

# Polycrystalline Thin Film Solar Cells<sup>+</sup>

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*Present status, manufacturing perspectives, and critical issues of polycrystalline thin film solar cells are reviewed. The paper is focused on CdTe and CuInSe<sub>2</sub> based heterostructure solar cells for which significant progress has been achieved in recent years. Material aspects and basic film characteristics that are important for good cell performance are discussed. Preparation methods of CdTe and CuInSe<sub>2</sub> films are presented.*

## 1. Introduction

Photovoltaics is a rapidly developing field with its advancing technologies and expanding markets. Thin film solar cells have been developed as a low cost option for single crystalline silicon cells. Huge efforts put in technology and research of thin film structures resulted in remarkable device performance achieved in last decade. Recent progress makes them viable alternative for single crystalline cells. Apart from amorphous and polycrystalline silicon, two compound semiconductors are the main contenders in this field: CdTe and CuInSe<sub>2</sub> with its alloys. Both materials are attractive for thin film solar cell applications because of their high optical absorption (direct band gaps) and their favourable electrical properties. They are used as absorbers in heterojunctions, preferably with CdS layer as a wide band gap window. Both types of cells can be produced by relatively cheap, scalable processes. Efficiencies achieved for the laboratory small area cells are approaching crystalline silicon: 16% for CdTe based cells and over 17% for CuInSe<sub>2</sub> cells (Fig.1). Also, acceptable conversion efficiencies exceeding 10% have been obtained for large area modules. Still, there are many problems to be solved before large scale manufacturing of such modules starts. They are specific for two considered types of structures and range from technology issues to environment implications. Also operation of the cells and especially role of defects is not fully understood yet.

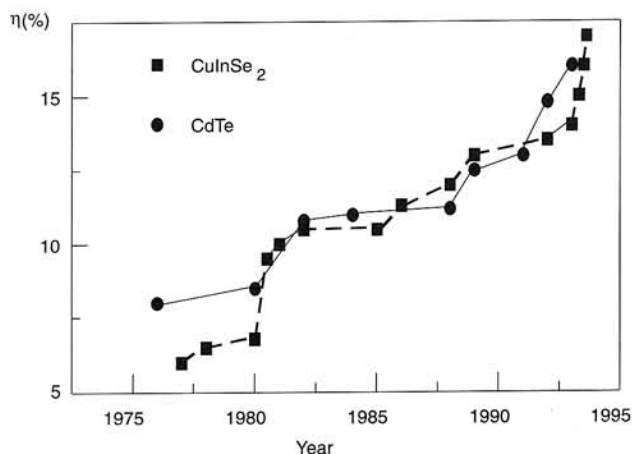


Fig.1. Progress in CuInSe<sub>2</sub> and CdTe solar cell efficiencies for last twenty years.

In this paper we present structures, processing techniques for film deposition and fabrication perspectives for CuInSe<sub>2</sub> and CdTe solar cells.

## 2. CuInSe<sub>2</sub> solar cells

CuInSe<sub>2</sub> crystallizes in chalcopyrite structure. It has direct band gap of 1.04 eV and is strongly light absorbing material. The band gap is well below the optimal value for photovoltaic conversion (about 1.4 eV). To increase the band gap an alloying of CuInSe<sub>2</sub> with CuGaSe<sub>2</sub> ( $E_g = 1.68$  eV) and CuInS<sub>2</sub> ( $E_g = 1.54$  eV) is employed. Complete miscibility of these compounds

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provides great flexibility for device design. Electrical properties of  $\text{CuInSe}_2$  are determined by large number of intrinsic defects. By controlled non-stoichiometry both n- and p-type material can be easily obtained.

For the first time  $\text{CuInSe}_2$  solar cell was demonstrated by Wagner in 1974 as a single crystal device with 12% conversion efficiency ( $\eta$ ). First thin film cell prepared as a heterostructure of p-type  $\text{CuInSe}_2$  with n-CdS was obtained by Kazmerski in 1978 [1] ( $\eta = 6.6\%$ ). In early eighties significant progress was achieved by the Boeing group [2] which invented concept of bilayer absorber in which the sequence of Cu-rich and In-rich layers of  $\text{CuInSe}_2$  is deposited. The deposition method was coevaporation of Cu, In and Se on Mo coated glass. High resistivity, In-rich material close to the heteroface prevents formation of the copper nodules. The Boeing group also recognised the importance of increasing band gap of both: window layer ( $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  was used instead of CdS) and absorber layer ( $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  instead of  $\text{CuInSe}_2$ ). It resulted in then-record conversion efficiency of 14.6%.

Since late eighties the best results have been obtained with the cell structure presented in Fig. 2.

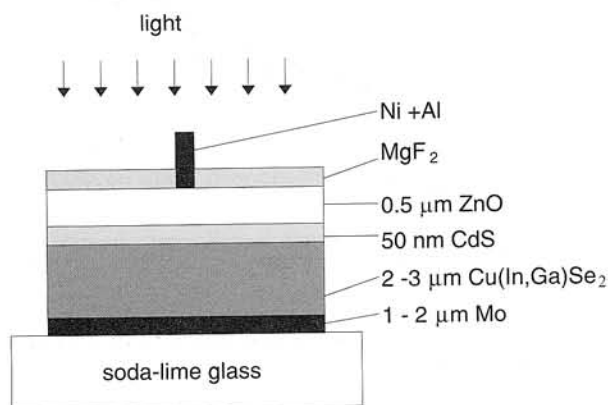


Fig. 2. Structure of  $\text{Cu(In,Ga)Se}_2$  based solar cell.

As a substrate soda – lime glass with the sputtered layer of molybdenum is usually used. It appears that the presence of sodium diffusing to the absorber layer is a vital factor for the absorber film quality. It was a major contributor to increasing the efficiency of  $\text{CuInSe}_2$  based solar cells over 15%. Sodium increases grain size of the absorber layer and the hole concentration in it.

The most critical process in fabrication of a good device is deposition of high quality absorber layer. Nowadays, it is usually  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  layer with the  $x$  value around 0.2 (the band gap is app. 1.15 eV). Higher contents of gallium in an absorber film does not produce a better cell performance. Sulphur substituting selenium is also used to increase the band gap [3].

There are certain characteristics of absorber films that are critical for good cell performance. The following conditions have to be satisfied:

- the overall Cu/In stoichiometric ratio of the  $\text{CuInSe}_2$  layer should be in the 0.9 – 1.0 range, stoichiometric uniformity of the film should be maintained across the substrate;
- formation of microscopic Cu-rich areas in the film should be avoided (low resistivity  $\text{Cu}_x\text{Se}$  inclusions are detrimental for the device performance);
- structure of the film should consist of columnar grains;
- good film adhesion to Mo coated substrate should be achieved;

There are several methods of the absorber layer deposition. They can be grouped under two main categories: single stage processes and two (or more) stages processes.

Single stage processing approaches for  $\text{CuInSe}_2$  and its alloys involve delivery of all components of this material at the same time onto a heated substrate. Examples of such methods are evaporation, sputtering or laser ablation from  $\text{CuInSe}_2$  source, coevaporation or cosputtering of Cu, In, Se, electrodeposition and spray pyrolysis. The last two methods although are low-cost processes have not produced high efficiency cells.

Evaporation and sputtering from compound sources have also been used to prepare  $\text{CuInSe}_2$  thin films. The major problem associated with both of these approaches was the lack of reproducible stoichiometric control resulting from Se and  $\text{In}_2\text{Se}_3$  loss in the vacuum environment. Another problem encountered for sputtering technique was the changing nature of a target. The highest efficiency cell (8.5%) fabricated by this family of techniques was demonstrated on a layer obtained by laser ablation of  $\text{CuInSe}_2$  target.

Coevaporation of the elements on the heated substrate was the first process to produce high quality films and high efficiency solar cells. There are several variations of this method related to constant or variable evaporation rates of the elements and different substrate temperature vs. time profiles. In one of the most successful version of the coevaporation method Cu and In rates were varied continuously to change composition from Cu-rich to In-rich. The resulting  $\text{CuInSe}_2$  film had a columnar grains of  $> 1 \mu\text{m}$  size and yielded devices with 17% efficiency [4, 5].

Multi-stage (sequential) processing approaches involve several (usually two or three) distinct processing steps. During the first stage of the process a precursor film containing some or all of the constituent elements is deposited. During subsequent stages of the process

the each constituent reacts with the other as well as with other species introduced from reactive atmosphere.

Among two-stage approaches selenization (and sulphurization for sulphur containing absorbers) of metal precursors is one of the most promising methods. In this approach metals (Cu, In, Ga) or selenium containing precursors (eg.  $\text{InSe}_x$ ) are deposited in a low temperature step by evaporation, electroplating, sputtering or e-beam deposition. In the second step precursor is selenized either in  $\text{H}_2\text{Se}$  atmosphere or in selenium vapour. There is a variety of solutions for this technique [4, 6]. The technique can be up-scaled to large substrate areas. About 15% percent cells and 11% modules were fabricated by using this approach.

Two (or three)-stage processes that yield the best quality  $\text{CuInSe}_2$  films manufactured nowadays involve vacuum processing. The last efficiency record for  $\text{CuInSe}_2$  solar cells (17.7 %) was achieved in NREL [7, 8] using an absorber deposition process with the following steps:

- 1) deposition of the  $(\text{In,Ga})_2\text{Se}_3$  precursor by the elements evaporation at the substrate temperature  $T_s = 250 - 300^\circ\text{C}$ ;
- 2) evaporation of Cu and Se ( $T_s = 550^\circ\text{C}$ );
- 3) evaporation of In, Ga and Se ( $T_s = 550^\circ\text{C}$ );

The graded band gap of the absorber film is achieved in this technique due to intentionally profiled Ga contents and by different diffusion mechanisms of In and Ga [7].

An attractive, potentially low-cost two-stage method is the screen printing involving deposition and heat treatment of pastes containing  $\text{CuInSe}_2$  powder. However, this technique has not produced acceptable quality devices yet.

The window layer in  $\text{CuInSe}_2$  based cells usually consists of thin film of CdS (buffer layer) formed by chemical bath deposition (CBD) and sputtered ZnO layer. Such a multilayer window prevents an absorption loss of the blue part of the solar spectrum in otherwise thick layer of CdS. The outer part of ZnO is a highly conductive n-type layer due to Al doping. For ecological reasons (cadmium toxicity) attempts have been made to replace CdS by no Cd containing layer. Efficiencies over 15% were obtained with  $\text{In}_x(\text{OH,S})_y$  as the heterojunction partner [9].

On the surface of a finished absorber film a thin layer of  $\text{CuIn}_3\text{Se}_5$  phase have been found [10]. This phase often defined to as the ordered vacancy compound (OVC) plays important role in a cell operation. As an n-type semiconductor it forms a buried homojunction within absorber film. It also affects the

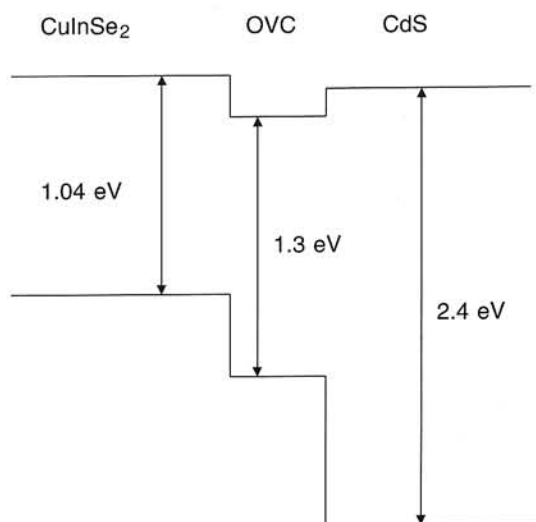


Fig. 3. Band alignment in  $\text{CuInSe}_2/\text{CdS}$  solar cell.

charge state of active defects and diminishes the carrier recombination. The band diagram of the  $\text{CuInSe}_2$  solar cell is depicted schematically in Fig.3. The main electron transport mechanism in the junction region is the thermionic emission.

It is interesting to analyse main sources of the progress that has taken place in recent decade. Figure 4. presents change of the  $I - V$  characteristics of good performance  $\text{Cu(In,Ga)Se}_2$  based cells between years 1987 and 1993 [11]. For comparison, the  $I-V$  curves for a 24% silicon cell and the theoretical one corresponding to the maximum efficiency for a semiconductor of the same band gap are shown. The

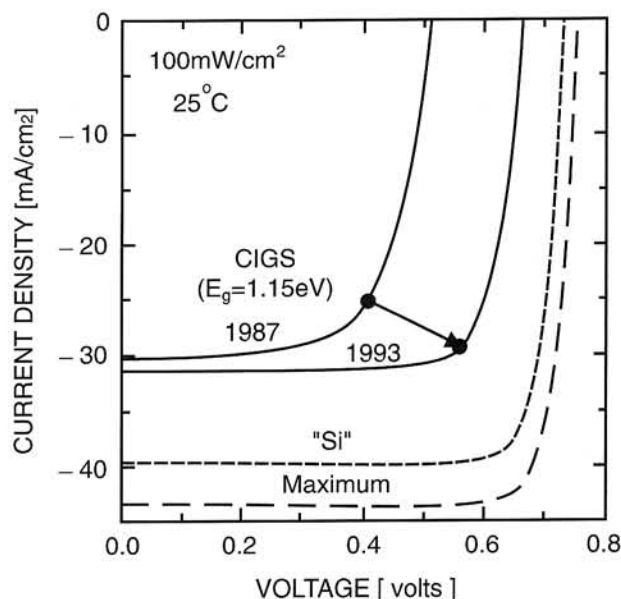


Fig. 4. Comparison of the  $I - V$  characteristics for  $\text{CuInSe}_2$  solar cells in 1987 and 1992 (after [11]).

Tab. 1. The parameters of the high efficiency Cu(In,Ga)Se<sub>2</sub> based cells

group	E <sub>g</sub> (eV)	V <sub>oc</sub> (mV)	I <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	efficiency (%)
EUROCIS	1.14	647	35.8	0.76	17.6
NREL	variable	652	33.18	0.77	16.8

progress has been related to the better control of deposition process and more efficient grain boundaries passivation. It resulted in decrease of the diode forward current 25 times, and decrease of the diode quality factor from 2 to 1.3 (thus improving fill factor). Also series resistance dropped from 2 Ωcm<sup>-2</sup> to 0.5 Ωcm<sup>-2</sup>. Table 1 compares the parameters of two high efficiency cells fabricated by the European consortium EUROCIS [5] and at the National Renewable Energy Laboratory in USA [7].

### 3. CdTe solar cells

CdTe presents the properties making it almost ideal material for photovoltaics. Its band gap 1.44 eV yields a perfect match for space and terrestrial solar spectra. Due to direct character of the band gap very high values of the absorption coefficient are reached ( $> 10^5$  cm<sup>-1</sup>). It means that 90% of the incident solar light is absorbed within a few micrometers of the material. CdTe is a single phase material with narrow range of stoichiometry that can easily be established at elevated temperatures due to a very low vapour pressure of the compound as compared to the elements. It can be doped to obtain both n-type and p-type conductivity. The films deposited at high substrate temperatures exhibit native p-type conductivity enhanced by the presence of oxygen. CdTe films like other II-VI films have very small grain boundaries recombination [12].

An obvious advantage of using CdTe as a photovoltaic material is availability of quite large number of techniques for thin film deposition. High rate deposition has been demonstrated for some of them.

Research on CdTe based solar cells started more than twenty years ago; the first thin film device was produced by Cusano in 1963 [13]. In the solar energy conversion heterojunctions are used because of difficulties in fabricating shallow homojunctions. The use of p-CdTe/n-CdS heterojunction deposited on SnO<sub>2</sub> coated glass was first reported by Andirovich et al. [14], who devised the device structure commonly employed today. Efficient CdTe based devices have been reported from early 80's [15].

All the highest efficiency CdTe/CdS cells have a standard structure shown in Fig. 5. It is so called super-

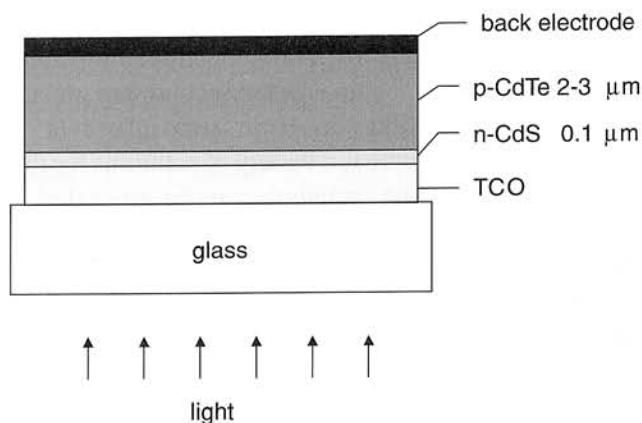


Fig. 5. Standard structure of CdTe/CdS solar cell.

strate configuration. In this configuration light illuminates cell from the substrate side through a layer of transparent conducting oxide (TCO). Usually it is indium-tin-oxide layer. The next layer (window) is CdS film prepared by CBD technique.

Numerous deposition techniques of CdTe absorber film [16, 17] can be divided into two groups:

- low temperature methods (substrate temperature below 350°C): thermal evaporation, electrodeposition, MOCVD, sputtering, atomic layer epitaxy etc.;
- high temperature methods ( $T_s = 500\div 700^\circ\text{C}$ ): compound sublimation and vapour transport (CSVT), atmospheric pressure chemical vapour deposition, spray pyrolysis, screen printing etc.;

One of the most frequently used deposition methods is the CSVT technique known also as the Close Spaced Sublimation (CSS) method. In this method the source material (usually CdTe powder) and substrate are placed close together ( $< 1$  cm) in the nitrogen or argon atmosphere at pressure within the range of 1 Torr (Fig. 6). Due to the temperature difference between the source and the substrate sublimated CdTe deposits on the substrate surface. Growth rates as high as 10 μm/min can be attained [18]. The highest efficiency cells have been prepared by this method at the University of Florida ( $\eta = 15.8\%$ ). Closely related to CSS method are Hot Elemental Deposition and Atmospheric Pressure Chemical Vapour Deposition methods [16].

No matter which deposition method is used for



Tab. 2. Performance of thin film photovoltaic modules (after [20]).

company	absorber	process	area (cm <sup>2</sup> )	efficiency (%)	power (W)
Siemens Solar	Cu(In,Ga)Se <sub>2</sub>	selenization	3830	11.2	43.1
Siemens Solar	Cu(In,Ga)(Se,S) <sub>2</sub>	selenization	3859	10.3	39.7
ZSW	Cu(In,Ga)Se <sub>2</sub>	evaporation	717	10.0	7.1
BP Solar	CdTe	electrodeposition	706	10.1	7.1
Solar Cells Inc.	CdTe	evaporation	6728	9.1	61.3
Matsushita	CdTe	screen printing	1200	8.7	10.0

CdTe film, thermal and chemical processing is necessary to produce good solar cells. It usually consists of three stages:

- 1) deposition of CdCl<sub>2</sub> layer onto the CdTe film (chemically or by evaporation);
- 2) annealing at 400°C;
- 3) removal of CdCl<sub>2</sub> excess;

This procedure leads to increase of the grain size and to diffusion of sulphur atoms into CdTe and tellurium atoms into CdS. It improves the cell performance and its uniformity.

The most difficult stage of the cell fabrication process is a deposition of a stable, low resistivity back contact on CdTe film. Usually first step in the back contact preparation is a modification of CdTe surface to produce Te-rich surface. Next, contact material (doped graphite, Cu alloy or Au) is deposited and heat treatment is applied. Alternatively, ZnTe is deposited. Most elaborated processes are proprietary procedures.

The I-V characteristics of 11.8% efficiency cell is shown in Fig. 7.

## 4. Manufacturing issues

From an industrial perspective the only driving force to develop thin film solar modules is to achieve considerably lower costs per Watt peak (Wp) than with traditional silicon wafer (c-Si) technology. According to different assessments it is possible to attain 1\$/Wp

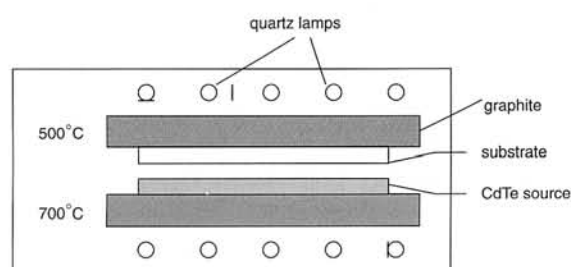


Fig. 6. Illustration of CSS deposition system.

for thin film devices, whereas for c-Si modules realistic target is 2\$/Wp. For European programme of photovoltaics development the goal is 1 ECU/Wp for thin film modules in year 2000 [19].

Two decisive parameters when determining cost of modules are efficiency and production yield. Since a module fabrication process involves about 15 steps, an overall module production yield set at 90% requires individual process steps with yields above 99%. These requirements are very difficult to meet. That is why thin film solar cells play a marginal role in photovoltaic market so far. Still, several industrial organizations are prepared for thin film module production and some of them already have entered the market with a pilot production. Table 2. presents the best results obtained for modules by some manufacturers.

Device stability is another crucial factor for potential manufacturing. In over 6 years tests CuInSe<sub>2</sub> based solar modules made by Siemens showed excellent stability [20]. Also in several months tests for CdTe devices no degradation was observed though some questions related to back contact stability remain.

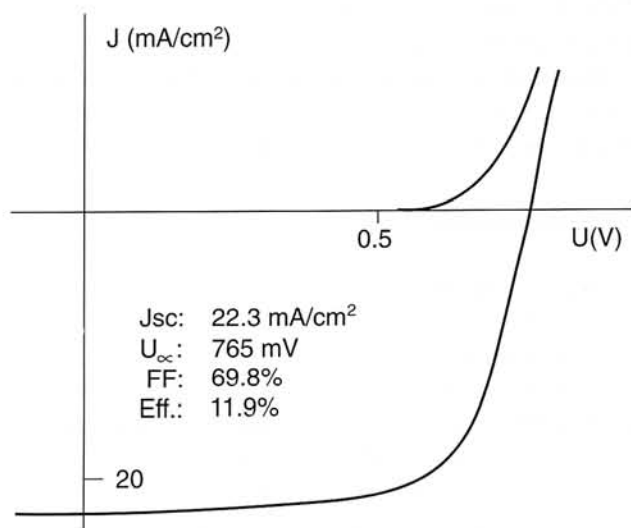


Fig. 7. The I – V characteristics of CdTe/CdS cell (after [17]).

Major issues confronting manufacture of CuInSe<sub>2</sub> based modules are: adhesion of the absorber layer to molybdenum and control of absorber composition, both in plane and perpendicular to the film surface. The present-day experience shows that the very high efficiency cells can be realised using coevaporation or selenization; other methods yield only moderate efficiencies. Films grown by coevaporation do not suffer from adhesion failure but their composition is harder to control than in sequential processes. Another problem to be solved concerns sodium diffusion through the Mo layer into absorber. Though beneficial for the cell performance, the diffusion process strongly depends on the chemical composition of the glass surface, thickness of Mo layer and deposition conditions of the absorber. These parameters have to be controlled over a large area to get an acceptable production yield. One possible solution is the use of a suitable barrier coating on the float glass and deposition of sodium containing layer on molybdenum to insure controlled Na diffusion into Cu(In,Ga)Se<sub>2</sub> absorber.

One of most attractive features of CdTe is the large number of methods by which good quality films may be prepared. Abundance of successful deposition techniques enabled a number of potential manufacturers to develop prototype products with relative ease and obtain modules with efficiencies in the range of 8%. Still some issues remain. One of the problems to be addressed is an annoying, costly step of heat treatment with CdCl<sub>2</sub> flux. This part of the process should be eliminated or combined with film formation. Another is a back contact issue with limited choice of contact materials.

Environmental aspect of CdTe based modules as cadmium containing devices has also to be considered. Production and recycling of such modules should take into account health and environmental hazards.

Both CuInSe<sub>2</sub> and CdTe are very radiation resistant materials so apart from terrestrial applications they can be also used in space power generation [21].

## 5. Conclusions

Remarkable progress has been made in developing polycrystalline thin film solar cells. Both, CuInSe<sub>2</sub> and CdTe based solar cells show great potential for further development and large scale manufacturing. Module efficiencies in the order of 15% seem to be realistic for a longer time frame. However, much remains to be done to insure long term reliability of thin film modules to successfully compete with crystalline silicon solar cells.

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