

## **ZNO IN THE DEVELOPMENT OF THIN FILM SOLAR CELLS**

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### **ABSTRACT**

ZnO doped with group III elements (ZnO-III) that had been developed by one of the authors (NNT) and his colleague in 1984 has been increasingly used in many optoelectronic applications. One of them is the photovoltaic (PV) solar energy, a new millennium industry which has fast growing market, potential accessibility to the billions of people worldwide, and is environmentally sound as a “green” source of energy. This new type of oxide has many valuable attributes: indium –free therefore cheaper, non-toxic, zinc source abundance, stability against hydrogen, low process temperature, a good balance between conductivity and transmission. Since its introduction to the PV solar community, several laboratories have adapted and studied this new type of oxide as a front contact, back contact, buffer layer for their research and development of solar cells. In the case of thin film solar cells, most of the commercial modules of amorphous silicon, microcrystalline/ nanocrystalline silicon and copper indium gallium selenide have at least one layer of ZnO-III in the device structures.

Recently, there is another development that is also technically challenging and economically attractive: the use of ZnO nanostructures grown on a TCO electrode in the dye sensitized solar cells (DSSC) which can potentially provide high efficiency due mainly to large surface and interface areas, therefore enhancing light absorption and charge separation, two important factors in PV solar cells.

In this paper, we will review some of the main R&D activities on ZnO –based thin film solar cell structures both in the world and in Viet Nam in the last two decades.

Keywords: transparent conducting oxide, ZnO, CIGS, solar cells, amorphous silicon.

### **INTRODUCTION**

Transparent conducting oxide (TCO) is a main component in the device structures of GaN based light emitting diodes, liquid crystal displays, organic light emitting diodes and solar cells. Indium tin oxide (ITO) has been widely used for TCO due to its high conductivity and high transmission in the visible spectral region. Indium however is toxic, chemically unstable, has become increasingly rare and therefore expensive. In 1984, while working at ARCO Solar in the U.S., one of the

authors (NNT) and his colleague Yu-Han Shing had developed a high quality indium –free, transparent conducting oxide film: ZnO doped with group III elements such as Al, B, and Ga [1]. This oxide is a n-type material; its conductivity is caused by the substitution of Zn<sup>2+</sup> ions with group ions for example Al<sup>3+</sup> ions, releasing excess electrons into the conduction band. For the sake of simplicity, let’s call the oxide family having III elements ZnO -III., ZnO doped with aluminum AZO; ZnO doped with boron BZO; whereas GZO is referred to as zinc oxide doped with gallium. The

obtained ZnO-III is a high band gap material which is non-toxic, stable against chemically reactive hydrogen (like plasma environment), less expensive, abundant in zinc source, low process temperature, has a low absorption coefficient, and high transmission, therefore can be made thick (2- 3  $\mu\text{m}$ ) for better conductivity; those are distinctive features that have not been readily realized with indium tin oxide (ITO) and fluorine -or sometimes doped with antimony- doped tin oxide (FTO), the two TCO's that have dominated the optoelectronic industry in the last forty years.

The ARCO's group had further incorporated this new type of oxide as a front contact layer, a back contact and a buffer layer in the development of amorphous silicon single junction (MTF modules), copper indium diselenide single-junction solar cells, transparent solar cells, copper indium diselenide- amorphous silicon tandem cells (BCLIPSE modules), MTF cell/ single crystal silicon tandem (ECLIPSE modules); some of them exhibited among the best conversion efficiencies at that time. Since then, many laboratories in the solar energy community have adapted this oxide in their research and development of thin film solar cells.

Recently, there is another development that is technically challenging and economically attractive: the use of ZnO nanostructures (such as nanowire, nanotips, nanorods, nanotubes) photoanodes on TCO in dye sensitized solar cells which can potentially provide high efficiency mainly due to large surface and interface areas, therefore enhancing light absorption and charge separation, two important factors in PV solar cells.

In this paper, we will highlight some of the R&D activities on ZnO - based thin film solar cell structures both in Viet Nam and in the world in the last two decades. Due to the scope of this article, we are not going to cover the application of ZnO-III in organic solar cells and single crystalline silicon / polysilicon solar cells, two other important members in the family of solar cells.

## RESULTS AND DISCUSSION

### History of the Development of Zinc oxide doped with group III elements

Before we discuss the on-going activities on the ZnO- based thin film solar cells in the solar industry, we'd like to take some time reviewing our original works on the development of this interesting yet important material. Our first ZnO transparent conducting oxide was zinc oxide doped with aluminum (AZO) which was prepared, using the RF, magnetron and reactive sputtering techniques. The sputtering targets were either a single ZnO target with about 2 wt% of  $\text{Al}_2\text{O}_3$  or ZnO target and Al target (Demetron); that gave an Al content in the range of 0.2- 6%. The sputtering systems were Perkin-Elmer, Torr-Vac II and in-line CPA sputtering. In the case of reactive sputtering, trimethylaluminum was employed for Al. The technical issue we had with the reactive sputtering was the existence of nodules on the metallic sputtering target after a certain period of utilization; that could create negative impact on the corrosion tracks and film uniformity. The substrate temperatures were in the range from room temperature to 350 C. One of our objective was to study the effect of hydrogen on the performance of AZO films for the two main reasons: (i) TCO is exposed to the hydrogen plasma in the process of making amorphous silicon (a-Si:H) solar cells and (ii) possibility of making ZnO-III in a CVD system. Therefore, AZO:H, high resistive ZnO:H films or a combination of the two were studied. Another approach to evaluate the impact of hydrogen on AZO was to post-anneal the film in the presence of hydrogen. Results indicated that hydrogen had not altered the characteristics of AZO, that led us to the study of ZnO using LP-CVD that would enable us to integrate the ZnO-III process in a full CVD coating line for amorphous silicon solar cells. We then further studied impact of other III elements (boron, gallium) on the characteristics of ZnO-III films. It was found that group III elements had increased the conductivity of

ZnO films by several orders of magnitude and a concentration peak was determined for each III element depending on the deposition conditions.

Optical and electrical properties of AZO are reported here as an example : Fig. 1 shows an average optical transmittance of 85% and an absorption of 5% over a wavelength range of 400 to 1100 nm and a resistivity of  $4.9 \times 10^{-4} \Omega - cm$ . The Hall mobility and the carrier concentration were measured in the temperature range from 77 K to 300 K, which was  $34 cm^2 / V - sec$  and  $2.8 \times 10^{20} cm^{-3}$ , respectively. Carrier concentration showed a peak with concentration of group III elements. That is, carrier concentration went up with increasing aluminum.  $Al^{3+}$  substitutes  $Zn^{2+}$ , giving free electrons; when aluminum content went beyond its peak, increase of Al content would result in a decrease in the carrier concentration. An x-ray orientation peak (002) in the c-axis orientation was observed, indicating that AZO had a hexagonal wurtzite structure with ions connected to four other ions in the tetrahedral bond  $sp^3$  hybrid [1].

With data of sputtered ZnO-III films in hands, we then went on to fabricate AZO and BZO, by means of CVD techniques (low pressure chemical vapor deposition LP-CVD with a home-built system and Watkins -Johnson system for the

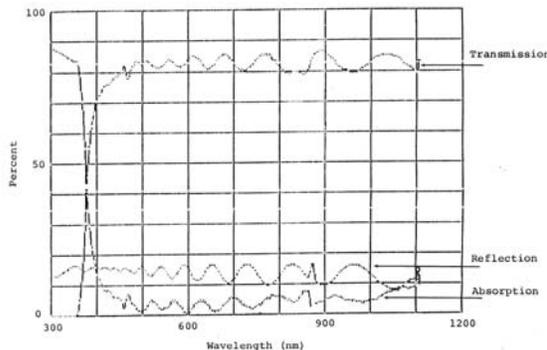


Fig. 1. Optical transmittance of sputtered AZO film as a function of the wavelength. The film was sputtered at room temperature [ARCO Solar, 1984].

atmospheric pressure chemical vapor deposition APCVD), using for example diethylzinc (DEZ), water vapor as the zinc and oxygen precursors. As for the dopants, trimethylaluminum and diborane diluted in hydrogen or helium were used for Al and B dopant in the ZnO matrix, respectively. It was found that performance of ZnO prepared from the sputtering and from LP-CVD were similar, except that surface of ZnO prepared with LP-CVD technique was rough with random trigonal prisms (from SEM). The best ZnO-III films we had achieved so far was GZO which had a resistivity of  $2.0 \times 10^{-4} \Omega - cm$  and a transmittance of 88%. In the case of LP-CVD, surface morphology depended on the content of water vapor. The same effect on surface morphology had been observed when we doped ZnO with boron and post-annealing could widen the optical band gap and alter the film crystallinity. AZO, BZO and GZO films had been tried as electrodes for CIS and a-Si solar cells. And all had exhibited essentially the same performance. Therefore, we decided to focus on AZO for our solar applications because aluminum is less expensive than gallium, boron and certainly indium. And, we will report the performance of AZO as a representative electrode in the thin film solar cell structures.

A novel device structure of AZO/CdS/CuInSe<sub>2</sub>/Mo as shown in Fig. 2 was fabricated on a glass substrate. A thick sputtered AZO (2.2 μm) was deposited onto the evaporated CdS/CuInSe<sub>2</sub> stack of films at an ambient substrate temperature. A 9.6% conversion efficiency over an area of 1.9 cm<sup>2</sup> was demonstrated, as shown in Fig. 3. It should be noted that the conventional ITO and FTO of a thickness of 2.2 μm had a low transmission, reducing the amount of current flowing through the solar cells. Besides, since CIS solar cell has a substrate-type configuration [Fig.7] which requires TCO at a low temperature such that the layers underneath would not be deteriorated; ZnO-III could be an ideal

candidate because its low process temperature.

As an option, in the CIS/ZnO structure shown in Fig. 2, a highly resistive ZnO layer (20- 100 nm with a resistivity of up to  $10^9 \Omega\text{-cm}$  by making oxygen rich to reduce the formation of zinc interstitials) was installed between CdS layer and AZO as a buffer layer to reduce the degradation of open circuit voltage  $V_{oc}$  and fill factor due to the shunt at the junction.



Fig. 2 A general schematic diagram of the AZO/  $\text{CuInSe}_2$  solar cell [Source : ARCO Solar] . A ZnO thickness of 2.2  $\mu\text{m}$  was much thicker than conventional TCO films for the same light transmission .

For the case of copper indium gallium selenide (CIGS) , the film was made , using the following procedure : a soda lime window glass was used, which was coated with a barrier/ protection layer silicon dioxide. This layer was to control and prevent sodium diffusion into the sputtered molybdenum (Mo) base electrode. Mo layer was chosen because it was able to stand the harsh condition in the selenization process at high temperatures and its ability to form an ohmic contact with CIGS layer. The Mo layer was patterned , using laser scribing . Copper, indium and gallium were formed by sputtering , using individual indium target and copper-gallium alloy target. The thus formed CIGS layer was then selenized in the presence of  $\text{H}_2\text{Se}$  at

400 C for 30-60 minutes . A thin layer of cadmium sulfide (CdS) was deposited using the chemical bath deposition (CBD) . A second patterning step was performed mechanically through CIGS layer to Mo layer to create vias. An AZO layer was then formed as a window layer using a LP-CVD technique on the exposed part of the Mo substrate in the interconnect via and thereby connects the Mo and ZnO electrodes of adjacent cells. A third and final patterning step was performed by mechanical scribing through the AZO and CIGS absorber to isolate adjacent cells. A cell-to-cell connection is tentatively shown in Fig. 4. CIS in this configuration can also be applied to CIGS.

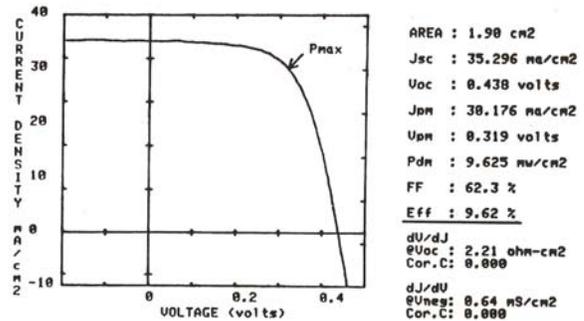


Fig.3. Illuminated current-voltage characteristics of the historic (AZO/CdS/ $\text{CuInSe}_2$ /Mo solar cell on a glass substrate [ARCO Solar, 1984,External publication No 85-22A/EA]

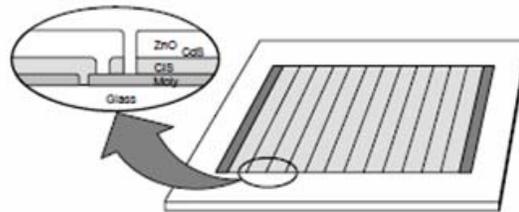


Fig. 4. A configuration of CIGS/AZO module [2]

ZnO-III was also studied for the bottom electrode and the window layer in amorphous silicon (a-Si) solar cells . A conversion efficiency (7.8 %) was also obtained on AZO/pin a-Si/AZO amorphous

silicon “see-through” solar cells over an area of 4 cm<sup>2</sup> as shown in Fig. 5.

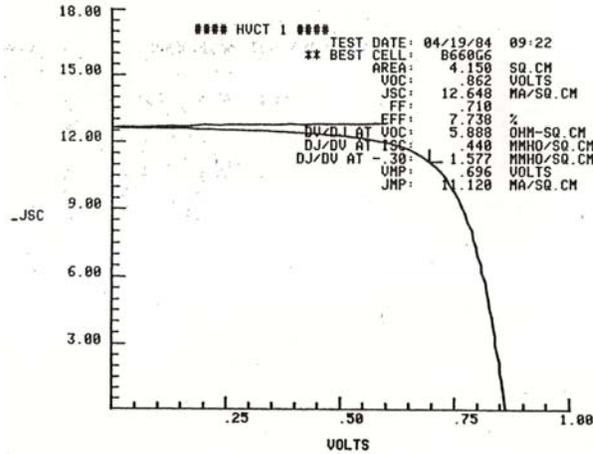


Fig. 5. Illuminated current-voltage characteristics of the historic AZO/pin a-Si/AZO “see-through” solar cell on a glass substrate [ARCO Solar, 1984]

The above numbers of solar cells with ZAO electrode were considered among the best conversion efficiencies at that time.

### ZnO doped with group III elements in the development of thin film solar cells .

Over period of 27 years since the material had been developed , ZnO-III has been tried for different optoelectronic devices such as light emitting diodes [3, 4], organic light

emitting diodes [5] , liquid crystal displays [6] and solar cells . Several deposition techniques have also been tried such as magnetron sputtering [7, 8], low pressure-chemical vapor deposition , atomic layer deposition [9], spray pyrolysis, MOCVD [10], pulsed laser deposition [11], arc plasma deposition [12], sol-gel [13] and ion plating [14]. .In all these techniques, sputtering and CVD , the two techniques that we had originally used in the development of our first ZnO-III series are perhaps the most suitable due to its large area deposition capacity, good adhesion and high deposition rate. In this review, we will discuss the development of ZnO-III only for thin film solar cells and modules of amorphous silicon (a-Si:H), microcrystalline silicon (μSi:H), nanocrystalline silicon (n-Si:H) , copper indium gallium selenide (CIGS), cadmium telluride (CdTe) and dye sensitized solar cells (DSSC).

Generally ,configurations of the thin film solar cells such as a-Si:H , micro/nanocrystalline silicon, (CIGS) cells and CdTe cells can be classified as in the chart shown in Fig. 6. The substrate can be of a rigid form such as glass substrate or a flexible form such as polyimide, stainless steel and the cells can be made discrete or monolithic.

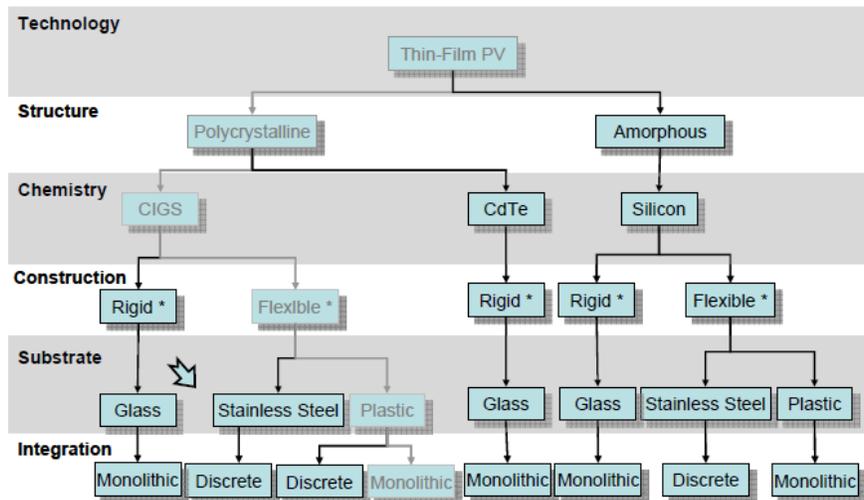


Fig. 6. Classification of the technologies of making thin film solar cells [Source : Honda]

Going further into the configurations, we can say that all thin film solar cells belong to one of the two main configurations, depending on the sun light incoming direction with respect to the

substrate : light coming from the substrate (superstrate) and light coming from the opposite direction of the substrate (substrate). Fig. 7 shows general features of the two configurations.

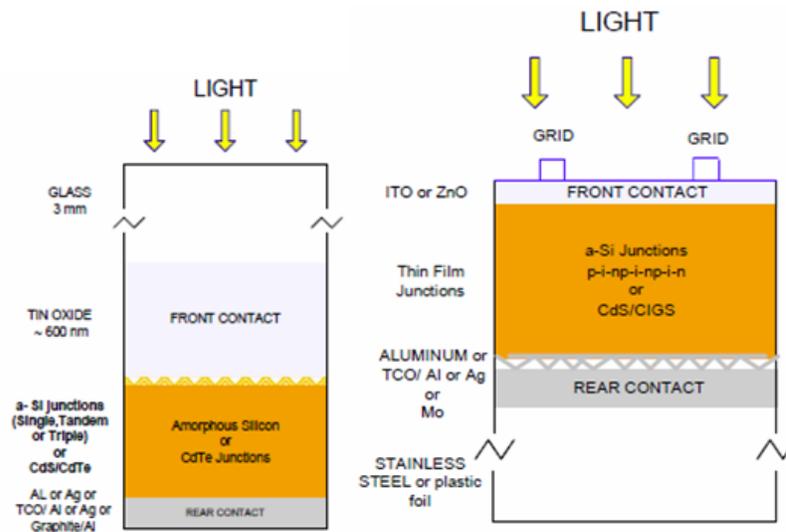


Fig. 7 . Superstrate configuration of thin film solar cells [Source : Rajeeva R. Arya] . Tin oxide in this configuration can be substituted with ZnO-III (as will be discussed later).

**Development of amorphous silicon and micro/nanocrystalline solar cells using ZnO doped with group III elements**

Amorphous silicon and its related devices are perhaps one of the most promising technology because they are built on the experience and process availability of IC industry. The players in the field of amorphous silicon solar cells are United Solar, Oerlikon Solar, Sharp, Mitsubishi, Canon, Applied Materials, Apollo Dupont, Power films, Energy PV, MV Systems, OptiSolar, Signet Solar, Nano PV, MWOE Solar, New Solar Ventures, Innovalight, Nanogram and Soltai. ZnO-III can be used either as a top electrode, a buffer electrode or a back electrode in amorphous silicon, microcrystalline/ nanocrystalline solar cells. The oxide film can also be textured to enhance light trapping, resulting in an increase in photocurrent, especially in the case of a-Si:H which is an indirect bandgap material, therefore the absorption coefficient near red and infrared spectral region is

relative small. For CIGS and CdTe solar cells, since both CIGS and CdTe are direct band gap materials, a textured ZnO-III might not be necessary. Fig. 8 shows a schematic model of amorphous/microcrystalline or nanocrystalline silicon solar cell where ZnO-III are used for both as a back reflector and a front layer. Here, ZnO-III with an index of refraction of 2, low reflectance at 600 nm is effective in light trapping for amorphous silicon cells. Texturing the surface of ZnO-III front layer will scatter the incoming light which increases the fraction of light absorbed in the layer, therefore increasing the light trapping in both single- and tandem-junction cells,

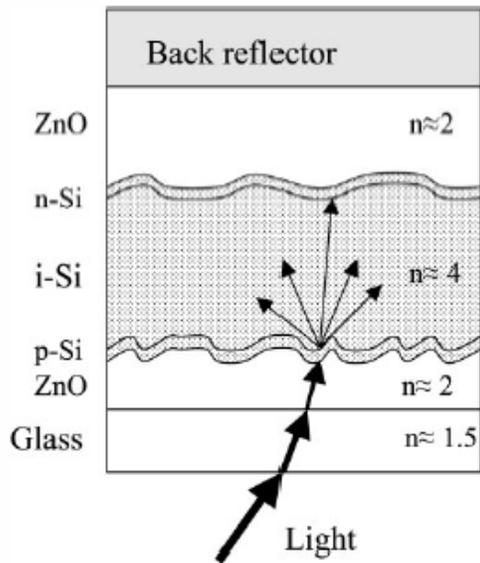


Figure 8. Schematic sketch of a  $p-i-n$  thin-film silicon solar cell, used both for  $a-Si:H$  and for microcrystalline silicon ( $\mu c-Si:H$ ) or nanocrystalline silicon ( $nc-Si:H$ ). The values for  $n$  indicated here give approximate values of the optical index of refraction, an important parameter for light trapping considerations. With a glass substrate; this corresponds to the so-called superstrate configuration [15].

The benefit of textured surface of ZnO-III films is to trap more light to the solar cells. A rough surface increases the length of light path and also the absorption of light by reducing reflection, thus increasing the quantum efficiency of the cell. Surface texturing can be formed by plasma or chemical etching which introduces an additional step or by self-texturing as in the case of chemical vapor deposition coating. Etching time is critical since over-etching would increase the sheet resistance of ZnO-III films [16].

Not only for  $a-Si:H$  single junction, ZnO-III has also been widely used for double junction and triple junction amorphous silicon cells. Fig. 9 shows a tentative structure of amorphous silicon tandem cells where ZnO-III films are used

As an example of how ZnO-III films have been used in the industry, AZO

as a back reflector, a buffer layer and a top layer. In this case, the tandem cell is a double-junction cell which consists of  $a-Si:H$  top cell and a  $\mu c-Si:H$  bottom cell (or  $nc-Si:H$  bottom cell). The same configuration can also be applied to a double-junction with  $a-Si:H$  top cell and  $a-SiGe:H$  bottom cell. The cell exhibited an initial conversion efficiency of 13-15% and a stabilized efficiency of 11-12%. In this structure the top cell is generally made small to reduce the Stabler-Wronski effect and therefore the device is top cell-limited.

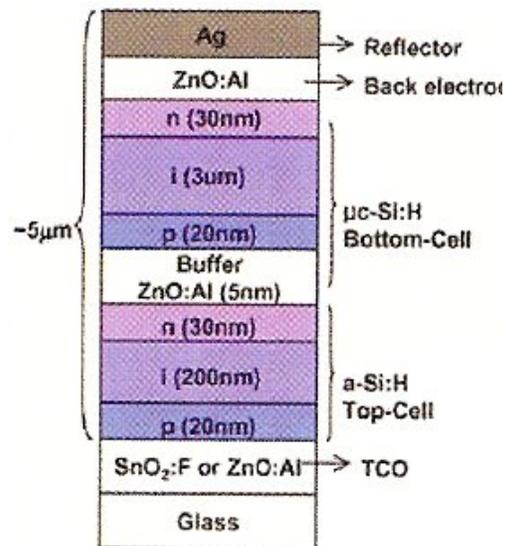
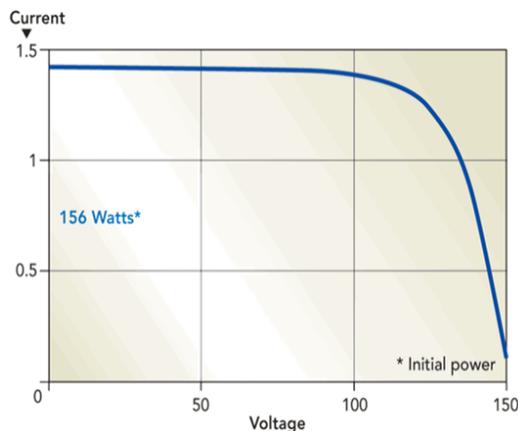


Fig. 9. A schematic configuration of amorphous silicon/microcrystalline (or nanocrystalline) tandem cells [17]

The low temperature process enables ZnO-III to be used as a buffer or top layer without damaging the performance of the layers underneath. Particularly, ZnO-III is more suitable than other TCO materials for the opaque substrate such as PET, polyimide or other substrate-type configurations.

$a-Si$  solar module of Applied Materials was used as a representative example. AZO

films were used as a bottom and top electrode of a-Si:H/  $\mu$ -Si:H tandem cells which were fabricated in the SunFab PV factory of Applied Materials . The AZO bottom electrode was sputtered on a sheet of glass substrate of a large area of 1 x1.3 m<sup>2</sup> (Generation 5) then etched in a solution of hydrochloric acid at different etching times to form a textured AZO film for light scattering at Si:H/ZnO interface. The top electrode was also sputtered AZO . The films had a transmission of 83.7% over a wavelength range of 400- 1100 nm with an uniformity of  $\pm 0.2\%$  uniformity and a sheet resistance of  $4.4\Omega/square \pm 3.1\%$  in uniformity . The etching time was varied between 5- 150 seconds to change the surface textured morphology with different crater sizes . And a module of 15.6 W with an aperture conversion efficiency of 11.5 % had been achieved, as shown in Fig. 10 .



gradient at the p/i interface . When dealing with polyimide , one has to pay special attention to the contamination which is caused by the two following mechanisms : (i) the web is not completely cross-linked and (ii) outgassed web will absorb water during the web transfer process. In our PTS system , the web was first sent through an oven section at 300 C for outgassing

*Fig. 10. I-V characteristics of a-Si:H/ $\mu$ -Si:H tandem module with AZO as top and bottom electrodes [Source: SunFab , Generation 5 , Applied Materials]*

In addition to the superstrate configuration , substrate configuration has also been studied. In an attempt to further reduce weight of the solar modules, in a cost-sharing contract with NREL (Department of Energy, 1984-1987), one of the author (TTN)'s group at 3 M ,had developed amorphous silicon solar cells on polyimide . As an example, cells of a p(200 A)-i(4,500 A) -n (300A) configuration were coated in-line on a moving web of 2 mil thick and 4 inches wide in a home-built plasma enhanced chemical vapor deposition, as shown in Fig. 11. The web was outgassed , cleaned , sealed and precoated with Al/TiN in a Web Pre-treatment System (PTS). Undoped layer (i layer) had photoconductivity values greater than  $1 \times 10^{-4} (\Omega - cm)^{-1}$  under AM1 illumination and the obtained cells had an efficiency of 9% over an area of 1 cm<sup>2</sup> . The p window layer was also a wide band gap p-SiC:H layer with a composition

trapped water and curing. And both sides of polyimide were coated with at least one layer of metal back electrode . Several other ZnO-based materials such as ZnO doped with fluorine or ZnO-III doped with fluorine and/or hydrogen, Ag/ZnO, ZnO-III/Ag/ZnO-III ,ITO/Ag/ZnO-III , CdZnO or SnZnO doped with group III elements had been tried for TCO [18] .

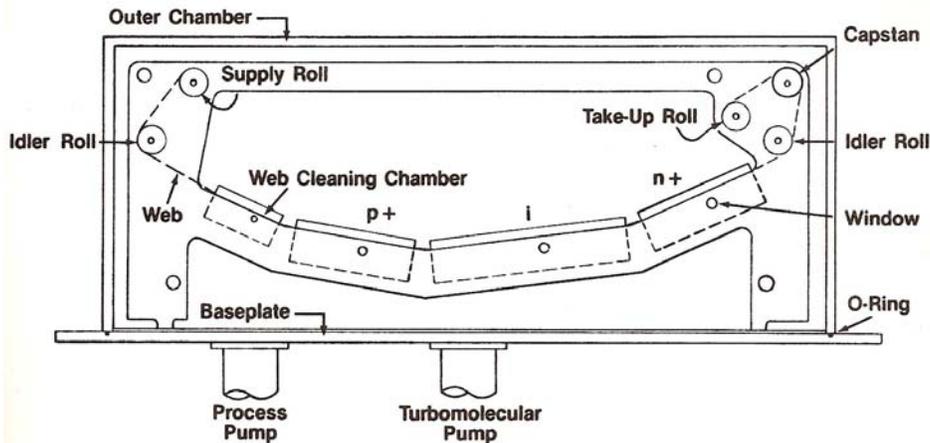


Fig. 11. An in-line plasma enhanced chemical vapor deposition (PECVD) for coating p, i, n layers of amorphous silicon. Standard deposition conditions : n-chamber :  $H_2 = 81$  sccm,  $SiH_4 = 0.6$  sccm,  $PH_3 = 0.006$  sccm, 30 W, 210 C, 1 Torr, deposition rate of 12 A/min. ; i-chamber :  $H_2 = 160$  sccm,  $SiH_4 = 56$  sccm,  $B_2H_6 = 56 \times 10^{-6}$  sccm, 30 W, 230 C, 1 Torr, deposition rate of 133 A/min ; and p-chamber :  $H_2 = 58$  sccm,  $SiH_4 = 0.3$  sccm,  $B_2H_6 = 0.006$  sccm, 40 W, 210 C, 1 Torr, deposition rate of 8.8 A/min. [19] Source: 3M & NREL].

A triple-junction amorphous silicon solar cells was developed by United Solar and Sharp. The United Solar's cells had an initial cell efficiency of 14.59% [20]. a-Si:H and a-SiGe films were used for the large bandgap and narrow bandgap, respectively and Ag/ZnO transparent conducting oxides was used for the back contact electrode. United Solar has also developed other configurations by substituting the middle cell and/or the bottom cell with nanocrystalline nc-Si:H. An initial active area conversion efficiency of 13.3% and 14.5% had been achieved on the a-Si:H/a-SiGe:H/nc-Si:H and a-Si:H/n-SiGe:H/nc-Si:H, respectively [21, 22]. Nanocrystalline silicon (nc-Si:H) which was achieved by hydrogen dilution in silane and by controlling the hydrogen profile possesses the following properties : band gap of 1.1 eV as supposed to 1.7 eV for a-Si:H, higher mobility than a-Si:H, low temperature process, large absorption in the red and infrared spectral region and stable due to less hydrogen.

#### **Development of copper indium gallium diselenide cells using ZnO doped with group III elements**

The players in the field of CIGS thin film solar cells are : Würth Solar, Global Solar Energy, Showa-Shell, Honda Soltec, Sulfurcell, Ascent Solar, Miasole, Avancis, Daystar, EPV, ISET, Nanosolar, Heliovolt, Solyndra, Solopower, ITRI, Flisom, Solibro (Q-cell), Odersun, CNRS, CIS Solar Technik, Solarion, and Scheulen Solar. The majority of the companies use ZnO-III as a front contact and the oxide films were deposited, using either sputtering or LP-CVD. Among them, Würth Solar, Global Solar, Honda, Showa Shell and Sulfurcell have a production capacity of 5-27 MW per year.

A general structure of CIGS/AZO is shown in Fig. 12 (a) which is similar to the structure of ARCO's cells shown in Fig. 2.. Although sputtering was mentioned here as the coating technique for AZO, other techniques such as LP-CVD, APCVD, nanoprinting and atomic layer deposition (ALD) can also be used.

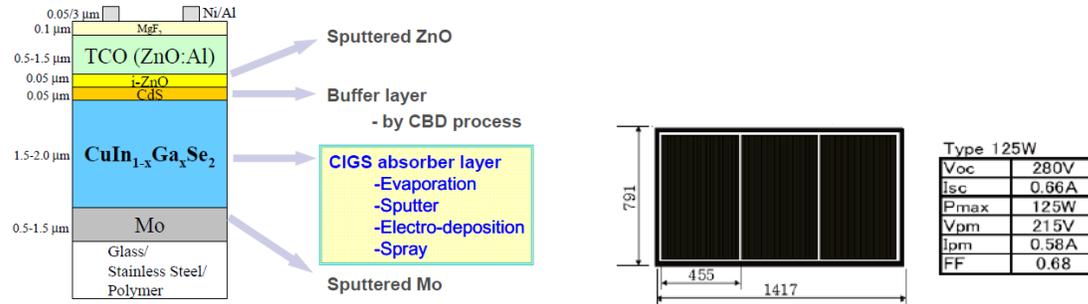


Fig. 12. General structure(a) and dimension (b) of CIGS/AZO solar cells [Source :Honda, ref.23]

Dimension and performance of a CIGS/AZO modules from Honda are shown in Fig. 12(b). [20]

Cell efficiencies and module efficiencies of representative CIGS/ZnO

modules are listed in Table 1 and Table 2, respectively.. Efficiencies of CdTe modules are also inserted in the Table for reference.

Table 1. Performance of CIGS and CdTe solar cells (source :NREL)

	Area (cm <sup>2</sup> )	V <sub>oc</sub> (V)	J <sub>oc</sub> (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	Comments
CIGSe	0.410	0.697	35.1	79.52	19.5	CIGSe/CdS/Cell NREL, 3-stage process
CIGSe	0.402	0.670	35.1	78.78	18.5	CIGSe/ZnS (O,OH) NREL, Nakada et al.
CIGS	0.409	0.830	20.9	69.13	12.0	Cu(In,Ga)S <sub>2</sub> /CdS Dhere, FSEC
CIAS	—	0.621	36.0	75.50	16.9	Cu(In,Al)Se <sub>2</sub> /CdS IEC, E <sub>g</sub> = 1.15 eV
CdTe	1.03	0.845	25.9	75.51	16.5	CTO/ZTO/CdS/CdTe NREL, CSS
CdTe	—	0.840	24.4	65.00	13.3	SnO <sub>2</sub> /Ga <sub>2</sub> O <sub>3</sub> /CdS/CdTe IEC, VTD
CdTe	0.16	0.814	23.56	73.25	14.0	ZnO/CdS/CdTe/Metal U. of Toledo, sputtered

Table 2. Module efficiencies of CIGS and CdTe solar modules from different laboratories [Source :NREL]

Company	Device	Aperture Area (cm <sup>2</sup> )	Efficiency (%)	Power (W)	Date
Global Solar	CIGS	8390	10.2*	88.9*	05/05
Shell Solar	CIGSS	7376	11.7*	86.1*	10/05
Würth Solar	CIGS	6500	13.0	84.6	06/04
First Solar	CdTe	6623	10.2*	67.5*	02/04
Shell Solar GmbH	CIGSS	4938	13.1	64.8	05/03
Antec Solar	CdTe	6633	7.3	52.3	06/04
Shell Solar	CIGSS	3626	12.8*	46.5*	03/03
Showa Shell	CIGS	3600	12.8	44.15	05/03

### ***ZnO in CdTe solar cells***

CdTe has a band gap of 1.4 eV, which is optimum for the efficiency of a single junction solar cell. Currently, First Solar and other solar companies have employed tin oxide FTO as a front electrode for their CdTe single-junction solar modules. However, since their closed-space sublimation technique is a high temperature process. Therefore, in consideration of the possibility of using CdTe multi-junction cells, Prof. Alvin Campaan and his group at The University of Toledo have studied sputtering as the technique to make CdTe/CdS and AZO electrode. A CdTe cell of a conversion efficiency of 14% at a sputtering temperature of 250 C was demonstrated [24]. CdTe/AZO was also fabricated on a flexible substrate [25]. The main players in this area are: First Solar, Primestar Solar, AVA Solar, Solar Fields, Canrom, Ascentool, Nuvo Solar Energy and Zia Watt Solar. The fast growth of CdTe thin film solar modules in the US (44% in 2006) lied perhaps with the aggressive growth in the manufacturing capacity of First Solar in Perrysburg in Ohio. This company is the leader of the solar cell with a production capacity of 90 MW in the US, 120 MW in Germany and 240 MW in Malaysia in 2009.

### ***ZnO in dye-sensitized solar cells***

Study indicates that advanced thin film solar cells such as dye sensitized solar cells, quantum dot solar cells have a potential to be less expensive than other types of solar cells because of the low temperature process, therefore flexible, and cheap substrates can be used. Three major advantages of nanostructured materials / nanoparticles-based DSSC over the conventional solar cells are: (i) large surface and interface areas, therefore enhancing light absorption and charge separation, two important factors in PV solar cells; (ii) tailoring optical properties by adjusting particle sizes and electrons and holes can be well confined and (iii) multiple exciton generation [26].

A dye sensitized solar cell (DSSC) with a solar power conversion efficiency of 8% at AM 1.5 was first reported by O'Regan and Grätzel in 1991 [27, 28]. This achievement was realized by using titanium dioxide nanoparticles abutted together to form a porous film which was coated with a layer of adsorbed dye. The dye was then filled with electrolyte. The historic DSC has five main components: a dye, a porous high surface area oxide (typically a 10 nm thick layer of TiO<sub>2</sub> nanocrystals), a collector electrode (fluorine doped tin oxide), a redox couple (usually iodide I<sup>-</sup>/triiodide I<sub>3</sub><sup>-</sup>) and a regeneration electrode (platinum). The advantages of TiO<sub>2</sub> are: low cost, availability, non-toxic and biocompatible. The working mechanism can be explained as follows: The dye absorbs the incident sunlight (not much light was absorbed in TiO<sub>2</sub> because this is a high band gap material), generating electrons into TiO<sub>2</sub>. The dye is rapidly regenerated from its oxidized state by electron transfer from I<sup>-</sup>. The photoinjected electrons diffuse to the back contact (Fluorine doped tin oxide electrode) and the regenerative cycle is completed by recycling tri-iodide I<sub>3</sub><sup>-</sup> at the platinum electrode to return it back to iodide I<sup>-</sup>).

In this type of device, photogenerated electrons travel to the electrode by hopping and there are thousands of hopping taking place which could increase the recombination rate, reducing the photocurrent. In order to reduce the hopping frequency, a direct path for electrons through for example nanowires, nanorods or nanotubes may be beneficial. As in the case of quantum dots in nanostructured dye-sensitized solar cells, the dot sizes determine energy levels; large dots are red and small dots are blue. Therefore, a mixture of quantum dots can practically cover most of the sun spectrum. Since quantum dots are confined in all three dimensions, one can tailor the absorption energy of the sun light by adjusting the dot sizes. As a result, conversion efficiency of

the quantum-dot based solar cells will not be constrained by the Shockley- Queisser limitation of 30% for a single junction , as in the case of the solar cells of Generation I and Generation II and can reach the theoretical limit of 63%. In addition , nanostructured dye- sensitized solar cells can be fabricated on a sheet of stainless steel , using the continuous roll-to-roll coating technique.

Figure 13 illustrates another type of dye sensitized solar cell which has been

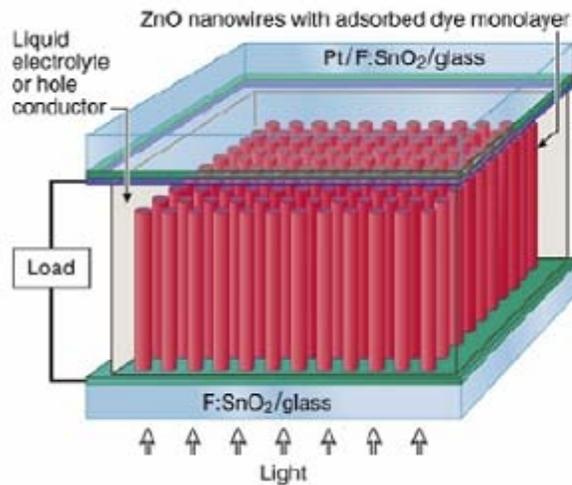
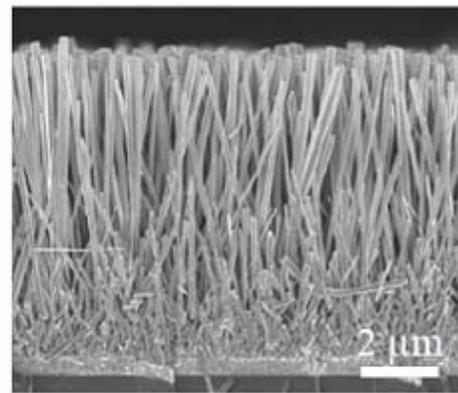


Fig. 13. Dye sensitized cell where ZnO nanowires were employed [28]

In this dye sensitized solar cell, ZnO nanowires which is the wide band gap semiconductor acting as an electron acceptor were grown vertically on a tin oxide coated from an aqueous solution of methanamine and zinc nitrate at a temperature at 95 C . CdSe quantum dots having quantum confinement effects are absorbed on ZnO nanowires as the sensitizer to convert light into the electrical current . CdSe quantum dots (nanometers in sizes) were synthesized separately and attached to the surface of ZnO for form a photosensitized anode . A space of 25 μm was formed between the platinumized transparent conducting oxide photocathode and the nanowire photoanode . The space was then filled with electrolyte containing  $I_3^- / I^-$  . Other ZnO nanostructured DSSC was studied as shown in Fig.14, where ZnO

studied by Prof. Eryl Aydil and his group at University of Minnesota. In this solar cell, TiO<sub>2</sub> was substituted with ZnO nanowires and commercially available fluorine doped tin oxide (FTO) were employed for both electrodes . Since process of fabricating nanostructured DSSC is at a low temperature and potentially can be coated on a flexible substrate, it is expected that ZnO-III can do the same job as or better than FTO as a collector electrode in this cell configuration.



nanorods were grown on a ZnO -III coated sapphire.

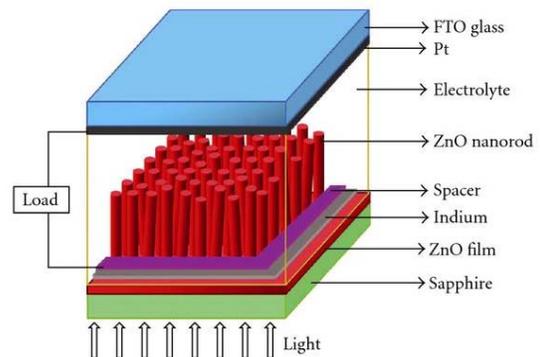


Fig. 14 A DSSC cell with ZnO nanorods [29]

In Fig. 14, the Pt coated FTO back electrode was replaced with ZnO doped with Gallium (GZO). A conversion efficiency of 1.9% was achieved for both types of cells. In another structure, ZnO nanotips and a Ga-doped GZO electrode were developed for DSSC applications. The n-type semiconductor ZnO nanotips provided large surface area for dye

### **Production of amorphous silicon solar modules in Viet Nam**

Viet Nam has an average solar radiation of  $5 \text{ kWh/m}^2/\text{day}$  which is more than that of Germany being about  $3 \text{ kWh/m}^2/\text{day}$ . The solar radiation varies from city to city and from month to month, peaks in July at the average radiation of 5-6  $\text{kWh/m}^2/\text{day}$  [German Federal Ministry of Economics & Technology]. Over a period of 28 years, the amount has jumped rapidly from 3 GWh in 1980 to approximately 60 GWh in 2008. Total electricity consumption per capita however remains at 1/10 of that in Germany, indicating a good business potential and enormous domestic demand for the solar electricity in Viet Nam. Viet Nam also has many remote areas, young work force, low cost labor, low SG&A. Last but not least, a PV industry can certainly set up a stepping stone in building the future semiconductor industry of the country.

Realizing the vast potential of solar energy in Viet Nam, Red Sun Energy was the first company who built a factory for single

anchoring in conjunction with direct conduction pathways for charge transport, while the GZO film acted as the transparent electrode. ZnO nanotips and GZO films were grown using the metallo-organic chemical vapor deposition (MOCVD). The obtained conversion efficiency of 0.77% [30]. ZnO nanotubes can also be used as photoanodes in DSSC cells [31, 32].

crystalline silicon solar panels in Long An in 2009. Unlike single crystalline silicon, thin film solar cells will consume less material by a factor of 1/600 of its silicon counterpart, therefore has potential of being less expensive. In 2011, two thin film companies have come into existence in the PV solar community in Viet Nam. Two months after First Solar broke ground to build a manufacturing plant for CdTe thin film solar modules, in May 14, 2011, Indochina Energy & Industry Co. or IC Energy - a wholly Vietnamese owned company - kicked off construction of a US\$ 390 million solar panel factory on a 11.5 hectare site (about  $115,000 \text{ m}^2$ ) in Chu Lai Economic Zone, Quang Nam to manufacture amorphous silicon solar modules at an annual capacity of 120 MW. In the first phase, the company plans to produce 30 MW, then triple the capacity to 90 MW in the second phase and the plant will be in full capacity by the end of 2015.

The steps of making IC Energy's amorphous silicon solar modules can be summarized in Fig. 15.

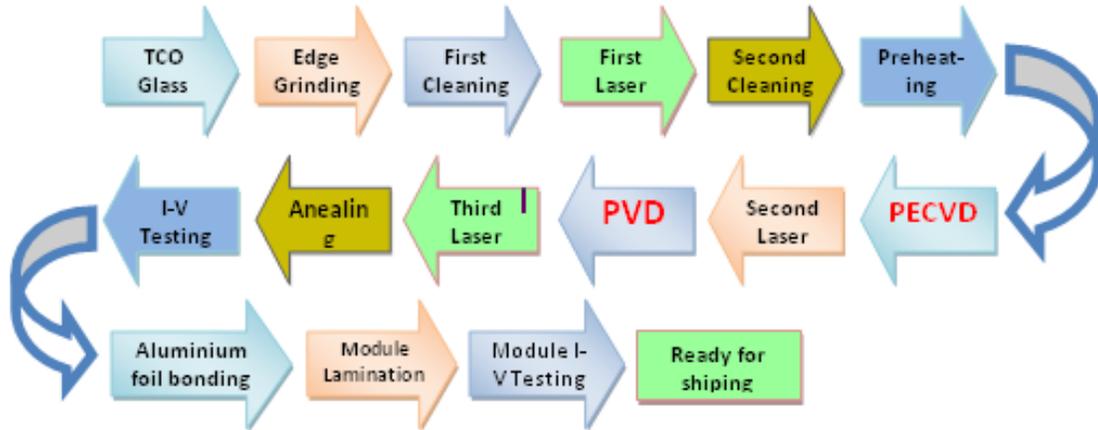


Fig. 15. Steps in manufacturing amorphous silicon solar modules [Source: IC Energy]

As shown in Fig. 15, the fabrication process consists of ten main steps :

- Step1: TCO coated glass plate is cut to desired dimensions , then washed with DI water (first cleaning) .
- Step 2: Laser patterning
- Step 3: Second cleaning with DI water.
- Step 4: The glass plate is heated to a predetermined temperature, then moved into a PECVD system to coat silicon layers.
- Step 5: Second laser patterning
- Step 6: ZnO coating in a PVD system.

- Step 7: Patterning with laser
- Step 8: First I-V measurement
- Step 9: EVA coating , frame set-up and electrical connections.
- Step 10: Second measurement before shipping.

Fig. 16 shows an amorphous silicon double junction module and its dimension (L 1245 mmx W 635 mm x D7.5 mm) that will be produced by IC Energy in the new plant. The module weight is approximately 14.4 kg.

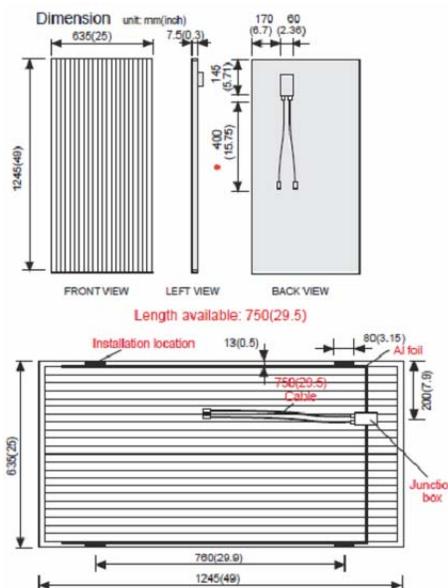


Fig. 16. IC Energy's amorphous silicon double-junction solar module [Source : IC Energy]

As shown in Table 3, the module produces 50 W with a stabilized conversion efficiency in the range of 7-8% at standard test conditions (STC). Electrical characteristics of the module at the normal operating cell temperature (NOCT) conditions are also listed for the testing

conditions in the field. NOTC is defined as the temperature of the cells in a module under the conditions : irradiance = 800 W/m<sup>2</sup>, air temperature = 20 C and wind velocity = 1m/s. NOTC is related to the module design, including module materials and packing density.

Table 3 . Performance of amorphous silicon module

Electrical Characteristics at STC (1000W/m <sup>2</sup> , 25°C, AM1.5)		
Maximum system voltage	V <sub>sys</sub> (V)	1000
Normal power (+/- 5%)	P <sub>max</sub> (W)	50
Voltage at P <sub>max</sub>	V <sub>mp</sub> (V)	43
Current at P <sub>max</sub>	I <sub>mp</sub> (A)	1.17
Open circuit voltage	V <sub>oc</sub> (V)	62
Short circuit current	I <sub>sc</sub> (A)	1.42
Maximum Source Circuit Fuse	I <sub>cr</sub> (A)	3

Electrical Characteristics at NOCT (800W/m <sup>2</sup> , 45°C, AM1.5)		
Maximum power	P <sub>max</sub> (W)	35.5
Voltage at P <sub>max</sub>	V <sub>mp</sub> (V)	38.6
Current at P <sub>max</sub>	I <sub>mp</sub> (A)	0.92
Open circuit voltage	V <sub>oc</sub> (V)	56.1
Short circuit current	I <sub>sc</sub> (A)	1.14

Temperature Coefficients	
Maximum output power (W)	-0.22% /°C
Open circuit voltage (V)	-0.33% /°C
Short circuit current (A)	+0.09% /°C

The above data represents stabilized electrical module performance at standard test conditions STC (irradiance of 1,000 W/m<sup>2</sup>, AM 1.5 and module temperature at 25 C). and at NOCT conditions [Source : IC Energy]

**CONCLUSIONS**

The role of TCO films in solar cells is two-fold: (i) diffuses the incoming light into the devices and (ii) creates a good electrical contact to collect generated current . Over the last two decades, ZnO doped with group III elements or ZnO-III has proved to be an important component in the optoelectronic devices due to its special features of being non-toxic, low cost, stability against hydrogen and low temperature process . Sputtering and chemical vapor deposition techniques CVD have worked effectively as production – oriented techniques for fabricating large area ZnO-III based modules. In particular,

LP-CVD is able to produce self- texturing for AZO and BZO. In the future, for further enhancing performance of thin film solar cells , one has to balance the performance of electrical conductivity and optical transmittance. That is, a high conductivity is related to an increase in the carrier concentration and mobility ; on the other hand, an increase in carrier concentration would increase the visible absorption, therefore reducing transmittance. The following aspects are suggested to study to further improve the performance of ZnO-III films : impurities and defects such as oxygen vacancies , stable interface between ZnO-III and active layers, low contact resistance , maximizing carrier mobility , deposition techniques, deposition conditions and high deposition rate. In the cell production environment, a high deposition rate is desirable especially in the case of superstrate devices , ZnO-III has to be

coated fast (high deposition rate) in order not to warp a large area glass substrate. As in the case of substrate device like amorphous silicon solar cells, large grains would help with the light trapping. Therefore, nucleation densities, surface reaction and process conditions (substrate temperature, pressure, impurities) have to be properly controlled and understood. In addition to ZnO-III, other ZnO-based TCOs such as Ag/ZnO-III, ZnO-III/Ag/ZnO-III, ZnO or ZnO-III doped with fluorine should be investigated.

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