Non-Silicon Thin-Film PV Materials Progress and Challenges.

SolarCon, Republic of Korea.

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Materion Advanced Chemicals

PRIMARY MARKETS SERVED

- LED Lighting
- Alternative Energy
- Optical and Semiconductor Coatings
- Specialty Battery
- Specialty Inorganic Chemical Applications
- Large Area Coatings
- Medical
- Research & Development

KEY PRODUCTS & SERVICES

- Phosphor Materials
- New Product Development Partnering
- High Purity Chemicals
- Thin Film Deposition Materials
- Large Format Sputtering Targets
- Precious and Non-precious Metals
- Precious Metal Refining & Recycling
- Materials for Research & Development

Milwaukee Facility leads the Business Unit and drives PV Material Development

First reported at AIMCAL in 2007 and SVC in 2009, thin film PV target and powder production has grown each year.

Topics Covered

- Cadmium Sulfide (CdS)
  - Introduced in 2005 is mature for evaporation and some sputtering processes.
- Copper Indium Gallium (di) Selenide (CIGS)
  - CIGS targets and powders
  - Binary compounds and metal alloys.
- Challenges of the sputtering of Se containing targets.

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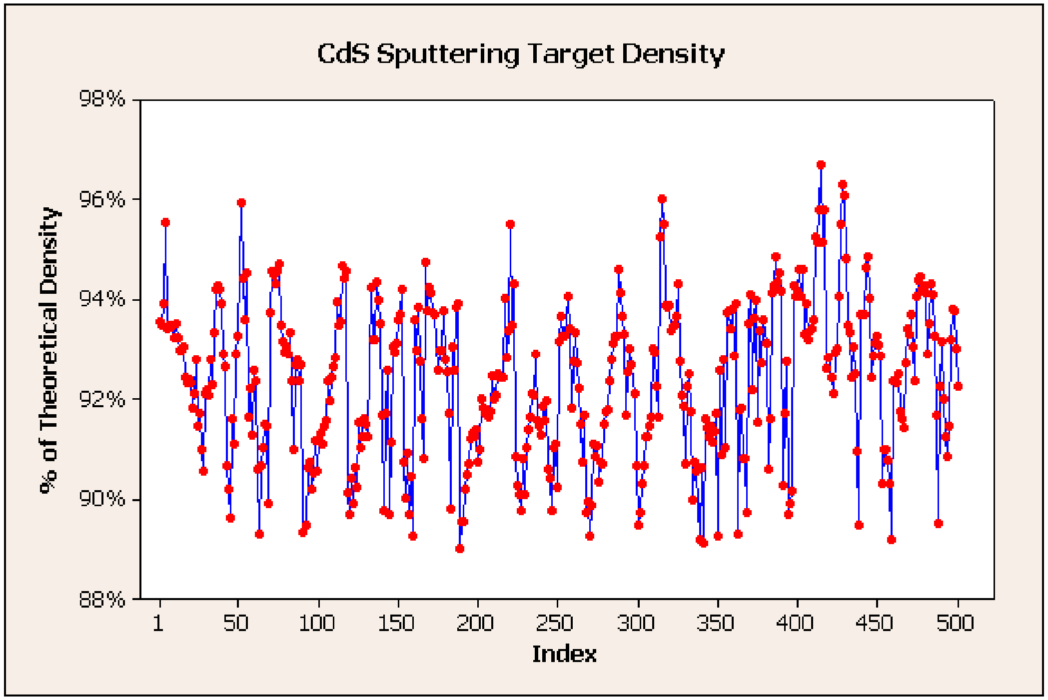
CdS Sputtering Targets

- Dense custom microcrystalline CdS powder is consolidated into tiles at high volume for sputtering.
- Indium bonding is the most efficient for reuse of the backing plates.
- Use of a digital multi-meter tests nature of the tile.
- CdS resistance is typically 1+ kilo-ohm.
- For this range, RF is common but some pulse DC processes have been reported.



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CdS Sputtering Targets

- Tiles with sizes up to 175mm x 200” at densities exceeding 89% are produced for bonding or direct use.
- Mosaic tile format is used for larger sputter tools.
- Tiles are Indium bonded onto rigid or reinforced backing plates.
- Target Performance considerations:
  - Management of re-deposition.
  - Sputtering power and arc sensitivity.
  - Temperature of target and process.

Sequentially bonded CdS tiles (on copper) for a large width sputtering process (March 2011).

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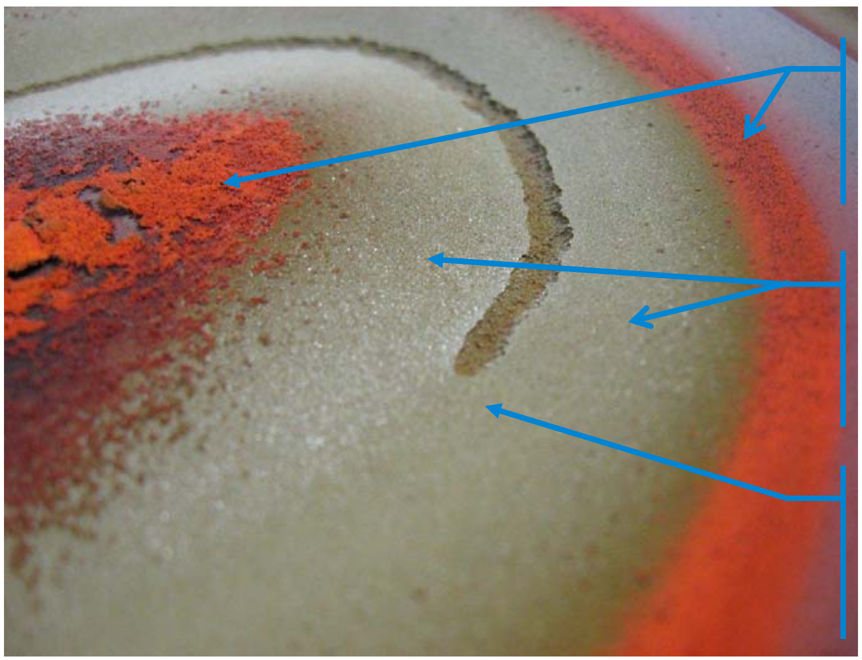
Effects of Power and Temperature on CdS

- Management of process conditions and surface/bulk temperature of the target is critical to lifetime of the target.

- Re-deposition of alternate phases and sulfur loss are key concerns.
- Local regions of higher conductivity can alter plasma density.



Re-deposition is lower density CdS. Aside from contamination - n, p or I type effects plasma.

Sulfur loss helps rate but also influences local conductivity.

Due to heat or dense plasma, local rate changes can shorten target life or effect uniformity.

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CIGS Sputtering Targets

- Standard single phase: $Cu(In_xGa_{1-x})Se_2$ powder is produced from a range of Copper, Indium and Gallium levels.
- Standard or Custom CIGS powders are manufactured and then consolidated into dense tiles for sputtering.
- More than 50 different customer specified composition powders have been made to order.
- Standard $Cu(In_{0.7}Ga_{0.3})Se_2$ tiles exceeding 88% density are available up to 125 mm x 125 mm or targets of 200mm in diameter.
- The machined tiles/targets are fit for elastomer or indium bonding to rigid backing plates.
- Final film properties are influenced by initial composition and process.
- Target Usability Contributors Include:
  - Sputtering approach.
  - Low melting sub-phases
  - Free metals

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Sputtering of CIGS and the CIGS Film

- Process conditions must be maintained to keep –Se in the compound.
- CIGS targets are fragile and sensitive to thermal and mechanical stress.
- With multi-meter readings in excess of 1 kilo-ohm resistance, RF sputtering is the most prevalent.
  - Novel pulse DC and DC techniques have been reported.

CIGS target after RF sputtering*

**all values are atomic %
**target composition, as measured by ICP
**as deposited and post anneal refer to film composition, determined by EDS
***EDS values are different than ICP bulk characterization values

	target	thin film as deposited	thin film post anneal
Cu	20 - 25	26.5 - 29.7	27.8 - 29.6
In	15 - 21	15.7 - 17.4	16.5 - 18.4
Ga	6 - 9	7.5 - 8.5	7.5 - 9.3
Se	50	45.9 - 48.8	44.2 - 46.5

**CIGS films obtained by Mr. Wen-Tsai Yen and Dr. Yi-Cheng Lin On SLG at 1Kw at Taiwan R.O.C National ChangHua University of Education Department of Mechatronics June 2008.*

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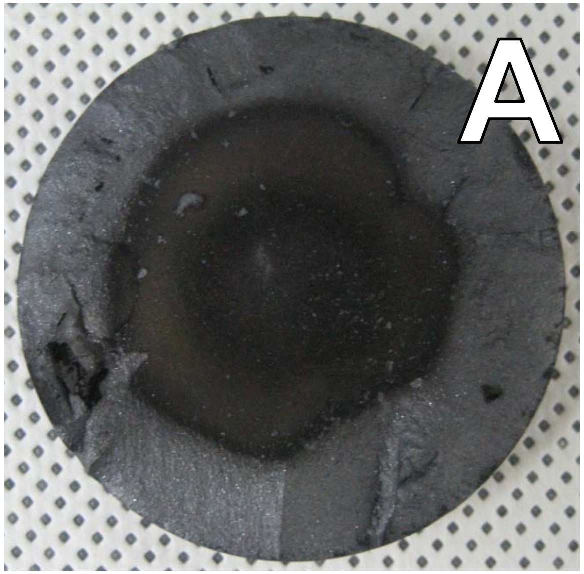
CIGS Compound Sputtering Targets

- Backing plate stiffness and bonding technique are important.
  - Backing plate bowing stress along with high temperatures can result in edge chipping. [A.]
  - In-plane chipped targets can sputter but excessive chipping can increase arcs and stability.
- High target temperatures can transform or embrittle targets.
  - Phase change, melting or glassy appearance indicate high temperature.
  - Shear overload failures along stressed regions can delaminate target from backing plate. [B.]
  - Selenium loss can lead to melt-out or increased arching.



CIGS Binary Sputtering Targets

- Commercial and academic demand has grown for the binary compounds.
  - Issues with controlling important In / (In + Ga) and Ga / (In + Ga) ratios in the CIGS layer led to requests for stable binary compounds.
  - Similar to the full CIGS target, -Se retention and control remains a key factor for the binary targets.
  - In_2Se_3 and Cu_2Se targets seem to have an even more dramatic conductivity vs temperature relationship.
  - With less sub-phases possible the onset of melting and poisoning of the target surface remain key hurdles for process development.
  - As with CIGS, the presence of Selenium in the compound limits target conductivity and makes use of pulse DC or DC sputtering difficult.
  - Process approach and conditions are less advanced than CIGS.
- Due to the complexities and limitations of sputtering –Se compounds, Industry has increased demand for conductive options.
  - Copper – Gallium and Copper-Indium-Gallium alloys have been developed for sputtering.

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Cu-Ga Alloy Sputtering Targets

- The CuGa Billet is cut/rolled into tiles or extruded for tubes.
- Conductivity of the alloy allows DC and pDC to be used
  - Limit of DC power is the stability of Gallium in the alloy.
- Up to 25 at% Ga. the alloy is stable and machined into segments up to 10mm thick.
- Large single piece or mosaic assemblies can be conventionally bonded.

A Typical machined CuGa25 billet

Typical CuGa25 targets for bonding.

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Cu-Ga Sputtering Targets for CIGS

- With increasing Ga. Content, the CuGa alloy is too brittle and required the development of a proprietary powder/press process.
  - Typical CuGa25+ at% Ga round target is up to ~190mm in diameter and 10mm thick.
  - Typical CuGa25+ at% Ga tiles are up to ~254mm long, 152mm wide and 6mm thick.

Single CuGa25+ round target.

3 CuGa25+ tiles ready for bonding.

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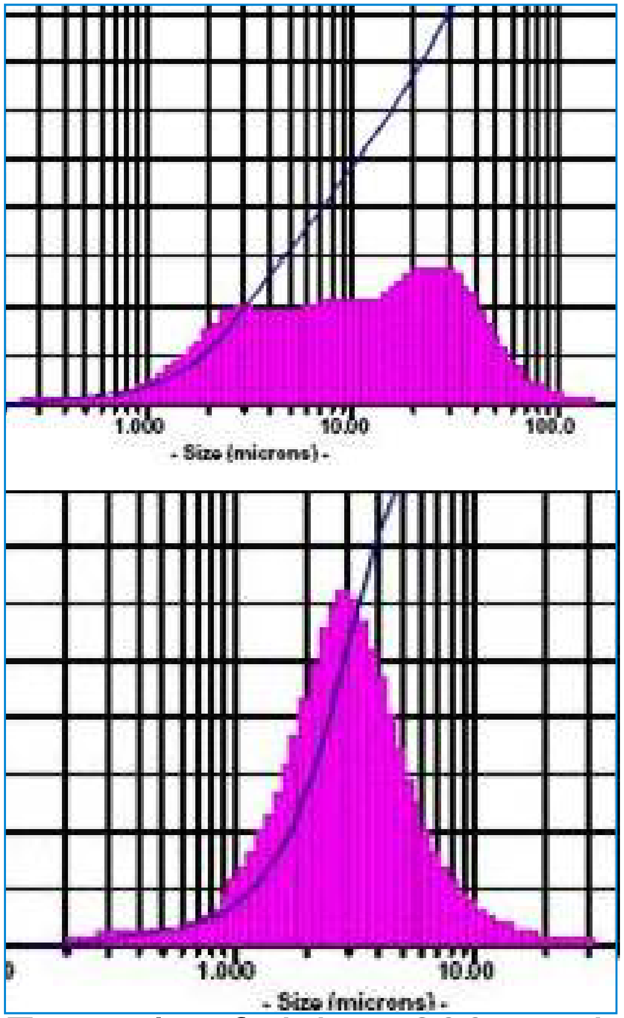
Cu-In-Ga Sputtering Targets

- Copper – Indium – Gallium targets require advanced manufacturing techniques due to large differences in constituent melting points.
  - Cu – ~1084 C In – ~430 C Ga – ~303 C
- With advanced manufacturing technology available, market trends show minimum composition variance of +/- 2.5 at%.
- Impact of Composition variances in a target:
  - Chance of sub-phases broadening the melting point range (of alloy) .
  - Soft regions near higher melting regions make machining difficult.
  - Inhomogeneous targets are likely to "melt-out" in-situ.
- Industry demands for higher composition control lead to a new process.
  - New process reduces composition variance to +/-1at%.
  - New process meets market demand for 500mm long,127mm wide and 10mm thick targets.

CIGS powders for Printing

- Standard -200 mesh $Cu(In_{0.7}Ga_{0.3})Se_2$ powders are sized in a custom process.
  - Sub-phases can complicate formulations.
  - Curing techniques may be sensitive to different metallic sub-phase impurities.
- Energetic sizing benefits from immediate immersion in a protective binder/ink or suspension.
- Internal techniques offer a starting composition and final D_{50} size < 5 microns.
- Materion continues to invest in developing other methods to size, protect and package finer powders.



Example of sizing -200 mesh CIGS to < 5 um.

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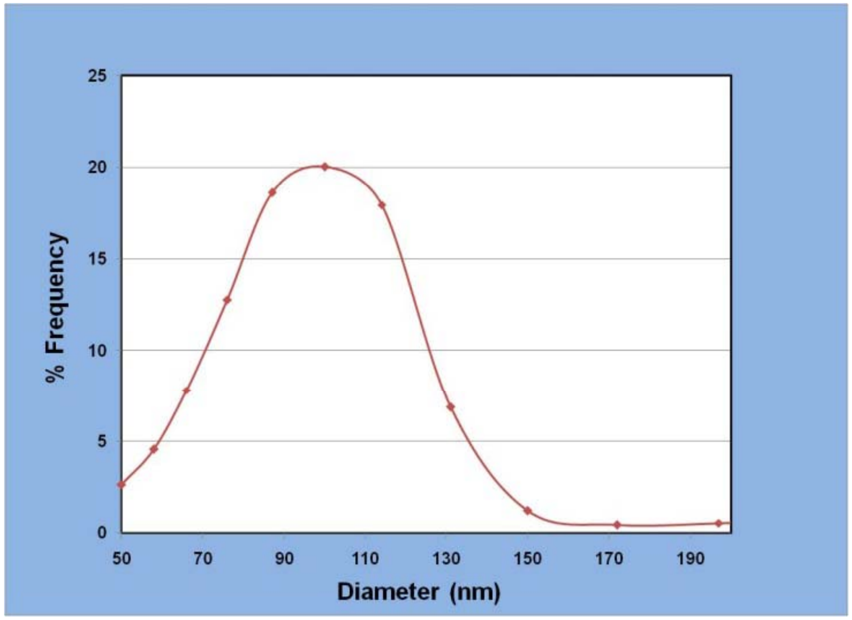
CIGS Nano Dispersions

- Standard $Cu(In_{0.7}Ga_{0.3})Se_2$ powders are further reduced and dispersed in a custom process.
  - Dispersions provided in water or alcohol
  - Available in 20 – 40wt% CIGS to liquid
  - Particle sizes <100nm possible
  - Additional compositions and dispersants possible.



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- Materion offers a large selection of metal/alloy and compound targets for CIGS efforts.
- Many materials for CIGS efforts require significant post deposition processing to achieve final film properties.
- The environment of each subsequent step must be weighed on the following step.
- Oxygen, moisture and temperature control is important between steps.

Material	Type	Purity (%)
Cu-In-Ga-Se	target	99.99
	6 mm pcs. & less	99.99
	-200 mesh	99.99
$CuInSe_2$	6 mm pcs. & less	99.999
Cu-In-Ga	target	99.99
Cu-In	powder	99.99
Cu-Ga	target	99.99+
Cu_2Se	target	99.5
	6 mm pcs. & less	99.5
CuSe	6 mm pcs. & less	99.5
In_2Se_3	target	99.9
	6 mm pcs. & less	99.999
Ga_2Se_3	6 mm pcs. & less	99.999
Cu	6 x 6 mm pellets	99.99*
	3 x 3 mm pellets	99.99*
	2-6 mm shot	99.99-99.999*
	-20, +50 mesh	99.95*
In	target	99.99, 99.999
	3mm shot	99.99 - 99.9999*
Ga	3 mm shot	99.99 - 99.9999
Se	3 mm shot	99.99, 99.999*

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Challenges for Sputtering Processes

Despite advances in producing and scaling of CdS, CIGS, CuGa, CIG and binary powders as targets, their delicate nature puts pressure on the process.

- Any time, any amount of Selenium is part of the compound, the target conductivity quickly drops.
- Selenium and Gallium also add the risk of –Se or –Ga vapor in the process.
  - Aside from Arcs (pDC, DC) the free metal interactions with the plasma (pDC, DC and RF) complicate sputtering.
- Selenium loss also reduces the integrity of the compound, which results in melting point reduction.
- Gallium loss in the alloys increases melt-out risk (CuGa) or destabilizes the composition and integrity of the CIG targets.

Challenges for Sputtering Processes

- Overheated targets can sag or melt:
  - Melting point reduction due to alloy melt-out or sub-phases.
  - High temperatures are associated with sputter process and cooling.
- For each compound to be maintained as a semiconductor, there must be special care to limit the target temperature.
  - Aggressive conditions or excessive arcs can liberate species.
    - Metals can coalesce (due to sweat or redposition) to make arcs unmanageable.
    - Metals can also create hot spots which can locally segregate or pool plasma.
    - Sulfides and Selenides can also redeposit as a non-ideal semiconducting or insulating phase which can “kill” or “poison” a target.

Challenges for Sputtering Processes

Adapting classical semiconductor/FPD procedures for thin film PV assumption #1 - bonding.

- It was assumed that conventional bonding would serve the needs of the new market.
  - — Indium bonds are adequate for systems that are well cooled or have durable, conductive targets in use.
  - — Most PV targets are semi-conducting at best and are made warm/hot by aggressive technique deployment.
  - — Elastomer, and epoxy bonds can be required for sputter down or sideways processes.
  - — Since cracking is also very common with the compound targets, elastomer bonding enables the target to be pushed even after many cracks/arcs.
  - — Hybrid bonding systems have been needed for the thermally unstable compounds or low melting point targets like CIG.

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Challenges for Sputtering Processes

Overlooking plate deflection due to temperature or water pressure destroys good targets.

- Backing Plate Selection and Specification.
  - It is important to note when the cooling water is in direct contact with the backing plate/target assembly as deformation can flood the chamber with water.
    - Typical water pressures are 1.5 to 3.5 Bar (1 Bar = 1kPa).
    - When there is a base plate, and no water contact, the thermal conductivity and cost of the material are most important (Cu, Mo, Ti).
    - Many compound targets or low melting point alloys provide very little or fleeting reinforcement to the backing plate assembly.
  - Oxygen Free – High Conductivity Copper has been standard but is too soft to be a safe water barrier at 2.5 – 3.5 bar of typical processes.

Challenges for Sputtering Processes

- Specifying temper is very important.
  - Conventional OFHC C101000 annealed copper has a low yield strength (11 ksi “kilo-pound[-force] per square inch”).
  - Work hardening C101000 increases the yield strength dramatically. (30-45 ksi).
  - Deformation of the backing plate can cause many issues.
    - — Assembly of the tool may be impossible if bolt holes are deformed.
    - — Any deformation by the backing can crack Sulfide or Selenide targets.
    - — Excessive deformation, even without water breech, can make re-using the backing plates difficult.
  - Other, more stiff materials (Molybdenum) or cheap (Stainless Steel) plates lack required thermal conductivity to minimize the risk to the thermally influenced –Se, –Ga or –In targets.
  - The Process Engineer should approve best choice to purchasing.

Challenges for Sputtering Processes

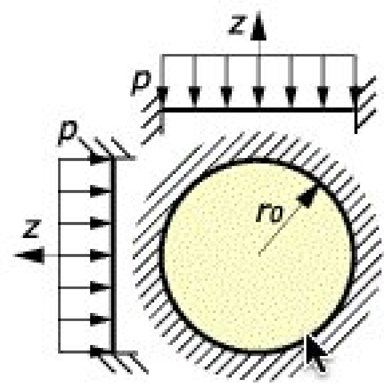
- Many Engineers use clamped plate calculations to calibrate their cooling strategy.

- The dimensions (ro, Lx, and Ly), load (Bar/Pascals) and modulus are known (or measured).

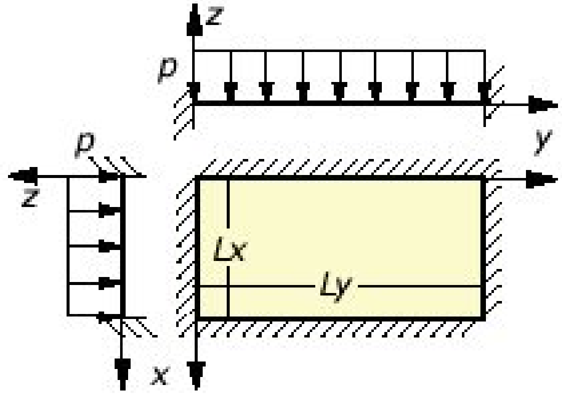
  - To protect against deflection and to maintain the best thermal conductivity Copper/Chrome C18200 is excellent with a yield strength of 40-60 ksi.

- The Elastic Modulus is the material property that describes stiffness.

  - known for most materials it should be tested from time to time as process conditions can “self anneal” the backing plate.



Clamped Circular Plate, Uniform Load



Clamped Rectangle Plate, Uniform Load

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Materion – Advanced Chemicals is your partner for PV materials

Our latest realignment is just the next step in providing the broadest experience and perspective to the quickly evolving PV thin film market.

We know we are an important part of both 1) this technology development and 2) the effort to give the solar marketplace more performance and value than before.

We will continue to produce and support the increasingly complex demand of the PV solar market.

CdS for evaporation and sputtering continues to grow and CdTe based approaches grow with utility scale supply projects

CIGS has met many challenges but tools are increasing in size and volume with many technologies to address them.

Challenges and Keys to Growth of Thin Film PV

Bonding and Backing plate specifications have to evolve to meet the needs of the more fragile and thermally sensitive compounds.

Many materials for CIGS efforts require significant post deposition processing to achieve final film properties.

The environment of each subsequent step must be weighed on the current step to assure an effective manufacturing strategy.

Oxygen, moisture and temperature control is important at every step.

CIGS on the large scale, by any current approach, is still very far from the theoretical nameplate of the system in terms of performance, cost and durability.

Many challenges remain in optimizing the right material and process for the right application.

Thank you for your attention!

Special Thanks to the Staff at Materion for the material calculations and product data/pictures used in this presentation.

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