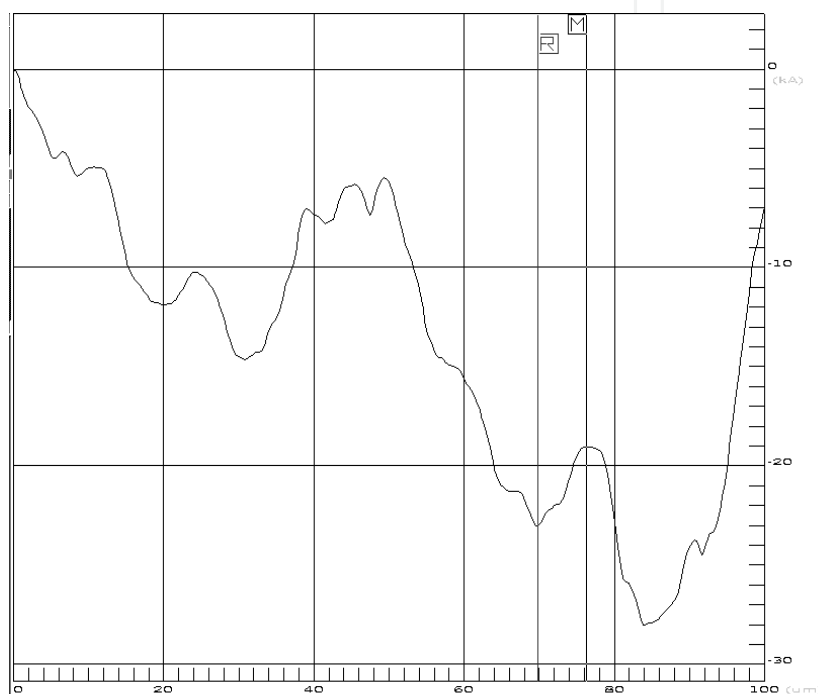


Fig. 11. Morphology of CdTe solar cell base absorber manufactured by screen-printing and subsequent high-temp. recrystallization.

Profilometry of screen-printed base (Figure 11) indicated very high thickness of investigated layer (even up to 20  $\mu\text{m}$ ), but also serious morphology defects. Typical roughness of obtained layers is beyond 3000 $\mu\text{m}$ , which exceeds 240% of average value for ICSVT and PVD techniques. Moreover obtained grains present different diameters from 1-2  $\mu\text{m}$  up to 10  $\mu\text{m}$ . Total layer thickness also varies strongly (locally up to 50%), which results in various optoelectronic parameters. Layers produced by screen-printing technology presents additionally high porosity, which prevents cadmium dichloride from volatilization and causes fast base oxidation and thus cell parameters degradation.

Considering the results obtained for three technologies aimed at manufacturing of CdS/CdTe solar structure on novel substrate material conclusion of their applicability and further development may be drawn.

ICSVT being the most complicated and so-far not commercialized method appeared to be the most efficient in creation of the proper polycrystalline base structure. The morphology of obtained layers confirms proper column grain structure of hexagonal CdTe crystals and thus high electrical parameters of final solar cell. Taking this into consideration further

development of this technique is desired in terms of non-flat architectonic elements as the solar cell substrate. First steps towards this goal have been undertaken.

Evaporation and post annealing of CdTe material in order to formation of proper base structure appeared to be less efficient. However simple and effective for various substrates technique leads to thin film base production only. Moreover the diameters of single grains obtained by the author are significantly lower than by ICSVT technology.

Screen - printing and sintering as the last investigated method appeared to be insufficient for the stabile cell-base production. The advantage of high layer thickness is seriously diminished by poor homogeneity, thickness instability and high surface porosity. Nevertheless screen printed layers can be effectively used as the in-production material for ICSVT or similar processes.

### 3. Innovative polycrystalline elastic structures, based on polymer substrates

Although CdS/CdTe cells have now entered the mass - production phase, but still there are many possibilities of their new applications fields. Basing on this idea, authors proposed the implementation of modified CdS/CdTe cell structure in universal, attractive application called BIPV (Building Integrated Photovoltaics) and also elaborated elastic cell structure [25]. The CdTe cell construction gives the opportunity of achieving these goals, under the conditions of the proper technology modifications, as well as proper substrate and contacts implementation. Due to successful application of CSS variants of CdS/CdTe manufacturing technology for effective solar cells production, further experiments towards new cell structure and properties became possible. Considering cell composition, two opposite configuration of CdTe cell became possible. Historically first one is a classical substrate configuration (Figure 12 a), whereas based on glass + ITO, emitter-based configuration is called superstrate (Figure 12 b).

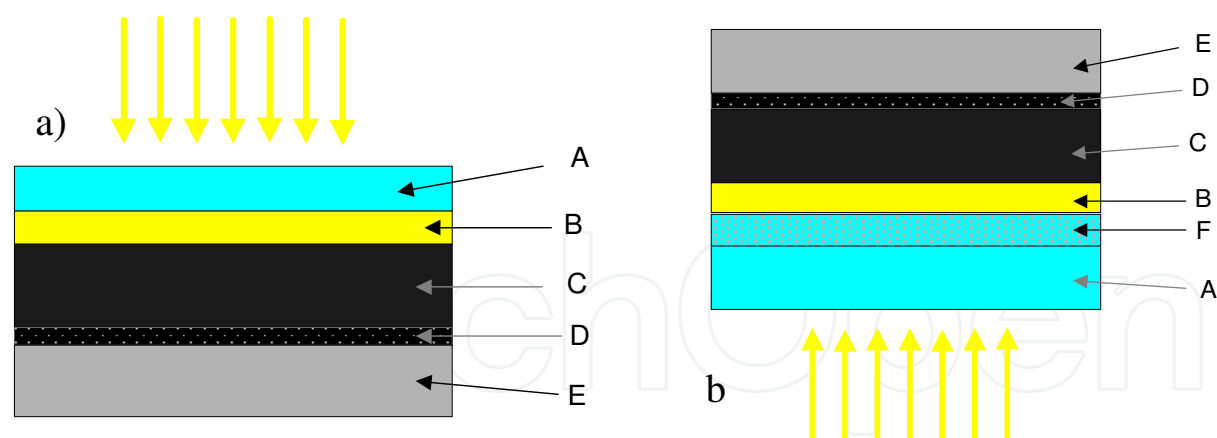


Fig. 12. Substrate a) and superstrate b) configuration of CdS/CdTe solar cell. A- glass cover, B- CdS emitter, C-CdTe base, D - base P+ sub layer, E-back contact, F-TCO layer, emitter metal contacts not visible.

Both of them possess some important advantages and technology drawbacks. Substrate configuration offers more mature manufacturing technology and lower substrate demands, while superstrate configuration ensures higher efficiencies (smaller surface shadowing) and better encapsulation. Adaptation of the described technology for new application and cell construction, demands deep consideration of all possible solutions.

Every introduced concept possesses some value according to different aspects of BIPV applications and each is subsequently investigated by Technical University of Łódź research group. Ceramic substrates could be recognized as the best platform for the complete integration of the photovoltaic element with the architectonic component. One may find the reports on practical investigation of this construction for other thin-film solar cells e.g. CIS devices [26]. However, for CdS/CdTe construction, there is still research and technology adaptation needed. Additionally this kind of application is strictly connected with one particular architectonic element type such as roof-tile or brick. Moreover it has to provide the complete modular interconnection and regulation system, since the whole installation is made of hundreds of elements, working in different conditions. Furthermore, different interconnection systems (series, parallel and series-parallel) are necessary for optimum power and load polarization. Finally, standard ICSVT/CSS technology needs some fundamental modifications, in case of implementation in profiled architectonic elements (roof tiles or ornaments), since the material transport occurs only between very closely positioned source and target.

Taking into account cadmium telluride solar cells, possessing flexible construction two base materials may be considered. One is thin metal foil, while the second is the polymer material. Implementation of metal foils, for example Mo substrates, for CdTe construction has been already investigated and reported [27]. In this work we focus on polymer foil implementation as the elastic solar cell substrate. Flexibility of this material, combined with polycrystalline thin-film structure properties, gives a promise that manufacturing of elastic solar panel, ready for integration with any shape architectonic substrate is possible. Moreover, it offers the opportunity of constructing both substrate and superstrate configuration of CdS/CdTe cell. Additionally, polymer foils are lightweight, high-durable materials, which enhances the possible application field of cells. Depending on the configuration, production technology and desired application different properties of the substrate foils will be demanded. Finding proper foil material and appropriate technology adaptation are the key to obtain efficient elastic PV cells.

To define the properties of polymer base foils, one may consider the specific of each configuration. So far, in the superstrate configuration highest conversion efficiencies were obtained. However, in this case, polymer substrates must meet several conditions. One can mention as the most important: high optical transparency in the full conversion range of CdS/CdTe cell, ability of TCO surface electrode covering, high thermal durability, high chemical and water resistance. Apart from these specific demands, substrate foil of any configuration is expected to be light-weight, have high elongation coefficient, thermal expansion similar to semiconductor polycrystalline layers (CdS and CdTe) and be low cost. In both cases elastic cells can be easily attached to different shape architectonic elements.

Taking this into account, also substrate configuration of elastic cadmium telluride cell was investigated. As the preliminary step possible polymer material options were verified. Polymers, as the materials, are constructed on a base of multi-modular chains of single, repetitive units called monomers. In the manmade polymers, even the number of a few thousand monomer types is being achieved. The properties of manufactured polymer material depend strongly, not only on its chemical content and even monomer construction, but also on the monomers interconnecting system. Due to complexity of the typical polymer construction, it is impossible to evaluate the physical properties of these materials using theoretical analysis. This gave the prompt to the series of experiments, aimed at



comprehensive evaluation of polymer foils physical parameters, potentially efficient as the CdS/CdTe cell substrate materials.

As the test group of polymer foils wide set of materials, including standard commercial solutions as well as high – temperature polyester and polyamide, was accepted. Among polyamide foils of high thermal durability, two materials - KAPTON® and UPILEX® foils were chosen. Both of them are commercially available high-technology materials implemented in specific applications (eg: space shuttles wings and nose cover, high power loudspeakers membranes). They are characterized by high mechanical and thermal durability, high dielectric constant and UV durability. Among the polyester materials high – temperature MYLAR® material was adopted. As the reference material, popular PET foil in standard and high - temperature production version was applied. First evaluation step of material properties is a verification of their mechanical parameters. Comparison of these results is presented in Table 2.

Parameter\Foil	PET/High temp PET	UPILEX®	MYLAR®	KAPTON® HN 100
Thickness [µm]	25.0	30.0	30.0	25.4
Weight [g/m²]	30.0	44.1	41.7	35.0
Surface mass coefficient [m²/kg]	31.2	22.7	23.98	27.9
Thermal expansion [%/ 1°C]	0.025	0.018	0.007	0.005
Standard elongation (25 °C) [%]	600.0	54.0	103.5	40.0

Table 2. Main mechanical parameters of tested polymer foils.

Obtained parameters suggest similar properties of all investigated materials. However, some important differences are evident. The most important is the value of the thermal expansion coefficient (TEC). In general, one may say that in the case of high-temperature materials the value of thermal expansion is lower. Exceptionally, in the case of UPILEX® the value of this parameter is close to standard PET foil. According to considered configuration, thermal expansion coefficient of substrate foil should be adjusted to the value of the semiconductor base or emitter and contact layer. In both cases of semiconductor materials (CdS, CdTe), the value of TEC is very low (at the level of  $5 \cdot 10^{-4}$  [% / 1°C]), but the most typical metal contacts present TEC value higher by the order of magnitude.

The critical parameter in the standard re-crystallization process, as well as in the ICSVT, is a thermal durability of layer material. The maximum values of declared operational temperature for each investigated foil are: 130°C for Standard PET, 185°C for High-temp PET, 254°C for Polyester MYLAR®, 380°C and 430°C for Polyamide KAPTON® foil. Basing on the declared temperatures and considering the ICSVT temperature demands, two most durable foils were accepted for further investigations. As the subsequent step the weight loss of KAPTON® and UPILEX® in higher temperatures was measured. The measurements of thermal durability were performed in the temperature range of a standard re-

crystallization process (450°C - 650°C). During the experiment, the percentage loss of the foil weight was measured. Additionally, plastic properties were tested as the indicator of usefulness for the elastic substrate application. For higher accuracy of obtained outcomes, as the additional test, the plastic properties of the materials for each temperature were estimated. Complete results of this test are presented in Table 3. Grey color of the table cell marks a permanent deformation or loss of elastic properties.

Weight in temperature:	UPILEX®		KAPTON®	
	12.5µm	25.0µm	12.5µm	25.0µm
480°C	91.82%	95.16%	96.70%	95.30%
500°C	91.36%	94.84%	96.00%	94.60%
550°C	89.55%	92.26%	74.70%	81.12%
600°C	70.00%	78.38%	Burnt	Burnt

Table 3. Temperature durability of examined foils. Dark-grey color indicates the loss of elastic properties or permanent deformation.

Analyzing obtained results, one may state that in the opposite to the manufacturer suggestions, the biggest weight loss in temperatures above 500°C, is observed in polyamide KAPTON®. Additionally, the loss of its elastic parameters occurs very rapidly. Contrary, UPILEX®, which melting point is declared below 400°C proved to be fairly resistant to temperatures until 550°C. In both cases thicker foils reacted slower for the temperature rise, which was expected due to their relatively high thermal resistance. It is worth mentioning that the experiment was conducted in conditions (time, equipment) similar to the manufacturing process. However, identified maximal allowable temperature is relatively lower than standard demanded temperature for ICSVT process. There were reasonable presumptions suggesting the possibility of re-crystallization temperature decreasing, in favor of longer process duration. Thus, examined foils were conditionally positively evaluated. Taking this into account, UPILEX® foil was accepted for further experiments, leading to manufacturing of the CdS/CdTe elastic layers. Considering possible configuration of designed cell, the light transparency characteristic of investigated foil was measured. The light transmission in the conversion range of CdS/CdTe cell both of KAPTON® and UPILEX® foils is presented in Figure 13.

Due to low transmission (below 60%) in the range 400 nm – 700 nm, which would decrease largely the total cell efficiency, for UPILEX®, substrate cell configuration was chosen. Basing on presented results, experimental sample of CdTe absorber, manufactured on 25 µm UPILEX® foil was prepared. Obtained semiconductor layer is based on Cu contact of 2 µm thick, made by PVD in pressure 5·10<sup>5</sup> Torr. The total area of the sample is 30 cm<sup>2</sup> and elastic properties of all manufactured layers are preserved (Figure 14). After the investigation, the average thickness of 2 µm and good uniformity of manufactured layer was confirmed. This makes proper base for CdS layer manufacturing and completing of the elastic CdS/CdTe construction.

Obtained results confirm the assumption that flexibility of polycrystalline cadmium compound layers may be employed in alternative applications, such as elastic cell structure. Finding the proper material for substrate of these devices is a key to manufacturing of efficient cell, however it demands considering of many technological aspects. Thermal and

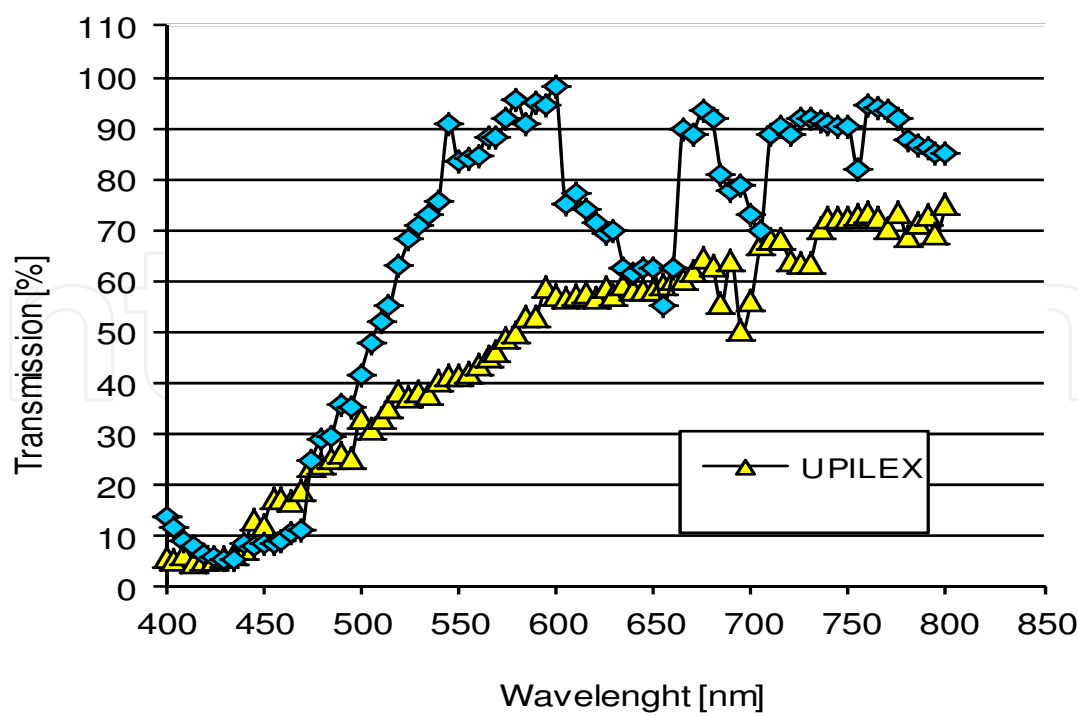


Fig. 13. Optical transparency of KAPTON® and UPILEX® foils in the wavelength range of CdS/CdTe cell effective photoconversion.



Fig. 14. Test structure of elastic CdTe layer based on UPILEX® foil and contacted by 2  $\mu\text{m}$  Cu layer.

mechanical properties of some high-temperature polymer foils give the possibility to construct complete solar cell with some technological modifications (particularly during the re-crystallization process). Another important factor is a proper, flexible and durable contacting system of such cell.

#### 4. Novel carbon nanotube contacts for proposed devices

An essential challenge in the development of flexible photovoltaic structures, excepting the elaboration of an appropriate semiconductor junction and optical properties of active layers, is providing suitable contacts. PV electrodes are required to be reliable, efficient, low cost and compatible with solar cell structure. An extremely frequently used solution is applying flexible transparent conductive oxides (TCO) as PV cell front (generally emitter) layer electrodes. As it was mentioned before emitter contacts are usually realized by using conductive transparent metal oxides, such as:  $\text{SnO}_2$ , ITO,  $\text{Zn}_2\text{O}_4$ ,  $\text{CdSnO}_4$ ,  $\text{In}_2\text{O}_3$ ,  $\text{ZnO:Al}$ , as well as  $\text{CdO}$ ,  $\text{ZnO}$  and  $\text{RuSiO}_4$ . In order to integrate solar cells into PV modules or for more convenient measurements execution, additional metal contacts attached to TCO are applied. The most popular among listed TCO compounds is indium tin oxide (ITO).

ITO is a mixture of tin (IV) oxide:  $\text{SnO}_2$  and indium (III) oxide:  $\text{In}_2\text{O}_3$  so called ITO. This material is characterized by high optical transmission of above 90% in visual range and relatively low electrical resistivity of  $10 \Omega/\text{square} \div 100 \Omega/\text{square}$  for thickness of  $150 \text{ nm} \div 200 \text{ nm}$ . Unfortunately, applying ITO and other TCO layers in flexible photovoltaics encountered a significant barrier. Those metal oxides indicate a lack mechanical stress resistance which leads to breaking and crushing of the contact. This disadvantageous characteristic was observed and reported also during the research on flexible diode display electrodes. Furthermore, thin ITO layers are predominantly manufactured by cost-consuming magnetron sputtering method [28], which increases the final cost of new PV cell and module. Moreover, the indium resources are strictly limited and expected to be exhausted within next fifteen years of exploitation.

A novel method of creating flexible transparent contacts for solar cells is to use carbon nanotubes (CNT). Due to the broad range of potential manufacturing techniques and diversified properties of obtained layers, carbon nanotubes are becoming increasingly popular in electronic applications. Especially CNT layers obtained using low-cost technologies such as screen printing or sputtering are potentially useful in flexible electronic devices [30] and smart textiles. This subsection presents the summary of experiments which were conducted up to now and led to adaptation of carbon nanotubes as thin transparent contacts of selected flexible photovoltaic structures.

To create CNT based transparent conductive layer (TCL), preparation of particular composite is necessary. Since there is a requirement of low cost material, multilayer carbon nanotubes, synthesized in catalytic chemical vapor deposition (CCVD), were used in tested compounds. CCVD process has a drawback which causes that not perfectly pure CNT material is obtained. Although, the material contains significant amount of non CNT carbon structures and metal catalyst, either purification or alternative fabrication methods, can increase costs up to a few orders of magnitude. The average dimensions of nanotubes in the material (determined by Scanning Electron Microscopy - SEM) are  $10 \div 40 \text{ nm}$  in diameter and  $0.5 \div 5 \mu\text{m}$  length, however longer structures have also been observed. Figure 15 presents HRSEM image of applied CNTs.

Carbon nanotube composites are printed on given substrates using, low cost screen printing technique. To specify a relationship between the content of CNT in the composition and the value of sheet resistance, electrical properties of printed layers was measured. Table 4 presents achieved results. All samples showed electrical conductivity and were much above the percolation threshold [11].

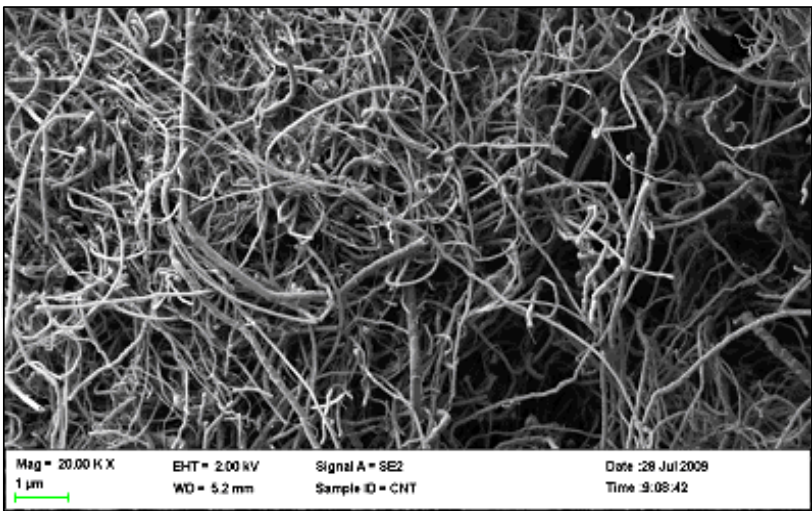


Fig. 15. HRSEM image of applied carbon nanotubes

Paste No	CNT content in the composition [%]	Sheet resistance [ $\Omega$ /square]
CNT.0.1	0.10	613 k
CNT.0.25	0.25	28 k
CNT.0.5	0.50	3.3 k
CNT.1.0	1.00	870

Table 4. Sheet resistance values for samples with different CNT amount [11].

Transparent conductive layers were prepared using four composites with various CNT content (Table 1). As a substrate borosilicate glass was used. In order to compare CNT and ITO layer parameters, an identical Bo Si glass sample, covered by 160 nm sputtered ITO, was taken. As a first step of carbon nanotubes TCL application in solar cell structure, transmittance of printed layers have been measured (Figure 16).

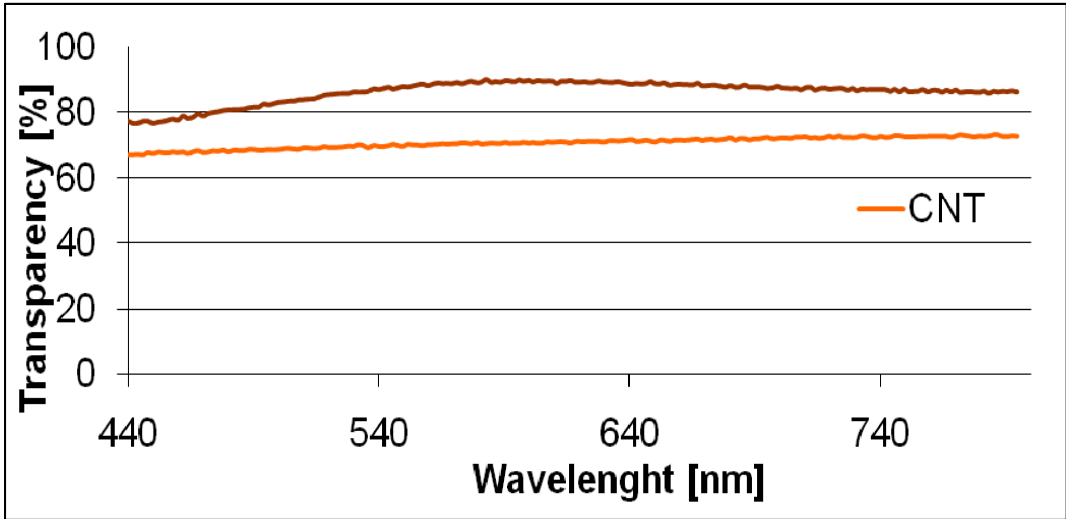


Fig. 16. Transmittance comparison of 0,25%, 1,5 µm CNT layer and 160 nm ITO on borosilicate glass, for standard solar cell absorption spectrum



A very important characteristic for printed CNT layers, is stability of the resistance while applying multiple mechanical stress. To verify this parameter for manufactured CNT layers, additional experiment was undertaken. TCL of 1.5  $\mu\text{m}$  thick was screen printed on polyamide Kapton® and tested by rapid mechanical bending in 80 cycles. The results of resistivity change (Figure 17a) was compared with literature outcomes, obtained for optical ITO layer (Figure 17b).

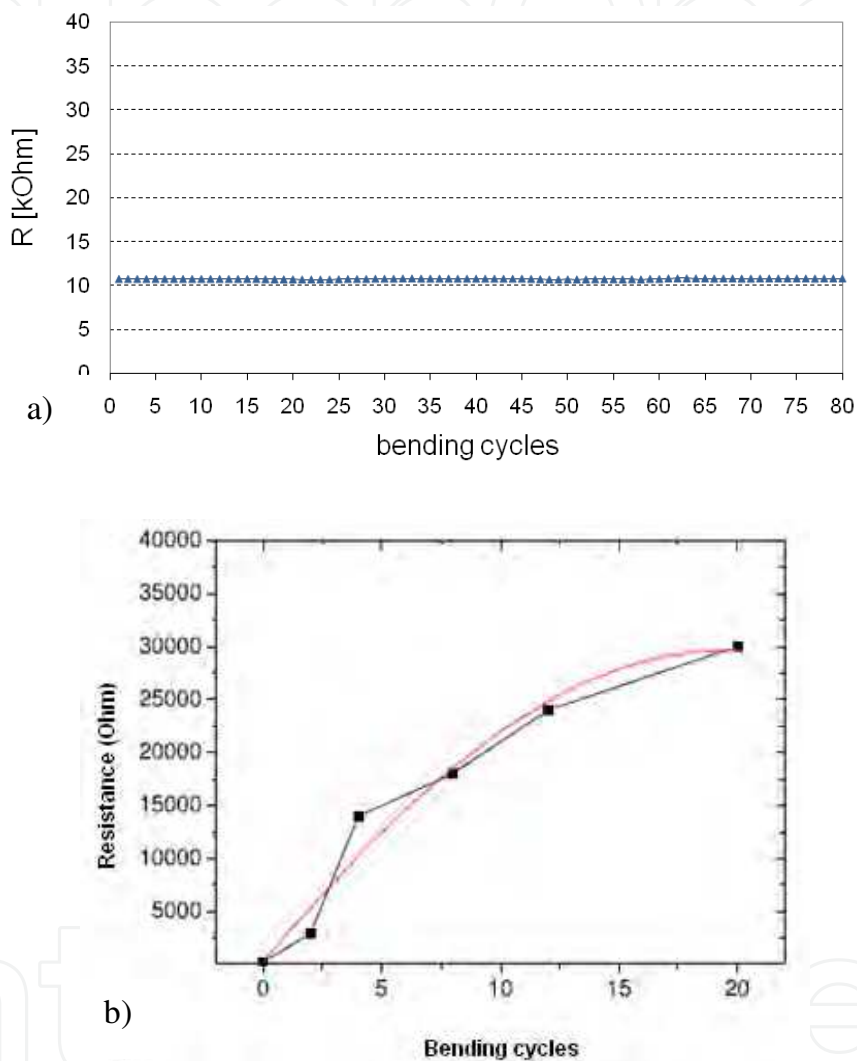


Fig. 17. Resistance changes of: a) CNT and b) ITO layers while bending [31]

After a positive estimation of CNT layers optical and electrical parameters, the possibility of implementation as a solar cell transparent conductive coating was verified. For creating models of screen printed CNT layer, as TCO replacement, in different PV cell structures, SCAPS simulator was used. Simulation models are generated by digital description of physical parameters of each structure layer, including contacts. Solar Cell Capacitance Simulator (SCAPS) is available free of charge for scientific research. Figure 18 shows I-V curves simulations, for CdTe/CdS solar cell structure with ITO and CNT contact layer. Operating parameters of simulated cells are presented in Table 4.

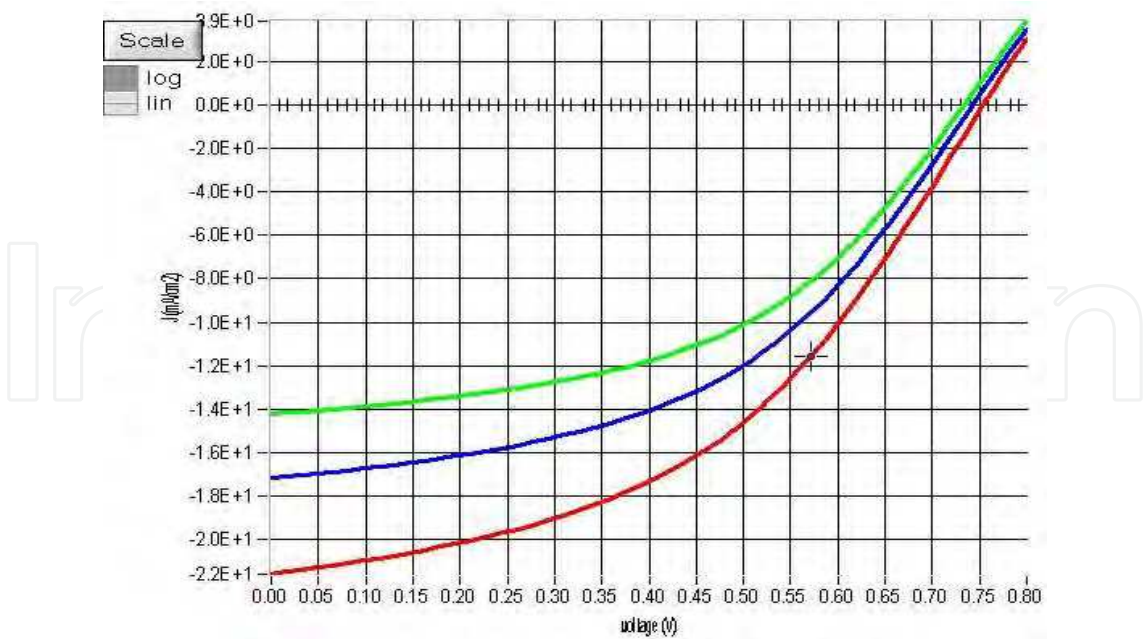


Fig. 18. SCAPS simulations of I-V characteristics of CdTe/CdS solar cell with filters: red- none, blue-ITO, green-CNT.

Filter	Open circuit voltage Voc [V]	Short circuit current Jsc [mA/cm²]	Fill Factor FF [%]	Efficiency η [%]
none	0.754	21.602	44.99	7.33
ITO	0.743	17.194	47.00	6.00
CNT	0.733	14.236	48.50	5.06

Table 5. Electrical parameters of CdTe/CdS solar cell

5. Conclusions

Carbon nanotube layers with relatively high optical transmittance were fabricated by inexpensive screen printing technique on glass and on elastic polymer substrates as well. The average difference of 10% in transmittance within standard CdTe cell photoconversion range between 160 nm ITO and 1.5 μm 0.25% CNT layer was observed. Sheet resistance of obtained layers are at relatively high level and should be diminished for efficient photovoltaic applications. To achieve this goal special technology and material compositions (including various CNT content) are tested. The resistance of CNT layers, in opposite to standard ITO, turned out completely independent on bending, which is critical in terms of flexible solar cells construction. According to SCAPS simulations the lowest  $P_m$  drop, caused by CNT layer implementation, was observed in case of thin-film cells, which is consistent with postulate of new construction flexibility. Preliminary practical experiments confirmed the presence of photovoltaic effect in solar cell equipped exclusively with CNT emitter electrode.

Presently, due to weaker optical and electrical parameters those layers cannot be a competitive alternative to the existing transparent conductive layers. Nevertheless, they

have much better elastic properties and high prospects for improving the optical and electrical parameters, and therefore they can be potential solar cells layers. Further experiments are planned for development of manufactured structure (including incorporation of main metal contacts) and manufacturing of thin-film cells with carbon nanotube emitter contacts. However, CNT composites obtain higher optical permeability at a lower carbon nanotubes content, which in turn, increases the resistivity of these materials. Thus, the simultaneous increasing of the permeability and reducing the resistivity is a difficult issue.

Flexible solar cells, based on thin film heterostructure are expected to be a natural development of currently produced devices. For elaboration of fully functional photovoltaic structure, ready for industrial production, many technological problems must be solved. Presented work is a small part of impact put in this process. It is highly probable that some of presented concepts will soon find the implementation in the commercially available elastic cells, based on II-VI compounds.

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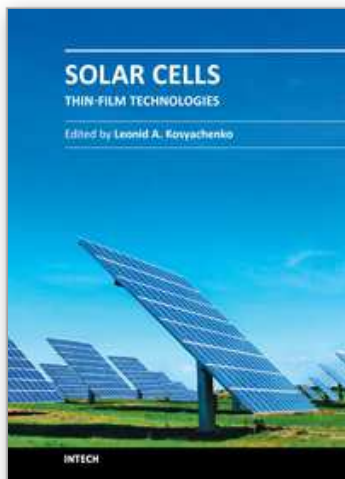
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## **Solar Cells - Thin-Film Technologies**

Edited by Prof. Leonid A. Kosyachenko

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The first book of this four-volume edition is dedicated to one of the most promising areas of photovoltaics, which has already reached a large-scale production of the second-generation thin-film solar modules and has resulted in building the powerful solar plants in several countries around the world. Thin-film technologies using direct-gap semiconductors such as CIGS and CdTe offer the lowest manufacturing costs and are becoming more prevalent in the industry allowing to improve manufacturability of the production at significantly larger scales than for wafer or ribbon Si modules. It is only a matter of time before thin films like CIGS and CdTe will replace wafer-based silicon solar cells as the dominant photovoltaic technology. Photoelectric efficiency of thin-film solar modules is still far from the theoretical limit. The scientific and technological problems of increasing this key parameter of the solar cell are discussed in several chapters of this volume.

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