

Developing and Assisting Next Generation Window and Absorber Solar Materials.

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Abstract

Since 2005 Williams Advanced Materials has been aligning resources to develop and scale-up products for a new generation of Solar Materials. The combined chemical and metallurgical capabilities continue to produce complex PVD materials for both rigid and roll-to-roll platforms. We continue to foster cooperation in order to reduce risk and produce the most effective partnering and R&D joint development activities with key vendors, customers and institutions.

Using in-house inorganic chemical synthesis and sintering capability, a new evaporation form of CdS for use as the *Window / Buffer* layer and CdTe for use as the *Absorber* in non-silicon Solar stacks is available. This low moisture, high density crystalline powder is ideal for consistent deposition behavior to very high volumes. Both of these products have allowed rapid development of dense tiles for assembly into many different sputtering configurations.

One especially challenging family of *Absorber* materials came in the form of the special requirements for stable CIS (Copper Indium diSelenide) and CIGS (Copper Indium Gallium diSelenide) powders and sputtering targets. At the Milwaukee, WI facility, carefully monitored chemical reactions were developed for the precursors and final compounds. The effort resulted in fine powders for printing, powder/pieces for evaporation and pressed targets/slabs for sputtering/CSS.

Introduction

With new developments in performance, cost and scale of Silicon based approaches – pressure is mounting on the non-Silicon approaches to fulfill their potential. While announcements in the equipment and process improvements hold the majority of the visibility for CdTe approach, the materials sector has also been working to influence the success and cost effectiveness of the varied approaches. The scaling up and development of lower cost, higher performing CdTe and CdS powders for the CdTe based cells have resulted in new compounds which help move novel CIGS approaches closer to champion elemental cell performance. The following discussion explains how each of these lessons led to a broad assortment of high grade specialty products to assist in the CIGS effort.

Discussion – CdS

Cadmium Sulfide (CdS) for solar applications has come a long way from its simple pigment beginnings. It can be said that in the mid 1800's techniques for heating acidic cadmium salt solutions in hydrogen sulfide gas to produce a brilliant powder/pigment were maturing and supplying the art industry with "cadmium yellow." As time progressed, the inorganic materials industry continued to refine precipitation, drying and manufacturing techniques to meet the growing industrial demand for this versatile direct band gap semiconductor. Into the 1970's Eastman Kodak and others experimented with techniques that manipulated optical grade powders to produce windows/substrates for the Infrared marketplace. These techniques continued to dominate well into the most recent Solar Initiatives.

In order to help the new Solar Marketplace deal with the various issues legacy to these large scale manufacturing processes, the ability to effect and optimize the crystallographic phase purity and maximize the chemical and light stability of new powders for evaporation or sputtering became an instant priority. Older precipitated CdS powders lacked the adequate density and strength to be properly evaporated and controlled for the very thin (60-400nm) and high performing buffer layers required for CdTe cell performance targets. The low powder density also kept target densities too low for proper consideration for PVD approaches. With inferior CdS, the relationship between hexagonal and cubic structures in the final film is uncontrollable making consistent n-type windows rare. Just as in those early pigments, if the cadmium sulfide is unstable the fading of the film in the presence of sunlight would alter the band gap and reduce cell performance.

The goal had to be higher density, highly ordered microcrystalline CdS. By focusing our efforts on a more solid state reaction and taking more care with sizing techniques we were able to produce an evaporation grade Solar CdS microcrystalline powder strong enough for both dilute and bulk phase transport. More sophisticated sizing techniques added to colorfastness during production which gives an important level of comfort for the operator. The higher density targets help the low rates of RF sputtering to be economical and effective for large area depositions. The higher strength and density target tiles can be elastomer bonded. The steady improvement of the CdS product line has allowed good processes to be developed for both Evaporation and Physical Vapor Deposition (PVD) of n-type CdS window layers. These larger area and/or high throughput routes rival the more common cadmium sulfate & thiourea Chemical Bath Deposition (CBD) option.

Discussion – CIGS (powders/targets)

As Dr. Rommel Noufi (now VP of Research at Solopower) captured so well at the 2006 IEEE 4th World Conference on PV Energy Conversion – Cu-chalcopyrite based solar modules are of significant importance to the thin film Solar sector. Even today, many look to CIS (Copper Indium diSelenide) and CIGS (Copper Indium Gallium diSelenide) based cells as the great hope for low cost, high performance modules to rival Silicon advances. Though many champion cells have been made via elemental evaporation processes – many have been asking for improvements in alloy and inorganic powder/target offerings in order to realize the true large area, lightweight or cosmetically enhanced processes available to alternate technologies. In this discussion, we will highlight our ongoing effort to increase the number and availability of products for this emerging technology marketplace.

To borrow from that same presentation [1], Dr. Noufi identified three main routes to make a CIGS based absorber layer:

- 1) $\text{Cu} + \text{In} + \text{Ga} > \{\text{Cu: In: Ga Intermetallic}\} \gg \text{He}_2\text{Se (or Se)}$ yields Cu(In,Ga)Se_2 or,
- 2) $\text{Cu}_2\text{Se} + (\text{In,Ga})_2\text{Se}_3$ yields Cu(In,Ga)Se_2 and finally,
- 3) $\text{Cu} + \text{In} + \text{Ga} + \text{Se}$ yields Cu(In,Ga)Se_2 .

Figure 1: Main routes to CIGS fabrication in Modules

While these were common for the laboratory and for in-situ films, these routes have little use – or economy, for the increasing demands for the binary, ternary or quaternary systems required by alternate techniques. By 2006 our Milwaukee facility had been steadily working for over two years on methods to produce the different reacted powders and compounds. We learned early on to overcome the inhomogeneous nature of the final compound due the varied melting points of the four components, a trait that dogs the

Bridgeman grown approaches for CIS and single crystal CdTe. It is important for us to always be cognizant of the spatial properties of an ingot if we expect to be able to harvest useful sized material for pressing or deposition applications. Furthermore, if we cannot fully scale up an ingot route there will be little hope to hit the ultimate cost/kg or cost/target requirements to meet the downward pressure on \$/watt requirements of the finished module.

All the way until 2007, work continued on optimizing the furnace/reactors to make the most stable reacted powders. As anyone who works with any CIGS or CIS process will explain, the Se content is troublesome to keep stable. It is a clear advantage for our process to have tight control of any deleterious exotherms during the reactions. All production lots of powder are carefully matched against X-ray diffraction (XRD) controls and Thermogravimetric (TGA) comparisons to carefully monitor crystal structure and screen for unreacted materials. The penalty for not having such tight controls is that there will be changes upon pressing that make the target unlike the tightly specified and agreed upon composition and state. It is our goal to provide the customer a consistent product on which to build a robust process. We take great care to assure the relationship between the target and the starting powder.

The benefit to such careful study and sensitive control development came in 2008 when we scaled our CIGS powder processes over seven times to meet demand for completely reacted CIGS targets. While it would be nice to have all customers/processes using one single CIGS composition, we have scaled up the ability to make a stable initial powder and final target comfortably in the below ranges:

Cu	20 – 25 at%
In	15 – 21 at%
Ga	6 – 9 at%
Se	50 at%

Figure 2: Cu-In-Ga-Se Preferred Compositions for Stable Powder and Target

By having defined, stable compositions, it is easier to imagine being able to control the composition of the as-deposited film better than if you had a system that changes uncontrollably. Below is an example of a CERAC CIGS target deposited 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 [2].

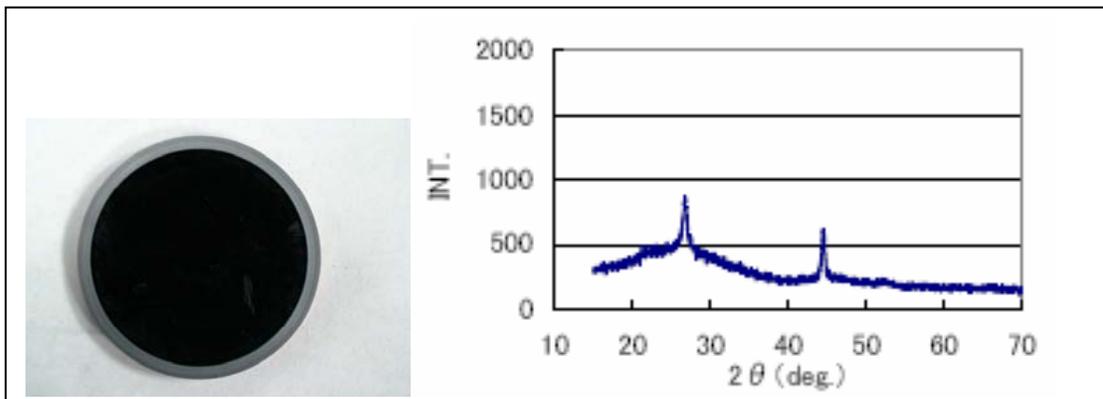


Figure 3: Cu-In-Ga-Se 25-17.5-7.5-50 at% and the As Deposited XRD

It is important to note that the as-deposited XRD of the sputtered CIGS layer shows the presence of structure and the characteristic peaks for $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$. As a quality step, the powder and target XRD scans are verified before shipping. The presence of peaks before any additional annealing or treatment step is a possible critical in-situ control point for Mr. Wen-Tsai Yen and Dr. Yi-Cheng Lin's process.

Discussion – CIGS (alloys/targets)

At the 2009 Society of Vacuum Coaters Techcon, Dr. Immo Kotschau [3] (head of R&D at Centrotherm Photovoltaics AG) voiced advances in the other side of the Cu-chalcopyrite based solar module arena. In another approach to hitting the low \$/watt and to minimize the total cost of ownership of a CIGS (Copper Indium Gallium (di)Selenide) turnkey, they are seeking to take advantage of a variant of Figure 1, Item #1 – Selenization of an Intermetallic. Over a year of focused effort has been devoted to developing and scaling several alloying methods at our New York facilities envisioned for use in such coating approaches.

One of the main components to this approach is the Cu-Ga alloy. With a glance at the Cu-Ga phase diagram [4], it is clear that keeping liquid Ga out of the cast part will be increasingly difficult as Ga content increases.

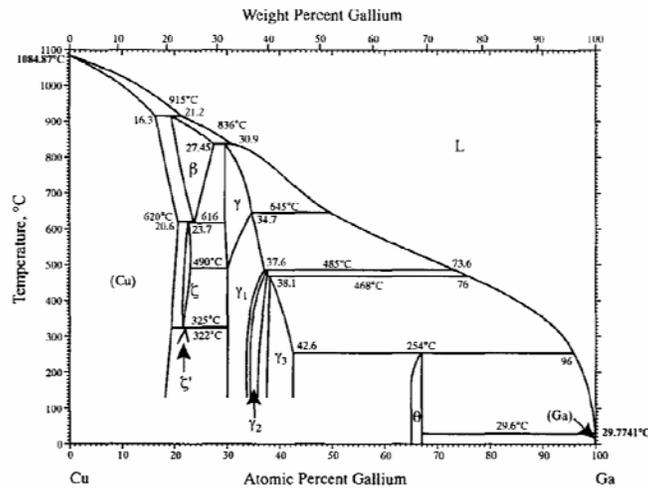


Figure 4: Cu-Ga Phase Diagram - Desk Handbook: Phase Diagrams for Binary Alloys

Where particle size distribution and powder density/structure and chemical stability dominate pressing considerations, we were able to take a fresh look on how to reach composition and productions techniques friendly to large volume such as continuous casting and cast/roll. Both New York facilities have extensive casting capabilities and experience. In order to get the best value going forward we focused on continuous casting and mold casting and hot roll as our two best options. The key to a successful sputtering product will be homogeneous composition, uniform and equiaxed grain structure and minimizing contamination. In order to make the most cost effective and longest life targets, we also knew that the target would have to be ductile enough to withstand cracking and be machinable.

In order to maintain the highest purity through the process, the elemental Copper and Gallium pure metals are placed in a Graphite Crucible, then into a Vacuum Induction Melting Furnace (VIM) and cast in Graphite mold with a Copper plate at the bottom. A custom cooling profile minimizes porosity and optimizes grain structure for machinability and solid phase purity. An important part of scale up is finding how to cut the cast ingot

in order to maximize the highest density, most uniform portion of the cast ingot to be rolled as the final product. For illustration, a typical Cu75Ga25 cast ingot is shown below. The purity remained consistent with standard higher purity processes from starting metals to final cast product.

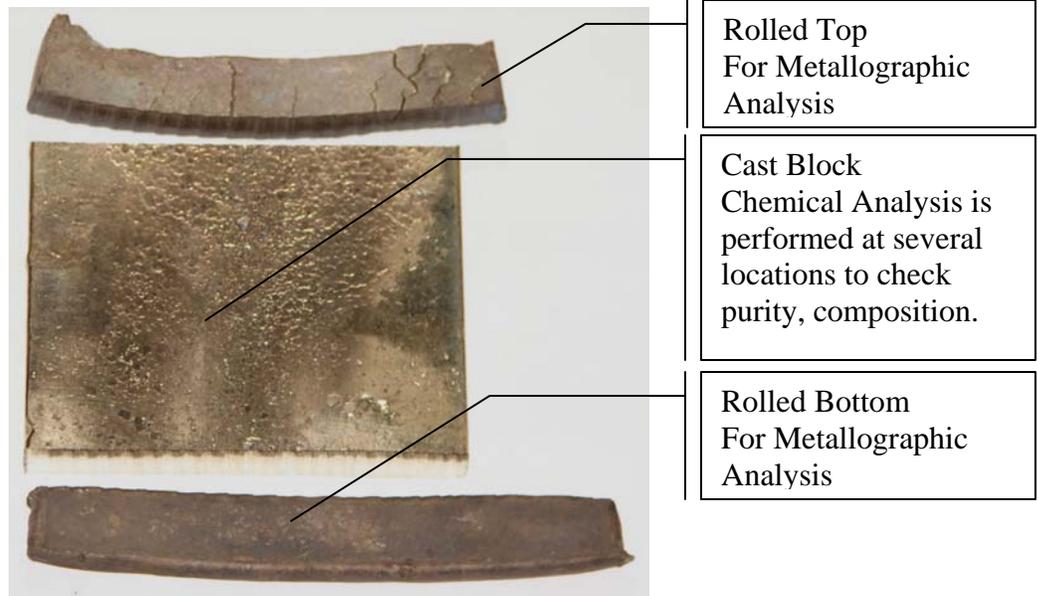


Figure 5: High Purity Cu75-Ga25 at% VIM Cast, Sectioned and Rolled Ingot (Critical Regions)

The process development cycle for such a process involves many runs and trials to optimize the rolling plan and to understand contamination control. It has become clear that the falling off point for Gallium content is 25% atomic. Above that, the Cu-Ga system becomes increasingly brittle and likely to contain liquid Gallium as an unwanted phase contaminant. For higher Gallium content requests, we employ a powder process (Cu70Ga30 at% for example) which is then pressed with techniques similar to the inorganic powders. The CuGa30 pressed parts are resistant to the cracking that we see in a CuGa30 cast product. The well behaved alloys at 25at% Gallium and below are good fits into various capacity expansion approaches within the organization. A project that lowers the cost and increases the size and thickness of the alternate powder varieties continues today. It is our goal to provide the size, performance and price required by the large sputtering cathodes that will make this approach to CIGS based Solar Cells successful.

Conclusion

Though the most robust development of non silicon Solar Module materials production capacity occurred in 2008, it was only the basis of more than seven years of detailed, thoughtful and careful exploration and development that enabled the growth. For all the solar materials, we have been able to use historical routes as solid basis for innovation. Rapid deployment of a novel microcrystalline CdS route coupled with special attention to particle size granular strength has yielded an excellent material for CdTe module manufacturing. This new material has also proven vital in making new CdS PVD targets where the high density and uniform structure help sputtering processes to yield reproducible thin films. Harnessing years of small scale chemical reactions led to a novel approach of making stable full Copper Indium Gallium (di)Selenide powders for direct use or as sputtering targets. These powder CIGS targets are complimented by Copper Gallium alloy targets for multistep PVD processes. It is our goal to offer reproducible, stable products that our customers can commercialize and control.

References

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