Prospects and Limitations in Thin Film Photovoltaic Technology R&D

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Deepest condolences to those who lost nears and dears due to COVID-19. Sincerest empathy to those who are still fighting to recover from COVID-19 and gratitude to all super heroes working round the clock around the world.

From Universiti Tenaga Nasional (UNITEN), Malaysia
Acknowledgement

- Thin Film Solar PV R&D Group of Universiti Tenaga Nasional (@The Energy University) of Malaysia.
- Solar Energy Research Institute of Universiti Kebangsaan Malaysia (@The National University of Malaysia).
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- All the useful literatures that are being referenced from various sources/journals/proceedings.

We are Committed for a Solar-Green-Earth
Our Collaborative Effort on Solar Photovoltaic Technology
Our Effort in High Impact Research on Energy

5 Research Institutes

- Institute of Power Engineering (IPE)
  - Transmission and distribution technologies
  - Power generation

- Institute of Sustainable Energy (ISE)
  - Solar energy
  - Wind technology
  - Energy based on biofuel

- Institute of Energy Policy & Research (IEPRe)
  - Energy economy
  - Regulatory policy
  - Social transformation

- Institute of Energy Infrastructure (IEI)
  - Geospatial intelligence
  - Energy water security
  - Disaster risk reduction

- Institute of Informatics & Computing in Energy (IICE)
  - Data analytics
  - Visual informatics
  - Energy security

Key Outcomes

- Increased publications
- Increased research grants / consultancy revenues secured
- Increased principal researchers
- Increased postgraduate students / postdoctoral researchers

Partnerships with:
- University of Strathclyde, Glasgow
- Imperial College, London
- MIT, Massachusetts Institute of Technology
- Deakin University, Australia
- Tokyo University, Japan
- The University of Queensland, Australia
- Kings College, London
- Dublin City University
- McMaster University, Canada
Institute of Sustainable Energy (ISE) @ UNITEN

- BIOFUEL
- SOLAR
- WIND
- HRES
- SUSTAINABILITY
OUTLINE

► Introduction
► Thin Film & Thin Film Deposition
► Solar Cells
► Implication of Thin Films into Solar Cells
  ► aSi
  ► CdTe
  ► CIS (CIGSSe, CZTS, CTS)
► Challenges and prospects
► Conclusion
A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications.

Thin film technology is a "self organizing" structural evolution. Ex: In ancient times, people already knew how to beat gold into a thin film (<1 μm thickness) with hammers and knew how use this "gold leaf" for coating all kinds of stuff.

Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media, electronic semiconductor devices, LEDs, optical coatings (such as antireflective coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin-film solar cells) and storage (thin-film batteries).

Applications:
Decorative coatings, Optical coatings, Protective coatings, Electrically operating coatings, Thin-film photovoltaic cells, Thin-film batteries
The act of applying a thin film to a surface is *thin-film deposition* - any technique for depositing a thin film of material onto a *substrate* or onto previously deposited layers.

"Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of *nanometres*. *Molecular beam epitaxy*, *Langmuir-Blodgett method*, *atomic layer deposition* and *molecular layer deposition* allow a single layer of *atoms* or molecules to be deposited at a time.

Thin film technology involves deposition of individual molecules or *atoms*. 
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Solar Cells

Solar cells operate by converting sunlight directly into electricity using the electronic properties of a class of material known as semiconductors and can be configured in many options like flexible, semi-transparent etc., besides rigid ones.
Solar Cell Development

First photovoltaic structure that converted light to electricity with reasonable efficiency (6%)


“Vast Power is Tapped by Battery Using Sand Ingredient”

...may mark the beginning of a new era, leading eventually to the realization of one of mankind’s more cherished dream—the harnessing of the almost limitless energy of the sun for the uses of civilisation”.

Vast Power of the Sun Is Tapped By Battery Using Sand Ingredient

MURRAY HILL, N. J. April 26—A solar battery, the first of its kind, which converts useful amounts of the sun’s radiation directly and efficiently into electricity, has been constructed here by the Bell Telephone Laboratories.

The new device is a simple-looking apparatus made of strips of silicon, a principal ingredient of common sand. It may mark the beginning of a new era, leading eventually to the realization of one of mankind’s most cherished dreams—the harnessing of the almost limitless energy of the sun for the uses of civilisation.

With improved techniques the efficiency may be expected to be increased substantially, they added. They observed that nothing is consumed or destroyed in the energy conversion process and there are no moving parts, so the potential savings over present methods could be substantial.

Special to The New York Times.
Evolution of Solar Panel Size

- Purchased in 1992

- 460Wp possible nowadays
PV Scenario till 2018 (2019)

Global Cumulative PV Installation: **500 GW**

620 GWp (by end of 2019)

Source: IEA-PVPS 2019 Snapshot of Global PV markets, April 2019

Source: International Renewable Energy Agency (IRENA), 2017
Photovoltaic (PV) Device/Cell

Solar cell is a semiconductor device (large area p-n junction) that converts sunlight directly into electricity.

Photovoltaic Conversion Efficiency (PCE %) = \( \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{I_{\text{sc}} \cdot V_{\text{oc}} \cdot FF}{P_{\text{in}}} \times 100\% \)

Basic Principle of Solar Cell Operation

EHP Generation and Carrier Transport in p-n Junction

Solar Cell I-V Curve Under Illumination
Solar Cell Essentials

- **Material** (Inorganic/Organic, Bulk/Thin Film/Dye)
- **Fabrication Process** (Physical/Chemical)
- **Structure** (Homo/Hetero/MIS/Schottky/Photo-electrochemical)
- **Economics**
What is essential for an ideal Solar Cell?

1. Cheap, Simple and Abundant Material
2. Integrated Large Scale Manufacturability
3. Cost, Long Durability as well as recyclability

- HIGH ABSORPTION COEFFICIENT > $10^5$ /cm with direct band gap ~1.5 eV
- JUNCTION FORMATION ABILITY
- HIGH QUANTUM EFFICIENCY
- LONG DIFFUSION LENGTH
- LOW RECOMBINATION VELOCITY
- ABUNDANT, CHEAP & ECO-FRIENDLY MATERIAL

- CONVENIENCE OF SHAPES AND SIZES
- SIMPLE AND INEXPENSIVE INTEGRATED PROCESSING/MANUFACTURABILITY
- MINIMUM MATERIAL / WATT
- MINIMUM ENERGY INPUT/WATT
- ENERGY PAY BACK PERIOD < 2 YEARS
- HIGH STABILITLY and LONG LIFE (> 20 Years)
- COST (< 1$/Watt or lower)
Abundance Chart (Elements)
Prospects of PV Materials

Spectral Response Characteristics of Solar Module

- GaAs
- c-Si
- CIS
- CdTe
- a-Si

Relative Spectral Response vs. Irradiance (W/m²)

Wavelength (nm)
Solar Cell Technologies

First Generation:
Crystalline silicon solar cell (200-500 micron)

Second Generation:
Thin film solar cell (1-10 micron)

Third Generation:
DSSC, Organic, Perovskite, Multijunction, Futuristic

Crystalline Silicon cells
- Mono-crystalline cells: Efficiency: 18%~25.6%
- Multi-crystalline cells: Efficiency: 17%~20.8%

Thin film PV
- CdTe cells: Efficiency: 18.3%~22.1%
- Amorphous silicon cells: Efficiency: 13.4%
- CIGS cells: Efficiency: 20.4%~22.6%

Perovskite cells
- Planar Structure
  - HTM
  - Perovskite
  - blocking layer
  - $\eta = 15.4\%$

Novel Hybrid
- Efficiency: 40%

Solar PV Applications
Controllers, Systems
About 1% Material of c-Si

Courtesy: Lawrence L. Kazmerski, NREL
Latest Chart Of Best Research-Cell Efficiencies (Up-to-date With The New World Record)

Source: NREL

Best measured cell efficiencies:
- 47.1% concentrator (6J, 143-sun)
- 26.7% crystalline silicon
- 23.4% thin films
- Perovskite 24.2%
- 11.9% dye cells
- 16.4% organic PV

Commercial modules
Typically only 50-80% of the these values

Bridging between Theoretical possibilities and empirical process optimization with better understanding on limits could lead to ultimate success

Future Prediction of Various Solar Cells Efficiency

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Thin Film PV

- THIN FILM SOLAR CELLS: 1-10 μm vs. Si 100-200 μm due to a higher optical absorption coefficient
- The thin film solar cells such as CdTe, a-Si and CIGS have greater advantages of significantly lower production cost over crystalline-silicon based cells
- Thinning will save material (About 1% Material of c-Si), lower production time and energy: all these factors will eventually decrease the cost and make it more popular

Key Issues:
- Long term stability (must be proven)
- Manufacturability (no off-the-shelf equipment)
- Performance (bridge gap between cells and modules)
  - Contacts
  - Buffers
  - Absorber
Thin Film

Thin film solar panels are made by placing thin layers of semiconductor material onto various surfaces, usually on glass. The term thin film refers to the amount of semiconductor material used. It is applied in a thin film to a surface structure, such as a sheet of glass. Contrary to popular belief, most thin film panels are not flexible. Overall, thin film solar panels offer the lowest manufacturing costs, and are becoming more prevalent in the industry.

There are three main types of thin film used:

- **Amorphous Silicon**

  Amorphous silicon is the non-crystalline form of silicon and was the first thin film material to yield a commercial product, first used in consumer items such as calculators. It can be deposited in thin layers onto a variety of surfaces and offers lower costs than traditional crystalline silicon, though it is less efficient at converting sunlight into electricity.

- **Cadmium Telluride (CdTe)**

  CdTe is a semiconductor compound formed from cadmium and tellurium. CdTe solar panels are manufactured on glass. They are the most common type of thin film solar panel on the market and the most cost-effective to manufacture. CdTe panels perform significantly better in high temperatures and in low-light conditions.

- **Copper, Indium, Gallium, Selenide (CIGS)**

  CIGS is a compound semiconductor that can be deposited onto many different materials. CIGS has only recently become available for small commercial applications, and is considered a developing PV technology.
Solar Cell Technologies

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Crystalline silicon solar cell (200-500 micron)

**Second Generation:**
Thin film solar cell (1-10 micron)

**Third Generation:**
DSSC, Organic, Perovskite, Multijunction, Futuristic

**Thin Film PV Research Focuses**

- **Crystalline Silicon cells**
  - Mono-crystalline cells
    - Efficiency: 18%~25.6%
  - Multi-crystalline cells
    - Efficiency: 17%~20.8%

- **Thin film PV**
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- **Perovskite cells**
  - Planar Structure
    - $\eta = 15.4\%$

- **Novel Hybrid**
  - Efficiency: 40%

Solar PV Applications
- Controllers, Systems

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**Solar PV Applications**

- Controllers, Systems

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**Thin Film PV Research Focuses**
Thin-Film PV Technologies

- Low materials use (~1 μm vs. ~300 μm for Si) – direct bandgap absorbers
- Low-cost substrates (glass, stainless steel, plastics)
- High-throughput deposition processes (batch or continuous)
- Lower processing temperatures (less energy use); some non-vacuum
- Fewer processing steps for modules; integral interconnection of cells during film deposition

In-line Manufacturing of Thin-Film CdTe Photovoltaic Modules

- Leading technologies:
  - Amorphous silicon (a-Si:H)
  - Cadmium telluride
  - Copper indium gallium diselenide (CIGS)
- Future technologies:
  - Thin (polycrystalline) silicon
  - Polycrystalline multijunctions

Choice of materials dictated by efficiency, materials availability, ease of manufacturing, module reliability, market acceptance
Thin Film PV R&D
Thin Film Photovoltaic Laboratory

Prof. Dr. Nowshad Amin
Prof. Makoto Konagai,
Tokyo Institute of Technology, Japan
Thin Film PV Fabrication Facility

- Annealing Chamber
- Ultrasonic Bath Sonicator
- Spin Coater
- Fumehood
- Thermal Evaporator
- Co-evaporation (MBE)
- Sputtering
- CBD Water Bath
- Deionized (DI) Water System
Thin Film PV Characterization

- Optical Spectrometer
- Hall Measurement System
- Integrated LIV with Class AAA Solar Simulator
- Surface Profilometer
- Integrated Semiconductor-PV Defect Measurement System
- Quantum Efficiency Measurement System
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Crystalline silicon solar cell (200-500 micron)

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**Second Generation:**
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**Third Generation:**
DSSC, Organic, Perovskite, Multijunction, Futuristic

**Perovskite cells**
- Planar Structure
  - HTM
  - Perovskite
  - Blocking layer

**Novel Hybrid**
- Efficiency: 40%

**Solar PV Applications**
Controllers, Systems

**Thin Film PV Research Focus:** a-Si
Why Amorphous Silicon as a PV Material?

- Amorphous Silicon has a very high absorption coefficient ($>10^5 \text{ cm}^{-1}$) over the major portion of the visible spectrum, making extremely thin film (100 – 500 nm) devices possible, leading to low material cost.
- Low temperature deposition process can be used to uniformly coat extremely large areas ($5.7 \text{ m}^2$).
- The deposition technique and by-products of the technique are environmentally benign making it a truly green manufacturing process.
- The optical Bandgap of 1.7 eV lies close to the peak (1.5 eV) where high efficiencies are expected.
- Monolithic integration of individual cells is simple and done by selective laser ablation – allows for module voltage optimization.
- Silicon and Hydrogen are abundant.
- The material can be doped p or n type (although not very efficiently) with boron or phosphorous respectively.
- The material possesses the necessary electron and hole transport properties for p-i-n type solar cells.

![Graph showing absorption coefficient of Si in different crystalline states](image)
Single, Tandem & Triple Junction Si Solar Cells

- **Single junction cell**
  - Module eff. 5-7%

- **Tandem cell**
  - Module eff. 7-10%

- **Triple cell**
  - Module eff. > 12%
Triple Junction a-Si:H/SiGe:H/nc-Si:H Solar Cells

Initial efficiency: 15.1%; Stable efficiency: 13.3%

Fabrication of a-Si:H Solar Cell (1J)

- PECVD is the best technique for a-Si:H Solar Cells

<table>
<thead>
<tr>
<th>Layer</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>Asahi Type-U, ~10 Ω/□</td>
</tr>
<tr>
<td>SnO₂:F</td>
<td>RF-PECVD, 18 nm, ~2.0 eV</td>
</tr>
<tr>
<td>p-a-Si:C:H</td>
<td>RF-PECVD, 2 nm</td>
</tr>
<tr>
<td>p-graded-buffer</td>
<td>VHF-PECVD, 500 nm</td>
</tr>
<tr>
<td>i-a-Si:H</td>
<td>1.75 eV</td>
</tr>
<tr>
<td>n-a-Si:H</td>
<td>RF-PECVD, 20 nm</td>
</tr>
<tr>
<td></td>
<td>~1.7 eV</td>
</tr>
<tr>
<td>ZnO:B</td>
<td>MOCVD, 70 nm</td>
</tr>
<tr>
<td>Ag</td>
<td>Evaporator, 60 nm</td>
</tr>
<tr>
<td>Al</td>
<td>Evaporator, 200 nm</td>
</tr>
</tbody>
</table>

Three chamber in-line PECVD system

Schematic diagram of PECVD with Load-lock and gas flow system

Substrates fixed in substrate holder

Plasma plume in PECVD chamber

PECVD is the best technique for a-Si:H Solar Cells
IV Characteristics & Quantum Efficiency

Photo and dark I–V characteristics of the $p$-$i$-$n$ solar cell

Quantum efficiency curve with wavelength in the range of 300-800 nm
## HIT Cells (Passivation Effect)

### Layer Configuration

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>280 um - p-Si (double-side-polished) (1–5 Ω.cm)</td>
<td>20 nm</td>
<td>n°-μc-Si:H</td>
</tr>
<tr>
<td>20 nm - p°-μc-SiOx:H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60-70 nm – ITO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500-700 nm – Ag/Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70nm - ITO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 nm - n°-μc-Si:H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-6 nm - a-SiOx:H</td>
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</table>
Minority Carrier Lifetime ($\tau$) was measured by quasi steady-state photo conductance (QSSPC).
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Thin Film PV Research Focus: CdTe
Advantages of CdTe Thin Film Solar Cells

- Bandgap 1.45 eV is almost optimum for PV
- The energy gap is ‘direct’- strong light absorption
  - CdTe has a high absorption coefficient \( >5 \times 10^5 \text{cm}^{-1} \)
- Simple and variety of low cost deposition techniques
- Polycrystalline materials and glass, cheaper...
- PV modules seal the cadmium, encapsulate and can be recycled
  - Thus safe, Cd is only 3.27 g/m² of PV

The total house weight is 60 tons as a value assuming a lightweight steel frame structure, two stories, and a floor area of 85 sq.m.
First CdTe-based Heterojunction Solar Cells was Reported on “thin film” CdTe heterojunctions, n-CdTe/p-CuTe as early as 1963 by …


CdTe Based Solar Cells

- **CdTe Single Junction Solar Cells**
  - 1960, Vodakov et al, Single crystalline CdTe wafer, Eff. 4%

- **Cu$_{2-x}$Te/CdTe Solar Cells**
  - 1963, Cusano et al, n-CdS/CdTe/p-Cu$_{2-x}$Te, Eff. 6%

- **CdS/single crystal CdTe Solar Cells**
  - 1969, Adirovich et al, SnO$_2$/CdS/CdTe, Eff. 1%
  - 1977, Yamaguchi et al, p-CdTe/n-CdTe/n-CdS, Eff. 11.7%
  - 1982, Barbe et al, n-CdTe/p-CdTe, Eff. 10.7%
Historical Background of CdTe (Deposition Process)

Thin Film CdS/CdTe Solar Cells

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Year</th>
<th>Authors</th>
<th>Composition</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen Printing</td>
<td>1984</td>
<td>Matsumoto et al</td>
<td>CdS/CdTe/C:Cu/Ag</td>
<td>12.8%</td>
</tr>
<tr>
<td>Electro-deposition</td>
<td>1991</td>
<td>Woodcock et al</td>
<td>CdS/CdTe</td>
<td>14.2%</td>
</tr>
<tr>
<td>Close-Spaced Sublimation (CSS)*</td>
<td>1982</td>
<td>Tyan et al</td>
<td>ITO/CdS/CdTe</td>
<td>10.5%</td>
</tr>
<tr>
<td></td>
<td>1992</td>
<td>Chu et al</td>
<td>SnO₂/CdS/CdTe/C:Cu</td>
<td>15.8%</td>
</tr>
<tr>
<td></td>
<td>1997</td>
<td>Aramoto et al</td>
<td>ITO/CdS/CdTe/C:Cu/Ag</td>
<td>16%</td>
</tr>
<tr>
<td>Magnetron Sputtering + CBD + CSS</td>
<td>2004</td>
<td>Wu et al</td>
<td>Cd₂SnO₄/Zn₂SnO₄/CdS/CdTe/Cu</td>
<td>16.5%</td>
</tr>
<tr>
<td>CSS Process</td>
<td>2005</td>
<td>Gupta et al</td>
<td>CdS/CdTe</td>
<td>11.8%</td>
</tr>
<tr>
<td>Undisclosed Process</td>
<td>2016</td>
<td>First Solar, USA</td>
<td>Eff. 22.1%</td>
<td></td>
</tr>
<tr>
<td>Undisclosed Process</td>
<td>2014</td>
<td>First Solar, USA</td>
<td>Eff. 21%</td>
<td></td>
</tr>
</tbody>
</table>
Glass: Borosilicate, soda lime. Inexpensive, good optical properties, compatible with deposition process (T).

TCO/Buffers: SnO$_2$, ITO, Cd$_2$SnO$_4$, ZnO, ZTO, In$_2$O$_3$ etc. Good electro-optical properties; compatible with subsequent processing steps; “buffers” important for thin CdS

CdS: $E_g = 2.42$ eV (510 nm); ~7 mA/cm$^2$ below 510 nm. Must be thin (600Å) and pinhole free. CdS:O used for record efficiencies

CdTe: versatility in deposition technology; thickness 3-8 µm; thickness why not ~2 µm? Can it be doped controllably?

Heat Treatment: “activation” process; improves bulk and interface properties; carried out in the presence of CdCl$_2$.

Back Contact: Various options most of which utilize Copper; doped graphite paste, ZnTe:Cu, etc. Stability? Cu-free Sb$_2$Te$_3$

Source: McCandless et al. 2004
Deposition Options and CSS

Source: McCandless et al. 2004
Temperature Profile of the CSS Growth Technique

Example: 3min 26sec  1min  1min
SEM Image of the CdS/CdTe Solar Cell Cross Section

3 µm
I-V Characteristics & Spectral Response of CdTe Thin Film Solar Cells

CdTe Thickness: 7 µm

I-V Characteristics

Area: 1 cm²
Voc: 0.81 [V]
Jsc: 26.3 [mA/cm²]
FF: 0.72
Eff: 15.3 [%]

Spectral Response
Spectral Response of the CdTe Solar Cell (The Effect of CdS Window Layer Thickness)

Quantum Efficiency [arb. Units]

Reflectance [%]

Wavelength [nm]

CdTe: 5 µm

CdTe: 1 µm

Cds: 55 nm
Cds: 60 nm
Cds: 65 nm
Cds: 75 nm
Cds: 90 nm
Research Prospects in CdTe Thin Film PV

CdTe Absorption Coefficient: $2 \times 10^4 \text{ cm}^{-1}$

Over 90% of Incident Spectrum Absorbed in 1 µm-CdTe layer

Insertion of Buffer Layer

CdTe Thickness Reduction to 1 µm

Back Surface Field Insertion

Vacuum Level

Electron Flow

Light Window/Buffer

Diffraction Light Absorption Layer

Ag

TCO

Window

CdS

CdTe

Ag

Recombination States

Back Contact

VB

CB

EF

Vacuum Level

Electron Flow

1.44eV

2.26eV

2.41eV

CdS

CdTe

ZnTe

Lig ht
SEM Images of the CdTe Surface with Different Thickness (Grown by CSS)

CdTe: 1 µm

CdTe: 2 µm

CdTe: 6 µm

2 µm

2 µm

3 µm
I-V Characteristics of 1 um-CdTe Thin Film Solar Cell

- CdTe Thickness: 1 µm
- $V_{oc} = 0.77$ [V]
- $J_{sc} = 23.11$ [mA/cm$^2$]
- F.F. = 0.63
- Eff. = 11.2 [%]

Active Area = 1.00 [cm$^2$]
AM-1.5, 100 mW/cm$^2$
Textured Tin Oxide (SnO$_2$:F) for Ultra-Thin CdTe

Dependence of Solar Cell Characteristics on CdTe Thickness

![Diagram]

Transmission [%]

Wavelength [nm]

CdTe: 0.6 µm

SnO$_2$:F (haze 37%)
SnO$_2$:F (haze 11%)
SnO$_2$:F (haze 3%)
ITO

Glass
TCO
Window
Ag
CdTe
BSF
Ag

![Diagram]

Voc [V]

Jsc [mA/cm$^2$]

FF

Eff [%]

CdTe Thickness [µm]
Continuous Fabrication Process

- Substrate Preparation
- Magnetron Sputtering Chamber Preparation
- Target Installation
- Operation of Sputtering Growth
- ZnO, CdS and CdTe deposition by RF Sputtering
- Back contact Deposition by DC Sputtering
Improving Performance: $J_{SC}$

- Most promising avenue to higher $J_{SC}$’s is via “thinner” CdS
- Approximately 7 mA below 510 nm (max. 30 mA/cm$^2$)

**Choice of Window material for CdTe solar cell is limited by several considerations:**

1. The heterojunction should be designed so that most of the absorption occurs within the CdTe bulk.
2. It must act as a highly transparent, and low-resistance window layer and not be responsible for carrier generation.
3. It should have wide band gap
4. It should have a small lattice mismatch with CdTe to avoid excessive interface recombination.
5. It should have long-term stability,
6. Finally, window material should be composed of elements that are slow to diffuse into CdTe.
Too thin CdS will lead to voids and shunt related losses - $J_{sc}$ may increase but FF will decrease.

In severe cases where voids lead to TCO/CdTe interface regions, $V_{OC}$ is also decreased.
Effect of Substrate Temperature

**Effect of source and substrate temperature**

i) Vary the source and substrate temperatures with constant temperature difference.

ii) Vary the substrate temperature, keeping the source temperature constant.

T_{substrate}: 550 - 620°C,
T_{source}: 560 - 700°C,
Ar Pressure: 1.8 - 2 Torr,
ΔT= 150, 100, 70, 75, 55, 25
Spacing: 1-2 mm,
Deposition rate: 500 nm/min

[15] Growth and characterization of CdTe by close spaced sublimation on metal substrates A. Seth!, G.B. Lush!, J.C. McClure!,*, V.P. Singh*, D. Flood#
Grain growth

As-deposited

CdCl₂ treated

Low temp deposition

High temp deposition
CdTe Layer Deposition at Different RF power

Values of the electrical parameters of as-deposited & CdCl₂ treated CdTe thin films

<table>
<thead>
<tr>
<th>RF-power (watt/cm²)</th>
<th>Resistivity x 10⁴ (Ω-cm)</th>
<th>Carrier concentration x 10¹³ cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>3.41</td>
<td>1.45</td>
</tr>
<tr>
<td>1.5</td>
<td>1.51</td>
<td>4.52</td>
</tr>
<tr>
<td>2.0</td>
<td>9.19</td>
<td>0.12</td>
</tr>
<tr>
<td>2.5</td>
<td>1.06</td>
<td>0.78</td>
</tr>
<tr>
<td>3.0</td>
<td>2.21</td>
<td>0.49</td>
</tr>
<tr>
<td>CdCl₂ treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>2.68</td>
<td>2.24</td>
</tr>
<tr>
<td>1.5</td>
<td>4.43</td>
<td>10.43</td>
</tr>
<tr>
<td>2.0</td>
<td>1.24</td>
<td>13.45</td>
</tr>
<tr>
<td>2.5</td>
<td>1.59</td>
<td>7.30</td>
</tr>
<tr>
<td>3.0</td>
<td>1.61</td>
<td>68.69</td>
</tr>
</tbody>
</table>

SEM images of CdTe thin films
CdCl₂ Treatment on CdS:O/CdTe Stacks

Schematic illustration of the CdCl₂ heat treatment in steps. (a) Glass/CdTe stack immersion in 0.3 M CdCl₂ solution for 10 sec, (b) SEM morphology of naturally dried sample (c) thermal annealing process with the temperature profile (samples annealed for 15 min. at 390 °C in vacuum with 66.66 Pa of N₂/O₂ pressure) and, (d) SEM morphology of the cleaned (by warm water) sample
J-V curves (left) of the fabricated CdTe solar cell with respect to the growth rate in Sputtering; External quantum efficiency (EQE) (right) of the solar cells (decrease of QE from 600 nm to 800 nm indicates the increase of carrier recombination at the bulk of CdTe)
Achievement in Novel Approach for CdTe Solar Cells

Table: Solar cell performance with FTO/ZnO:Sn/CdS:O/CdTe/Cu:C/Ag configuration

<table>
<thead>
<tr>
<th>RF power (CdTe)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
<th>Cell area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 watt/cm²</td>
<td>0.56</td>
<td>18.58</td>
<td>59</td>
<td>6.14</td>
<td>0.25</td>
</tr>
<tr>
<td>2.0 watt/cm²</td>
<td>0.72</td>
<td>20.11</td>
<td>65</td>
<td>9.41</td>
<td></td>
</tr>
<tr>
<td>2.5 watt/cm²</td>
<td>0.68</td>
<td>21.89</td>
<td>62</td>
<td>9.23</td>
<td></td>
</tr>
<tr>
<td>3.0 watt/cm²</td>
<td>0.67</td>
<td>22.55</td>
<td>68</td>
<td>10.27</td>
<td></td>
</tr>
</tbody>
</table>

Cross sectional image & J-V curves of the ZnO:Sn/CdS:O/CdTe/Cu:C/Ag solar cells
Back contact of CdTe

- Forming back contact to CdTe is problematic owing to the high electron affinity $\chi_S = 4.5\text{eV}$.

- For Ohmic contact require a work function of $> 6\text{eV}$ - No such metal exists!

- May contact with high work function metals (e.g. Au $\sim 5.1\text{eV}$) but a barrier still exists.

\[ \phi_m \geq E_g + \chi \quad \text{Ohmic contact} \]
\[ \phi_m \leq E_g + \chi \quad \text{Rectifying contact} \]

Ohmic and rectifying metal/p-semiconductor contacts.
Pseudo-Ohmic Contact – A Potential Key to Success

CdTe absorption coefficient: $2 \times 10^4$ cm$^{-1}$; 1 µm-CdTe absorbs 90% of the incident spectrum.

- **Efficiency Improvement**

- **Reduction of Carrier Recombination Area.**
- **Enhancement of Optical Confinement.**
- **Reduction of Carrier Recombination at the Back Contact.**
I-V Characteristics of CdS/CdTe/ ZnTe Solar Cell

Voc: 0.74 [V]  
Jsc: 22.98 [mA/cm²]  
FF: 0.49  
Eff: 8.31 [%]  

Voc: 0.71 [V]  
Jsc: 18.94 [mA/cm²]  
FF: 0.43  
Eff: 5.76 [%]  

Active Area: 0.5 cm²  
AM 1.5, 100 mW/cm²  

Corning 1737  
ITO  
Ag  
1 µm  
0.2 µm  
CdS  
CdTe  
ZnTe  
Carbon  
Ag  

N₂ doped  
undoped
I-V Characteristics of CdTe/ Cd_{0.5}Zn_{0.5}Te Thin Film Solar Cell

Corning 1737
ITO
CdS
CdTe
Cd_{0.5}Zn_{0.5}Te
Au

Area: 0.086 cm²
Voc: 0.68 [V]
Jsc: 22.60 [mA/cm²]
FF: 0.49
Eff: 7.46 [%]
Ag & Na Doping Effect in CdTe Thin Film Solar Cells

- $V_{bi}$ is correlated to device performance ↔ $V_{oc}$
- Increase of acceptor concentration, $N_A$ will shift Fermi to near $E_v$ and shift up the $E_c$ higher $V_{bi}$ ↔ $V_{oc}$.

Doping (Ag, Na, Cu) + Back Contact + Anneal

Mask + Etch + remove mask

Characterize

Copper (II) chloride ($CuCl_2$) and silver nitrate ($AgNO_3$) dip coating

Nd:YAG laser at wavelength of 532 nm

Experimental procedures:

- Characterize
- • $V_{bi}$ is correlated to device performance ↔ $V_{oc}$
- • Increase of acceptor concentration, $N_A$ will shift Fermi to near $E_v$ and shift up the $E_c$ higher $V_{bi}$ ↔ $V_{oc}$.
Ag & Na Doping Effect in CdTe Thin Film Solar Cells
A lot of opportunity in Voc improvement.

Primary research of in Voc improvement:
- Interface optimization (back/front contact)
- Improve carrier lifetime – better CdTe film quality (grain size, grain boundary, defects, fabrication process, etc.)
- Understand of doping capability of CdTe and improve carrier concentration.

- Thinner CdTe Absorber layer
- Improvement of the back contact
- Insertion of bi-layer
- Optimizing process steps
- Low temperature deposition techniques
- Deposited layer quality improvement
- Annealing (CdCl₂) treatment optimization

2016 highest Eff 22.1%* record cell from First Solar

M. Gloeckler, I. Sankin, and Z. Zhao, "CdTe Solar Cells at the Threshold to 20% Efficiency", J. of Photovoltaics 3(4) 1389 - 1393 (2013)
First Solar
Kulim, Malaysia

- 6 Manufacturing Plants
- Over 4,000 Skilled Associates
- Over 3 Million Square Foot of Floor Space
- 2016 Total Annualized Capacity 2.5 GW
First Solar on CdTe Thin Film Solar PV

1. CdTe cell efficiency reaches > 22% and module performance > 18%
2. Largest Module is over 460 Wp to date
#9 Topaz Solar Farm, USA

The plant could power 160,000 average California homes and displaces 377,000 tons of carbon dioxide annually which is equivalent to 73,000 cars being removed.

Highlights:

- **Location:** California, USA
- **Capacity:** 550 MW
- **Area:** 24.6-square-kilometer
- **Year:** 2014
- **Cost:** $2.5 billion
- **Modules:** First Solar CdTe

2nd Generation CdTe Based
CdTe Field Performance

• Independent test by TÜV Rheinland Photovoltaic Testing Lab shows CdTe has better than c-Si and comparable or better performance to c-Si bifacial cells technology.

• Data collection – 1 year

• 3 different sites:
  • Tempe – hot climate, module temperature > 45 deg. C
  • Davis – Moderate climate, module temperature ~25 de. C.
  • Toronto – cold climate

OUTLINE

- Introduction
- Thin Film & Thin Film Deposition
- Solar Cells
- Implication of Thin Films into Solar Cells
  - aSi
  - CdTe
  - CIS (CIGSSe, CZTS, CTS)
- Challenges and prospects
- Conclusion
Thin Film PV Research Focus: CIGS, CZTS, CTS

Solar Cell Technologies

First Generation:
Crystalline silicon solar cell
(200-500 micron)

Second Generation:
Thin film solar cell
(1-10 micron)

Third Generation:
DSSC, Organic, Perovskite, Multijunction, Futuristic

Crystalline Silicon cells
- Mono-crystalline cells
  - Efficiency: 18%~25.6%
- Multi-crystalline cells
  - Efficiency: 17%~20.8%

CdTe cells
- Efficiency: 18.3%~22.1%

Amorphous silicon cells
- Efficiency: 13.4%

CIGS cells
- Efficiency: 20.4%~22.6%

Perovskite cells
- Planar Structure
  - HTM
  - Perovskite
  - Blocking layer
  - η = 15.4%

Efficiency: 40%

Thin film PV Applications
Controllers, Systems

Novel Hybrid

Solar PV Applications
Controllers, Systems
Brief History of CIGS Solar Cells

1839: Photovoltaic effect discovered by Becquerel

1950: 6% efficient silicon solar cell was fabricated in Bell Labs

1954: Photovoltaic effect was discovered in CdS/CuS₂ devices

1960: 14% efficient silicon solar cell was made

1974: First chalcopyrite solar cells with CuInSe₂ absorbers were made

1975: 12% efficient CdS/CuInSe₂ solar cell was made by scientists at Bell Labs

1980s: Corporations and research laboratories started developing CIGSe solar cells
Absorber

- **Cu(In,Ga)Se$_2$** is an alloy of CuInSe$_2$ and CuGaSe$_2$.
  - Classified under I-III-VI$_2$ group of semiconducting materials (direct bandgap).
  - Crystallizes in the tetragonal chalcopyrite structure **homogeneously**.
  - Cu-based chalcopyrites span a wide range of bandgap energies that cover most of the visible wavelength spectrum.

![Crystal structure of CuInSe$_2$](image1)

![Crystal structure of Cu(In,Ga)Se$_2$](image2)

![Bandgap energies (E$_g$) vs. lattice constant (a) of the Cu(In,Ga,Al)(S,Se)$_2$ alloy system](image3)

Advantages of CIGS Solar Cells

• Minimum use of materials

Advantages of CIGS Solar Cells

- Monolithic connected modules offer better stability than soldered or bonded PV modules
- Modules are more aesthetically pleasing too

Monolithic integrated (MLI) CIGS PV module

Advantages of CIGS Solar Cells

• Short energy payback time

CIGS modules require 60% less energy to produce than crystalline silicon panels.

LCoE (€ct/kWh) of power plants

Source: Fraunhofer ISE/ IPA Dec. 2013


Advantages of CIGS Solar Cells

- CIGS PV modules possess lower temperature coefficient than crystalline Si

- CIGS PV modules has higher tolerance for shading

Advantages of CIGS Solar Cells

- CIGS modules generate higher electricity (comparing with c-Si) in real world conditions (data from 4 different sites).

Successful Commercialization

<table>
<thead>
<tr>
<th><strong>Founded</strong></th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Headquarters</strong></td>
<td>Tokyo, Japan</td>
</tr>
<tr>
<td><strong>Technology</strong></td>
<td>Lead and Cadmium-free CIGS modules</td>
</tr>
<tr>
<td><strong>Employees</strong></td>
<td>~ 1,300</td>
</tr>
</tbody>
</table>
| **Product** | • R&D and Production of CIGS modules  
• Sale of Solar Power Systems  
• Development of Power Plant Projects  
• Power Generation and Management |
| **Investment** | JPY 113 B |
| **Capacity** | 1050 MW per annum |

Highly automated production process
Solar Frontier (now IDEMITSU Kosan) on CIGS PV
Current Status of CIGS PV

Highest recorded efficiency for CIGS PV device to date:

- **Cell**: 22.6%
  - Reported by ZSW.
  - Size 0.5 cm².

- **Mini-module**: 19.8%
  - Reported by Solar Frontier (now IDEMITSU KOSAN).
  - Size 7.5 cm × 5 cm.

- **Module**: 19.2%
  - Produced by Solar Frontier (now IDEMITSU KOSAN).
  - Size: 30 cm × 30 cm.

---

CIGS solar cells with intentional surface treatment with K-sources, coupled with the unintentional Na diffusion from the glass substrate, have consistently shown an improved open-circuit voltage ($V_{OC}$) and fill factor (FF).

Researchers compared the device characteristics of their previous world record holding solar cell of 20.9% efficiency with their, at the time, record breaking cell of 22.3%.

Also tested was a solar cell with Cd-free buffer.

Cell area: 0.5 cm$^2$

K-treatment was found to enhance $V_{OC}$ in all surface treated solar cells.

Recombination analysis suggests that the recombination rates at the interface and in the depletion region were largely reduced compared to untreated device.

The reduced recombination rates are likely due to a decreased defect density on the absorber surface and depletion region.
Recent Advances

<table>
<thead>
<tr>
<th>Paper#2</th>
<th>Authors</th>
<th>Journal</th>
<th>Significant Findings</th>
</tr>
</thead>
</table>
| Record Efficiency for Thin-Film Polycrystalline Solar Cells Up to 22.9% Achieved by Cs-Treated Cu(In,Ga)(Se,S)_2 | Takuya Kato, Jyh-Lih Wu, Yoshiaki Hirai, Hiroki Sugimoto, and Veronica Bermudez | IEEE Journal of Photovoltaics Year: 2019 (IF: 3.398, Q1) | • Researchers at Solar Frontier further improved their solar cell from 22.3% to 22.9% by replacing K-treatment with Cs-treatment during absorber layer preparation  
• Conventional sulfurization-after-selenization (SAS) process was also replaced with a Rapid Thermal Process (RTP) by increasing the temperature ramp rate from 8–10 to 200–300 °C/min  
• New SAS process led to better quality absorber layer manifested as reduced V_{OC} and the extended minority carrier lifetime  
• The combination of the modified absorber and Cs treatment enables an absorber having wider E_{g,min} to increase V_{OC} more efficiently with increased carrier density, reduced defect density, and suppressed carrier recombination  
• Cell area: 1 cm²  
• Type of buffer layer: extremely thin CBD-CdS (10 nm)  
• The alkali treatment improves tolerance for reduced CdS thickness |
<table>
<thead>
<tr>
<th>Paper#3</th>
<th>Authors</th>
<th>Journal</th>
<th>Significant Findings</th>
</tr>
</thead>
</table>
| Improving the lateral homogeneity of Cu(In, Ga)Se\(_2\) layers fabricated by RF magnetron sputtering from a quaternary ceramic target | Linquan Zhang, Longlong Zeng, Chunhong Zeng, Yunfeng Liang, Ruijiang Hong | Ceramics International | • Authors subjected the as-sputtered Cu(In,Ga)Se\(_2\) films to annealing treatment at atmospheric pressure with added Se pellets  
• Annealing duration was 30 minutes  
• Annealing temperature investigated: 475, 500, 525 and 550 °C  
• The annealed films were compact and composed of well-faceted grains with sizes of approximately 500–1000 nm  
• The crystallinity of the annealed films was significantly enhanced without phase separation nor formation of secondary phases  
• Single-layered and compact films were formed by recrystallization of columnar grains during the annealing process (FESEM images are on the next slide)  
• Authors also reported that tensile stress that was introduced into the CIGS films during the sputtering process and was subsequently eliminated by annealing treatment  
• Tensile stress is usually the cause of delamination of the CIGS layer from the Mo back contact  
• The results indicate that annealing treatment, with the addition of Se pellets, is a feasible way to improve the lateral homogeneities in composition and morphology of sputtered Cu(In,Ga)Se\(_2\) films |
Recent Advances
<table>
<thead>
<tr>
<th>Paper#4</th>
<th>Authors</th>
<th>Journal</th>
<th>Significant Findings</th>
</tr>
</thead>
</table>
|         | Rebekah L. Garris, Steve  | Solar Energy Materials and Solar Cells        | • The researchers studied the similarities and differences between high quality CIGS solar cells made with various structures and fabrication techniques  
• The underlying electrical behavior governing the performance of these CIGS-based solar cells were investigated  
• CIGS solar cell samples were obtained from different research laboratories and industrial companies (see Table 1 on the following slide)  
• Performance parameters of the CIGS samples, shown in Table 2, indicate that despite significant differences in cell structures, fabrication techniques, carrier-density depth profiles, and activation energies, the device performance was similar  
• Cross-sectional EBIC signals overlaid on FESEM images showed that the different growth processes and composition variations affected the electric field distribution in the CIGS devices (see Figure 1 on slide 8)  
• This is a strong indicator that current collection profile in a device is influenced by the type substrate and the absorber deposition process |
|         | Johnston, Jian V. Li,    | Year: 2018                                   |                                                                ,assignments to the authors were not made in the text. Year: 2018 further provides context for the journal publication but was not used in the analysis.                                                                 |
|         | Harvey L. Guthrey,       | (IF: 6.019, Q1)                               |                                                                ,assignments to the authors were not made in the text. Year: 2018 further provides context for the journal publication but was not used in the analysis.                                                                 |
|         | Kannan Ramanathan,       |                                              |                                                                ,assignments to the authors were not made in the text. Year: 2018 further provides context for the journal publication but was not used in the analysis.                                                                 |
|         | Lorelle M. Mansfield     |                                              |                                                                ,assignments to the authors were not made in the text. Year: 2018 further provides context for the journal publication but was not used in the analysis.                                                                 |
Recent Advances

Table 1
Summary of cell structures and fabrication processes for six different fabricators, reprinted from [1].

<table>
<thead>
<tr>
<th>Fabricator</th>
<th>Substrate</th>
<th>Absorber process</th>
<th>Absorber</th>
<th>Buffer</th>
<th>Cell structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Glass</td>
<td>Three-stage Co-evaporation</td>
<td>Cu(In,Ga)Se₂</td>
<td>CdS</td>
<td>ZnO:Al/i-ZnO/CdS/CIGS/Mo</td>
</tr>
<tr>
<td>B</td>
<td>Glass</td>
<td>Three-stage Co-evaporation</td>
<td>(Ag,Cu)(In,Ga)Se₂</td>
<td>CdS</td>
<td>ITO/i-ZnO/CdS/ACIGS/Mo</td>
</tr>
<tr>
<td>C</td>
<td>Stainless steel (R2R)</td>
<td>Co-sputtering</td>
<td>Cu(In,Ga)Se₂</td>
<td>CdS</td>
<td>ZnO:Al/i-ZnO/CdS/CIGS/Mo</td>
</tr>
<tr>
<td>D</td>
<td>Stainless steel (R2R)</td>
<td>Three-stage Co-evaporation</td>
<td>Cu(In,Ga)Se₂</td>
<td>CdS</td>
<td>ITO/i-ZnO/CdS/CIGS/Mo</td>
</tr>
<tr>
<td>E</td>
<td>Glass</td>
<td>Metal-precursor reaction with H₂Se/H₂S</td>
<td>Cu(In,Ga)(S,Se,S,Se)₂</td>
<td>Thin CdS</td>
<td>ZnO:B/ZnO/CdS/CIGSSe/Mo</td>
</tr>
<tr>
<td>F</td>
<td>Glass</td>
<td>Metal-precursor reaction with H₂Se/H₂S</td>
<td>Cu(In,Ga)(S,Se,S,Se)₂</td>
<td>Thin Zn(O,O,S)</td>
<td>ZnO:B/ZnO/Zn(O,O,S)/CIGSSe/Mo</td>
</tr>
</tbody>
</table>

Table 2
Parameter table from J-V curves of representative devices, reprinted from [1].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{DC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>$E_{g}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>701</td>
<td>34.3</td>
<td>80.7</td>
<td>19.4</td>
<td>1.17</td>
</tr>
<tr>
<td>B</td>
<td>742</td>
<td>33.0</td>
<td>77.8</td>
<td>19.1</td>
<td>1.22</td>
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<tr>
<td>C</td>
<td>698</td>
<td>32.3</td>
<td>77.4</td>
<td>17.5</td>
<td>1.22</td>
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<tr>
<td>D</td>
<td>656</td>
<td>34.3</td>
<td>69.3</td>
<td>15.6</td>
<td>1.18</td>
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<tr>
<td>E</td>
<td>571</td>
<td>34.6</td>
<td>72.3</td>
<td>14.3</td>
<td>1.09</td>
</tr>
<tr>
<td>F</td>
<td>669</td>
<td>38.3</td>
<td>73.2</td>
<td>18.8</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Device Fabrication (CRUCIAL)

- **Window**
- **Buffer**
- **Absorber**
- **Back Contact**
- **Substrate**

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-ZnO/n-ZnO</td>
<td>0.25 – 1 µm</td>
</tr>
<tr>
<td>Buffer</td>
<td>50 nm</td>
</tr>
<tr>
<td>Cu(In,Ga)(S,Se)₂</td>
<td>1 µm</td>
</tr>
<tr>
<td>Mo</td>
<td>1 µm</td>
</tr>
<tr>
<td>Glass, metal, polymer</td>
<td></td>
</tr>
</tbody>
</table>

Co-evaporation
Co-Evaporation System (MBE) for CIGS Thin Film Growth - 1

- Substrate holder (2 inch, 800°C, rotation)
- Growth chamber ($\phi 406 \times 600$, Liq N2 shroud)
- K-cell (Max 1200°C, 5~25cc, PBN crucible, shutter)
- Valved cracking cell (Max 500°C, shutter)
Prospects of CIGS PV Device

- The ability to tailor the bandgap of CIGS devices to create larger bandgap absorber layers opens up the possibility of using CIGS in tandem PV devices.
CZTS (Se) Cell

- Band Gap: 1.4-1.6 eV – Direct
- Deposition Techniques: PVD; Sputtering; Spray Pyrolysis; Electrodeposition; Screen Printing
- Theoretical Efficiency: ~30%
- Efficiency Obtained: up to about 9.6% → 11%
- Abundant, cheap and green materials

Problems:
- Multiphasic; Mixed Phases (monoclinic, orthorhombic, cubic, tetragonal, stannite)
- Multistructural; Structural and Electronic Inhomogeneities
- Difficult to control complicated synthesis process
- Time and temperature stability questionable
CZTS Solar Cells by Sulfurization of a stack of evaporated Zn/Sn/Cu films

\[ \text{H}_2\text{S/N}_2, \quad 500 \degree \text{C} \]

\[ \text{Cu}_2\text{ZnSnS}_4 \]

Current Density [mA/cm²]

\[ J_{sc} = 6 \, \text{mA/cm}^2 \]
\[ V_{oc} = 400 \, \text{mV} \]
\[ \text{FF} = 28\% \]
\[ \eta = 0.66\% \]

CZTS Solar Cells by Sulfurization of co-sputtered Cu, SnS and ZnS film

ZnS
SnS
Cu
Mo

H₂S/N₂
580 °C

Cu₂ZnSnS₄
Mo

Current density (mA/cm²)

Jₑc = 17.9 mA/cm²
Vₑc = 610 mV
FF = 62%
η = 6.77%

Voltage (V)

IPCE (%)

Wavelength (nm)

CZTS Device Fabrication

Step by Step CZTS Device Fabrication Process

1. Single Step RF-Sputtered CZTS Precursor
2. Sulphurization Process
3. KCN Etching

Photon, E=hu

TCO (400 nm)
i-ZnO (50 nm)
n-CdS (50 nm)

-(+) ve Mø (1 µm)

(+) ve Mo (1 µm)

Soda Lime Glass

- Thermally Evaporated

- RF-Sputtered

- Chemical Bath Deposited

- DC-Sputtered

- Ultrasonification & N₂ drying

Front contact

Back contact

Practical CZTS Device
THIN FILM DEPOSITION & CHARACTERIZATION OF CZTS

Scanning Electron Microscopy (SEM)
CZTS at Present

**Sulphurization Process Parameters**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack Configuration</td>
<td>SLG/Mo/CZTS</td>
</tr>
<tr>
<td>Heating Ramp-Rate</td>
<td>5 °C/Minute</td>
</tr>
<tr>
<td>Cooling Rate</td>
<td>Natural cooling</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>0.0001 ATM (90 mTorr)</td>
</tr>
<tr>
<td>Working Pressure</td>
<td>0.5 ATM (380 Torr)</td>
</tr>
<tr>
<td>Background Gas</td>
<td>Purified N$_2$ (99.99 %)</td>
</tr>
<tr>
<td>Sulphur Content</td>
<td>62.50 mg</td>
</tr>
<tr>
<td>Holding Time</td>
<td>45 Minutes</td>
</tr>
</tbody>
</table>

**KCN Etching** 10 wt%, 2 Minutes

**CdS by CBD**, 68 °C to 70 °C

**i-ZnO, ITO & Al Layers**

**Mechanical Scribing**

**Current Density J (mA/cm$^2$)**

- $J_{sc} = 14.83$ mA/cm$^2$
- $V_{oc} = 0.631$ V
- FF = 41.98
- $\eta = 3.93$ %

**External Quantum Efficiency, EQE (%)**

- EQE at 1.50 eV: 70%
- EQE at 1.35 eV: 60%

**Open Circuit Voltage, V$_{oc}$ (V)**

- Toyota Central: 8.78 V
- This Work: 8.13 V

**Short Circuit Current Density (mA/cm$^2$)**

- Toyota Central: 26.84 mA/cm$^2$
- This Work: 14.83 mA/cm$^2$

**Fill Factor**

- Toyota Central: 61.90%
- This Work: 61.90%

**Photoanode Efficiency (%)**

- Toyota Central: 9.19%
- This Work: 9.43%
CZTS Flexible Solar Cells
Recent Advances

Cu2ZnSnS4 solar cells with over 10% power conversion efficiency

Table 1: Detailed device performance parameters estimated for a two-device model.
High Efficiency CTS and CTGS Thin-Film Solar Cells

Fig. 1. (a) Structures of stacked precursors, CTGS thin film, and CTGS solar cell, as well as (b) schematic of three-zone tube furnace for sulfuration of the stacked precursors to form the CTGS thin films under S and SnS$_2$ vapors.

Table 2
Photovoltaic performance parameters, $J_{SC}$, $V_{OC}$, $FF$, and $\eta$ of the CTGS solar cells at each Ge thickness of 0, 200, 275, and 420 nm in Fig. 5. The $E_g$ of the CTGS absorbers was estimated from the first EQE derivative.

<table>
<thead>
<tr>
<th>Ge thickness (nm)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (CTS)</td>
<td>31.1</td>
<td>0.251</td>
<td>45.4</td>
<td>3.6</td>
</tr>
<tr>
<td>200</td>
<td>29.3</td>
<td>0.370</td>
<td>51.2</td>
<td>5.6</td>
</tr>
<tr>
<td>275</td>
<td>29.4</td>
<td>0.344</td>
<td>49.7</td>
<td>4.9</td>
</tr>
<tr>
<td>420</td>
<td>23.9</td>
<td>0.311</td>
<td>37.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Ref: Hayashi et al., SOLMAT 2020
OUTLINE

- Introduction
- Thin Film & Thin Film Deposition
- Solar Cells
- Implication of Thin Films into Solar Cells
  - aSi
  - CdTe
  - CIS (CIGSSe, CZTS, CTS)
- Challenges and prospects
- Conclusion
Market share of c-Si PV panels is projected to decrease from 92% to 44.8% between 2014 and 2030.

The third-generation PV panels are predicted to reach 44.1%, from a base of 1% in 2014, over the same period.
**Thin Films: The commercial leaders**

**Cu(InGa)(S,Se)₂ Thin Film Cell**
Best Research: 22.9% - Solar Frontier

- Front Contact
  - Al (0.3 µm) on Al (0.05 µm)

- Mo (1 µm)

- CIGS (2-4 µm)

- CdS, ZnSnO, or InSe (0.05 µm)

- ZnO (~0.5 µm)

- MgF (~0.1 µm)

**CdTe Thin Film Cell**
Best Research: 21.1% - First Solar

- Glass Superstrate (3-4 mm)

- CdsSnO₄

- Zn₂SnO₄

- ZnₓCd₁₋ₓS

- CdS (0.05 µm)

- CdTe (1.6 µm)

- ZnTe (0.1 µm)

- Ni (0.01 µm)

- Al (0.03 µm)

- Encapsulant

- Glass Substrate (3-4 mm)
  - Also, stainless steel, polymer

---

**Front Contact**
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**CdS, ZnSnO, or InSe**
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  - Also, stainless steel, polymer
First Solar (CdTe) dominates the thin film module manufacturer segment with 3.1GWp annual capacity in 2016.

- From 2012, First Solar capacity increase with module efficiency improvement without new plant investment [1].
PV Technology Comparison: Thin Film vs Multicrystalline Silicon

<table>
<thead>
<tr>
<th></th>
<th>a-Si</th>
<th>CdTe</th>
<th>CIGS</th>
<th>Multi c-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial module efficiency</td>
<td>10.0% (Sharp) [3]</td>
<td>17.0% (First Solar) [5]</td>
<td>14.2% (Solar Frontier) [2]</td>
<td>17.3% (Trina) [6]</td>
</tr>
<tr>
<td>Module Temperature Coefficient (Pmpp)</td>
<td>-0.24%/°C [3]</td>
<td>-0.28%/°C [5]</td>
<td>-0.31%/K [2]</td>
<td>-0.41%/°C (Trina) [6]</td>
</tr>
</tbody>
</table>

**Advantages**
- a-Si: Mature technology, Excellent for small devices (e.g. pocket calculators), Low cost manufacturing, Lower temperature coefficient
- CdTe: Low cost manufacturing, Lower temperature coefficient
- CIGS: High efficiency, Glass or flexible substrates, Lower temperature coefficient
- Multi c-Si: Mature technology, High volume production, competitive cost.

**Disadvantages**
- a-Si: Low efficiency, High cost equipment, less popular now as lower Si price
- CdTe: Medium efficiency, Rigid glass substrates, Cd toxicity is a concern
- CIGS: High cost & traditional process, Quarternary compound, complicated process control. No Cd
- Multi c-Si: Medium efficiency, Poorer temperature coefficient

**Major manufacturers (2016 production capacity)**
- a-Si: Sharp**, Uni Solar**
- CdTe: First Solar (3100MW) [5], Calyxo (85MW)
- CIGS: Solar Frontier (1110MW) [2]
- Multi c-Si: Trina Solar (4825MW*) [6], Hanwha Q-Cells (4583MW*) [9], Canadian Solar (5232MW*) [7], JA Solar (4920MW*) [8]

- CdTe and multicrystalline Si are competing best research cell and module efficiency and translate to commercialize module’s efficiency.
- CIGS slow adoption to commercial.
- Temperature coefficient of thin films are better.

*Crystalline Si supplier capacity includes total mono and multicrystalline.
**No data available, estimate a-Si production capacity is very low with Si price reduce tremendously in the past several years.
Best Efficiency Record: Snapshot of CdTe, a-Si, CIGS & c-Si

- Rapid development of CdTe and CIGS in the past 6 years.
- CdTe has the highest development with +4.8% efficiency improvement in 6 years. CIGS has +3% increment over the past 7 years.
- Corporate spending for R&D and commercialize fund: First Solar utilized 4% - 5% of annual revenue. Spent $130M or 4.2% of total revenue in 2016 [1].
- Multicrystalline Si has some momentum recently with n-type high performance cells [2] from Fraunhofer Institute for Solar Energy Systems ISE. Still slow efficiency improvement compare to thin film.
- Monocrystalline Si and amorphous Si performance has very less efficiency improvement in the last 5 years.

Source: https://www.nrel.gov/pv/assets/images/efficiency-chart.png
The Casualties

Bankability
The capacity or capability to manufacture or produce a product competitively (e.g., with an acceptable profit, reliability, etc.)
Challenges to Thin Film Technology Commercialization

1. Technical:
   - Continue adopt and translate record cells/module efficiency to high volume production → involve high capital investment.
   - Possible risk and challenge in high volume manufacturing, product performance and customer acceptance. Needs to deliver cost structure as forecast to remain competitive.
   - New innovation – potential commercialization of new disruptive technology (Perovskite/c-Si Tandem junction) that could produce higher efficiency at lower cost.
   - Innovation of lower cost c-Si raw material (fluidize bed poly, cheaper lower energy/higher purity ingot).

2. Economical:
   - Cost per watt pressure: Chinese manufacturers expansion and domestic demand will be the key. Cost per watt crash in 2H-2016 might be repeated if China’s domestic demand shrink as 13th 5-year plan exceeded the target 3 years ahead.
     - Cost per watt < $0.30 – thin film manufacturers have to increase production capacity and produce at cheaper cost to maintain return margin and sustain competitive.
   - International trade barrier – introduction of impose tax to PV module in high PV demand countries will slow down the PV sector growth.

3. Political:
   - Governments abrupt energy policy change and benefit energy sources other than PV, e.g: US pulling out of Paris Agreement, promote traditional energy sources.
   - Unstable political regions delay the PV adoption: Middle east.
End of Life Recycling R&D Prospects

Industry standard warranty from Tier 1 manufacturers
Preferred options for PV waste management

- As research and development (R&D) and technological advances continue with a maturing industry, the composition of panels is expected to require less raw material.

- Rapid global PV growth is expected to generate a robust secondary market for panel components and materials.

- As current PV installations reach the final decommissioning stage, recycling and material recovery will be preferable to panel disposal.

Source: IEA, End-of-Life PV 2016
Innovation in Approach: *Materials by Design + Artificial Intelligence*

“Edisonian Approach” - *Conventional trial-by-error science*

“Materials-by-Design” - *Inverse process: Define desired materials functionalities and work backward to computationally define (determine) best-of-class materials*

Courtesy: Lawrence L. Kazmerski
Conclusion

1. Thin Film PVs are finally demonstrating their potential to provide affordable solar generated electricity

2. Leading thin film PV material - CdTe & CIS - have come a long way since its inception
   - The devices are becoming significantly more complex
   - Although much is known about the leading thin film PV, unresolved issues and open questions remain

3. Further advances in performance require improved understanding of the materials that comprise the solar cell, the key interfaces, and the device operation models (AI may be implemented)
   - Control of absorber properties
     - improve carrier lifetimes (therefore collection)
     - control doping concentration
   - Better contacts (front and back)
     - to improve yield
     - to improve performance

4. Scopes for Industry
   - Off-the-shelf manufacturing equipment
   - In-line diagnostics for improved quality control/yield
   - Validation of long term reliability
   - Bridge the performance gap between small cells and commercial modules
   - Sustainable Recycling process of end-of-life PV panels

Current R&D Priorities
- Materials and Devices
- Manufacturing
- Reliability
Our mission “Solar-Green-Earth”
Adopting & adapting all-solar solutions...
in days to come...for our future generation....

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