Polycrystalline Thin Film Photovoltaics: Research, Development, and Technologies

Preprint

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ABSTRACT

II-VI binary thin-film solar cells based on cadmium telluride (CdTe) and I-III-VI ternary thin-film solar cells based on copper indium diselenide (CIS) and related materials have been the subject of intense research and development in the past few years. Substantial progress has been made thus far in the area of materials research, device fabrication, and technology development, and numerous applications based on CdTe and CIS have been deployed worldwide. World record efficiency of 16.5% has been achieved by NREL scientists for a thin-film CdTe solar cell using a modified device structure. Also, NREL scientists achieved world-record efficiency of 21.1% for a thin-film CIGS solar cell under a 14X concentration and AM1.5 global spectrum. When measured under AM1.5 direct spectrum, the efficiency increases to 21.5%. Pathways for achieving 25% efficiency for tandem polycrystalline thin-film solar cells are elucidated. R&D issues relating to CdTe and CIS are reported in this paper, such as contact stability and accelerated life testing in CdTe, and effects of moisture ingress in thin-film CIS devices. Substantial technology development is currently under way, with various groups reporting power module efficiencies in the range of 7.0% to 12.1% and power output of 40.0 to 92.5 W. A number of lessons learned during the scale-up activities of the technology development for fabrication of thin-film power modules are discussed. The major global players actively involved in the technology development and commercialization efforts using both rigid and flexible power modules are highlighted.

INTRODUCTION

Polycrystalline thin-film compounds based on II-VI binary thin-film CdTe solar cells and I-III-VI ternary thin-film CIS-based solar cells have made remarkable progress in the past few years. World record total-area efficiency of 16.5% has been achieved by NREL scientists for a thin-film CdTe solar cell using a modified device structure of CTO/ZTO/CdS/CdTe/contact. The several advantages of this novel structure as compared to the conventional structure of TO/CdS/CdTe/contact are highlighted below. A new O2-alloyed CdS layer whose bandgap varies with the O2 content has been developed at NREL labs. Contact stability and accelerated life testing (ALT) of these devices is the focus of research at several laboratories. NREL scientists also achieved world-record, total-area efficiency of 21.5% for a thin-film CIGS under 14X concentration and AM1.5 global spectrum. When measured under AM1.5 direct spectrum, the total-area efficiency increases to 21.5%. Details of the cell processing are given below. The Institute of Energy Conversion (IEC) at the University of Delaware has set a world-record, total-area efficiency of 16.9% for a thin-film copper indium aluminum diselenide (CIAS) solar cell, verified by NCPV/NREL. Also, n- and p-type transparent conductors (TCs) used in thin-film solar cell fabrication are described below. n-type TCs used in thin-film solar cell applications are ITO, CTO, TO, ZnO, and ZTO; p-type TCs that are in the early stages of development are CAO, CIO, CSO, and ZnO. When fully developed, p-type TCs will have some unique advantages in solar cell fabrication, especially in a tandem device. It has been established that the efficiency of single-junction polycrystalline thin film solar cells has a practical limit of about 20% under 1-sun illumination. In order to move the technology forward in the next 5 to 10 years, tandem junction thin-film solar cells are the logical choice to advance the state-of-art efficiency to about 25%. Pathways for achieving this long-term goal are elucidated. R&D issues relating to CdTe and CIS materials and devices are also presented.

A number of organizations worldwide are involved in the technology development of thin-film CdTe and CIS modules. Power modules in the efficiency range of 7.0% to 12.1% and power output of 40.0 to 92.5 W have been fabricated by several groups worldwide. Numerous lessons learned in the design, development, processing, and encapsulations/packaging of thin-film module fabrication is also discussed in detail. A number of applications based on CdTe & CIS have been deployed worldwide with grid-connected system sizes varying from 10.0 to 250 kW.

TRANSPARENT CONDUCTORS

An important component for making high-efficiency thin-film solar cells are n-type current-carrying TCs. The basic properties for making high-quality TCs are: high conductivity, high optical transmission, low surface roughness, thermal stability, chemical stability, work function, crystallinity, hardness, and cost. This is depicted in Table 1. Typical n-type TCs used in solar cell fabrication are ITO, TO, CTO, ZnO, and ZTO. The typical values for...
bandgaps are in the range of 3.3 to 3.8 eV; carrier concentration is in the range of $10^{20}$ to $10^{21}$ cm$^{-3}$; conductivity of $10^4$ (ohm-cm)$^{-1}$; sheet resistance about 5 to 10 ohms per sq.; and optical transmission greater than 85% over the visible part of the solar spectrum. ZTO is mainly used as a buffer layer in cell fabrication. ITO, SnO$_2$, and ZnO are currently used for module fabrication. ITO is fabricated by sputtering, SnO$_2$ by CVD and spray deposition, and ZnO by MOCVD and sputtering. CTO is deposited by sputtering and is currently being used for fabricating world-record laboratory cells. CTO has superior electrical and optical properties when compared to conventional SnO$_2$ [1].

Recently, p-type TCs have emerged and could potentially have a significant impact in fabricating tandem polycrystalline thin-film devices. The most commonly used p-type TCs are CAO, CIO, CSO, and ZnO. They are mainly, but not exclusively from the crystallographic family of delafossite [2]. The main drawback of p-type TCs is its lower carrier concentration, which is several orders of magnitude lower compared to n-type TCs. The typical value varies from $10^{16}$ to $10^{17}$ cm$^{-3}$, mobility is in the range of 0.1 to 10 cm$^2$V$^{-1}$s$^{-1}$, and bandgaps are about 3.5 eV. Major doping improvements are needed to improve the carrier concentration and also the mobility without a loss in optical transmission. Both n- and p-type TCs are listed in Table 2.

### Table 1. Transparent Conductors (Requirements)

- High optical transmission
- Low electrical resistivity
- Low surface roughness
- Thermal stability to withstand processing temperature
- Chemical stability
- Adhesion - Thermal coefficient match
- Crystallinity
- Hardness
- Cost

### Table 2. Transparent Conductors (Types)

<table>
<thead>
<tr>
<th>n-type</th>
<th>p-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO*</td>
<td>CuAlO$_2$ (CAO)</td>
</tr>
<tr>
<td>SnO$_2$: F, Cl, Sb* (TO)</td>
<td>CuInO$_2$ (CIO)</td>
</tr>
<tr>
<td>ZnO: Al, B, Ga, In*</td>
<td>Cu$_2$SrO$_4$ (CSO)</td>
</tr>
<tr>
<td>CdO: F</td>
<td>ZnO: N, Ga</td>
</tr>
<tr>
<td>Cd$_2$SnO$_4$ (CTO)</td>
<td>Cu$_2$SnO$_4$ (ZTO)</td>
</tr>
</tbody>
</table>
| In$_2$O$_3$ (IO) | * Commercial Products
| In$_2$O$_3$: Mo |

### II-VI THIN-FILM SOLAR CELLS

II-VI binary thin-film solar cell based on CdTe is one of the most promising thin-film solar cell. CdTe has an optimum bandgap of 1.45 eV, which is an excellent match for the solar spectrum. Also, its high absorption coefficient implies that a few microns of the absorber film are sufficient for cell fabrication. A typical thin-film CdTe solar cell structure is glass/SnO$_2$/CdS/CdTe/ contact and is shown in Fig. 1. Several back contacts investigated worldwide are reported elsewhere [3]. A world record total-area efficiency of 16.5% has been achieved by NREL scientists using a modified device structure of glass/CTO/ZTO/CdS/CdTe/graphite [4]. There are several advantages of this new structure as compared to the conventional device structure. The CTO has higher optical transmission, lower resistivity, and smoother surface roughness as depicted from AFM investigation.

Table 3 highlights the accelerated life testing (ALT) that is currently under way within the National CdTe R&D Team to address these issues. The several variables that have been investigated imply that a few microns of the absorber film are sufficient for cell fabrication. A typical thin-film CdTe solar cell structure is glass/SnO$_2$/CdS/CdTe/ contact and is shown in Fig. 1. Several back contacts investigated worldwide are reported elsewhere [3]. A world record total-area efficiency of 16.5% has been achieved by NREL scientists using a modified device structure of glass/CTO/ZTO/CdS/CdTe/graphite [4]. There are several advantages of this new structure as compared to the conventional device structure. The CTO has higher optical transmission, lower resistivity, and smoother surface roughness as depicted from AFM investigation.

One of the critical processing steps for high-efficiency devices is a CdCl$_2$ heat treatment, which may be either a wet chemical process or a dry vapor process. The current trend is to move toward a dry vapor process because it has better process control, and it eliminates the handling of wet chemicals in the laboratory environment. Fig. 2 is an AFM image of a CdTe film that depicts the significant grain growth after the vapor CdCl$_2$ heat treatment done at about 400°C for 15 - 20 minutes, which minimizes grain boundary defects for achieving high efficiency devices. Another important effect that is observed is the intermixing that takes place at the CdS/CdTe interface. The amount of sulphur in the solid solution varies from 2% to 12% depending on the deposition temperature of the absorber layer for cell fabrication [5]. A new O$_2$-alloyed CdS layer whose bandgap varies from 2.42 to 3.17 eV with the O$_2$ content has been developed by NREL scientists [6].

![AFM micrograph of before and after vapor CdCl$_2$ heat treatment.](image_url)
are illumination, temperature, ambient condition, bias, time, etching prior to depositing the back contacts, and CdCl₂ process details. More specifically, researchers are studying effects of micro-non-uniformity, capacitance-voltage measurements, chlorine issues stated above, back barrier height, defect chemistry, Cu movement in the device, the effect of O₂, and the role of S at the CdS/CdTe interface.

**Table 3. CdTe – Accelerated Life Testing**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illumination</td>
<td>0.5 Sun, 1 Sun, 2 Sun, Dark</td>
</tr>
<tr>
<td>Temperature</td>
<td>60, 70, 80, 90, 100, 110, 120°C</td>
</tr>
<tr>
<td>Ambient</td>
<td>Air, Ar, He, N₂, O₂</td>
</tr>
<tr>
<td>Bias</td>
<td>I_SC, V_OC, P_MAX, P_REV, F_FOR</td>
</tr>
<tr>
<td>Time</td>
<td>1 to 4000 hours</td>
</tr>
<tr>
<td>Etching</td>
<td>BM, BDH, NP, no etch</td>
</tr>
<tr>
<td>Measurements</td>
<td>I-V, Q-E, C-V, PL</td>
</tr>
<tr>
<td>Characterizations</td>
<td>AES, AFM, EDS, SEM, SIMS, XPS, XRD</td>
</tr>
</tbody>
</table>

I-III-VI THIN-FILM SOLAR CELLS

I-III-VI ternary thin-film solar cell based on CIS and related alloys and materials is another promising thin-film solar for both space and terrestrial applications. CIS is a direct-bandgap material and has a bandgap of about 0.9 eV. When Ga is introduced into the absorber layer, the bandgap increases to about 1.12 eV with a Ga content of less than 30% (Ga/Ga+In). A typical thin-film CIS based solar cell substrate structure is ZnO/CdS/CIS/Mo/glass and is shown in Fig. 3. A world-record total-area efficiency of 21.1% under 14X concentration and global AM1.5 spectrum has been achieved by NREL scientists [7]. When measured under AM1.5 direct spectrum, the efficiency increases to 21.5%.

**Fig. 3. Thin-film CIS solar cell structure.**

Under 1-sun condition, the total-area efficiency of thin-film CIGS solar cell is 18.8%. To enhance the efficiency to 20% under 1-sun condition, improvements need to be made to minimize defects in the CIGS absorber film. Fig. 4 is a TEM cross section showing dislocations near the CdS/CIGS interface that need to be eliminated or minimized by optimizing the deposition conditions. Additionally, the Institute of Energy Conversion at the University of Delaware, Newark, Delaware, has set a world-record, total-area efficiency of 16.9% for a thin-film CIAS solar cell, verified by NCPV/NREL. Here the Ga is replaced by the Al. The bandgap of this device is 1.15 eV. The Al/Al+In is less than 30%. The CIAS film is grown by the physical vapor deposition method [8].

**Fig. 4. TEM cross section of thin-film CIGS solar cell showing dislocations.**

One of the most active area of research is alternate buffer layers. A comprehensive list of buffer layers investigated by various groups worldwide is reported elsewhere [9]. The performance characteristics and process robust-ness of these devices using alternate buffer layers is not comparable to CBD CdS. The most compelling research issue related to CIS devices is the role of moisture and its impact on long term reliability. Moisture ingress appears to have a detrimental effect on device performance. Other areas of scientific research is the development of superstrate structure, development of wide-bandgap chalcopyrite absorber films, low-temperature processing of absorber film, in-line process diagnostics, and modeling. Alternate substrates such as stainless steel, polymers, and metal foils are also being investigated for fabricating lightweight, flexible CIGS devices for space applications. CdS/CIGS interface studies done by NREL researchers have shown that Cd diffuses into the CIGS absorber and may play a significant role in junction formation [10].

**TANDEM THIN FILM SOLAR CELLS**

The efficiency of single junction polycrystalline thin film solar cells efficiency has a practical laboratory limit of about 20% under 1-sun illumination. To move the technology forward in the next 5 to 10 years, tandem-junction solar cells are the logical choice for advancing the state-of-art efficiency to 25%, based on the scientific knowledge developed for single-junction devices. The theoretical limit for the conversion efficiency of tandem thin-film solar cells with two junctions is about 29%. Modeling work done by Fan of Kopin [11] and Kuwano of Sanyo in the early 1980s indicate that the ideal bandgaps for high-performance cells are 1.7 eV for the top cell and 1.1 eV for the bottom cell. A typical solar cell structure could be ITO/CdS/(CGS, CIAS, CIGSS, CdZnTe, CdSe)/p-ZnO/ITO/CdS/CIGS/Mo/glass for a two terminal device; it is shown in Fig. 5. Major challenge in developing this tandem-junction solar cell is the development of a top cell with a bandgap of 1.7 eV using low-temperature absorber
processing. Other challenge is to develop a transparent, heavily-doped, low-resistance tunnel junction connecting the top and bottom cells. Alternately, the growth of low carrier concentration and high-mobility TCs to minimize free-carrier absorption for tunnel junction formation is needed. The research is in the very early stages of development with much of the focus being on fabricating the top cell with a bandgap of 1.7 eV.

Fig. 5. Tandem thin-film solar cell structure.

TECHNOLOGY DEVELOPMENT

From a technology development standpoint, a number of groups worldwide are actively involved in developing thin-film rigid and flexible power modules for various applications. Three companies are currently in the early stages of CdTe product commercialization; Antec Solar (AS), Germany; BP Solar (BPS), USA; and First Solar (FS), USA. The major players for thin-film CIS-based module development are Energy Photovoltaics, USA; Global Solar Energy, (GSE), USA; Honda Engineering, Japan; Shell Solar Industries (SSI), USA; and Wurth Solar, Germany. Table 4 summarizes the champion thin-film CdTe and CIS modules fabricated by several industrial group worldwide.

Table 4. Polycrystalline Thin Film Photovoltaic Modules

<table>
<thead>
<tr>
<th>Organization</th>
<th>Material</th>
<th>Area (cm²)</th>
<th>EFF (%)</th>
<th>Power (W)</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP Solar</td>
<td>CdTe</td>
<td>6360</td>
<td>11.0%</td>
<td>92.5%</td>
<td>06/01</td>
</tr>
<tr>
<td>Wurth Solar</td>
<td>CIS</td>
<td>6623</td>
<td>10.4%</td>
<td>68.9%</td>
<td>11/01</td>
</tr>
<tr>
<td>First Solar</td>
<td>CdTe</td>
<td>6612</td>
<td>10.1%</td>
<td>67.1%</td>
<td>12/01</td>
</tr>
<tr>
<td>Matsuishi Battery</td>
<td>CdTe</td>
<td>5413</td>
<td>11.0%</td>
<td>59.0%</td>
<td>05/00</td>
</tr>
<tr>
<td>Global Solar</td>
<td>CIS</td>
<td>7714</td>
<td>7.4%</td>
<td>57.3%</td>
<td>01/03</td>
</tr>
<tr>
<td>Antec Solar</td>
<td>CdTe</td>
<td>6633</td>
<td>7.0</td>
<td>46.7%</td>
<td>11/01</td>
</tr>
<tr>
<td>Shell Solar</td>
<td>CIS</td>
<td>3651</td>
<td>12.1%</td>
<td>44.3%</td>
<td>03/99</td>
</tr>
<tr>
<td>Energy PV</td>
<td>CIS</td>
<td>3518</td>
<td>6.2%</td>
<td>19.7%</td>
<td>04/97</td>
</tr>
</tbody>
</table>

Table 5. Lessons Learned

The highest power output for any thin-film monolithic module is 92.5 W with an aperture-area efficiency of 11.0% for an Apollo thin-film CdTe module made by BPS using the electrodeposition technique [12]. FS has fabricated a 10.1% efficient thin-film CdTe power module using the vapor transport deposition method [13]. The highest efficiency of any thin-film module is a 12.1% efficient CIGSS module fabricated by SSI using the two stage process of depositing the precursors -Cu, In, Ga by sputtering (Fig. 6) followed by the selenization process [14].

The highest efficiency for a flexible, lightweight, thin-film CIGS module is 7.4% with a power output of 57.3 W made by GSE uses the PVD technique [15] for absorber formation; it is shown in Fig. 7. The manufacturing cost of thin-film module fabrication is reported elsewhere [16].
Also, we report temperature differential in going from room temperature to low and medium temperatures and finally to high-temperature regimes for depositing the absorber films. Other lessons learned are monolithic integration using laser and mechanical scribes, the sputter drift of targets, machine process drift due to residual coatings, control of external dopants, film adhesion, encapsulation/packaging of modules to prevent corrosion and moisture ingress, and last but not least the important issue of ES&H in a large scale manufacturing environment.

APPLICATIONS

A number of thin-film PV arrays based on CdTe and CIS modules which are either rigid or flexible are being tested worldwide. The PV systems are either stand-alone or grid-connected. The system sizes vary from 10 to 250 kW. Fig. 8 show a rooftop, grid-connected 10-kW thin-film CdTe PV array installed on the WAPA building in Folsom, CA. A 40.8-kW thin-film CIGSS PV array has been installed in Salzburg, Austria and is shown in Fig. 9. Flexible, lightweight, thin-film CIGS arrays have been deployed on tents (Fig. 10) and are used by the U.S. Army and Marines. Two solar fields using “experimental” thin-film CdTe module, whose system sizes are 175 kW and 250 kW, respectively, have been deployed in Springerville, Arizona, and Dublin, California.

SUMMARY

Major technical advances have occurred in the field of polycrystalline thin film compounds such as CdTe and CIS that have propelled photovoltaic research, development, and technology deployment. A world record total-area efficiency of 16.5% has been achieved for a thin-film CdTe solar cell using a modified device structure of CTO/ZTO/CdS/CdTe/graphite by NREL scientists. Researchers at NREL have also set a world record for a thin-film CIGS solar cell with a total-area efficiency of 21.1% under 14X concentration and AM1.5 global spectrum. When measured under AM1.5 direct spectrum, the total-area efficiency increases to 21.5%. The absorber film was grown using the three-stage process and the PVD technique. A key CdTe-related stability issue is being rigorously investigated using the ALT to understand the mechanisms and modes that causes changes in the device performance under various stress conditions. Several buffer layers to potentially replace the CBD CdS in thin-film CIS solar cells have been highlighted. The role of moisture on thin-film CIS-based devices has been addressed. World-record power output of 92.5 W and aperture-area conversion efficiency of 11.0% has been achieved by BPS for a thin-film CdTe power module. For a thin-film CIS power module, SSI demonstrated an aperture-area conversion efficiency of 12.1%. For flexible, lightweight, thin-film CIGS module, an aperture-area conversion efficiency of 7.4% and power output of 57.3 W has been fabricated by GSE. Many companies worldwide are actively involved in building manufacturing capacity for both CdTe and CIS module fabrication. Several thin-film grid-connected PV arrays in the range of 10 to 40.8 kW have been installed and are being tested. Two thin-film CdTe solar fields using “experimental” modules, whose system sizes are 175 and 250 kW, respectively, are being tested in Springerville, Arizona, and Dublin, California.

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REFERENCES


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**Subject Terms:** PV; II-VI binary; thin-film solar cells; cadmium telluride (CdTe); I-III-VI ternary thin-film; copper indium diselenide (CIS); device fabrication; power modules;