CIGS Deposition: A Crucial Challenge

Manufacturers are employing a wide range of evaporation deposition techniques during cell fabrication.

■ Robert G. Wendt

Recently, copper indium gallium diselenide ($CuIn_xGa_{(1-x)}Se_2$, or CIGS) thin-film photovoltaics have drawn the interest of several industrial organizations for commercialization. Much of this attention was sparked by the remarkable lab results that have been achieved in academic and institutional organizations around the world.

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CIGS currently exhibits the highest solar energy-to-electrical energy conversion efficiency of all the thin-film solar cell devices. In fact, the laboratory record efficiency of 20% - which is now reported as worldwide official results - now approaches that of multicrystalline silicon (20.4%).

The high-efficiency advancements allow CIGS to compete head-to-head with silicon from a performance standpoint, but with the potential of lower cost due to the thin-film nature of the solar cell device.

The basic CIGS structure is multilayered thin film deposited onto a carrier substrate made of glass, metal foil or polymer foil. The p-n semiconductor materials of CIGS and cadmium sulfide (CdS), respectively, are sandwiched between the molybdenum positive electrical back contact and the transparent conductive oxide (TCO)

negative electrical contact. Options for the TCO include aluminum-doped zinc oxide (AZO) or indium tin oxide (ITO).

Along with their high conversion efficiency, CIGS cells exhibit several other attractive features, including tolerance to a wide range of chemical compositions expressed in terms of the Cu/(In+Ga) and Ga/(In+Ga) stoichiometric ratios.

CIGS exhibits a high solar absorption coefficient, requiring a layer thickness of ~2.5 micrometers, compared to ~170 micrometers to ~250 micrometers for silicon solar cells, thus making CIGS less susceptible to commodity pricing of raw materials or to material shortages.

Additionally, CIGS does not exhibit the light-induced instability that is found in some other thin-film solar devices.

All thin-film solar cells also substantially benefit from the manufacturing technology developed in other thin-film arenas, including the flat-panel display, architectural plate glass and hard-disk-drive industries. Some of these industries have had to endure incredible price erosion and both responded by applying new, efficient technologies for both manufacturing tools and deposition.

Selenization

Although excellent CIGS laboratory efficiencies have been achieved,

translation of these results into successful manufacturing has proven challenging. There are several techniques currently under investigation for manufacturing CIGS cells, including the following methods:

■ selenization of metal precursors that are in the form of either stacked layers (Cu-Ga/In), nanoparticles, or inks consisting of Cu, In and Ga;

■ sputtering from metal selenide targets (Cu_2Se, In_2Se_3, $(In,Ga)_2Se_3$);

■ thermal evaporation from pure metals; and

■ hybrid processes involving a combination of the above.

Each option presents both benefits and challenges. Selenization of metal precursors was the focus within both the industry and academia in the early stages of CIGS development and commercialization, and this process resulted in consistent performance - with cells and modules exceeding a 10% conversion efficiency.

Conceptually, the process is straightforward and controllable: Sputter Cu or Cu-Ga, followed by sputtering In, react the Cu and In to form a Cu_xIn_y intermetallic, finished by reacting the intermetallic with either hydrogen selenide, hydrogen sulfide or both. The ink and nanoparticle processes are usually deviations of how the Cu and In are deposited.

However, selenization of metals typically requires long reaction times, ranging from several minutes to sometimes hours, which presents several manufacturing challenges - especially for deposition on moving metal or polymer foils. Each reaction operation has fundamental reaction rate constants that fundamentally control the CIGS reaction kinetics.

Sputtering from metal selenide targets offers simplification of the

selenization of metal precursors by avoiding some steps for forming Cu_XIn_Y intermetallics. Additionally, formation of the metallic selenide targets is straightforward and is offered by several target manufacturers.

But with this method, target stability can cause problems during the energetic sputtering process. During sputtering, selenium (Se) can be lost, and uncontrolled Cu_XSe_Y and In_XSe_Y species can form on the target sur-

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face, causing the chemical composition of the sputtered film to vary.

Overall, although successful results have been achieved using the selenization of metal precursors and sputtering from metal selenides, record conversion efficiencies achieved by researchers worldwide have been through thermal evaporation. There are two primary thermal evaporation techniques employed - one is a three-stage process, and the other is a two-stage process.

In the three-stage process developed by the U.S. Department of Energy's National Renewable Energy Laboratory, the first stage involves evaporating In, Ga and Se to deliver approximately 70% of total amount of In and Ga required in the final CIGS film.

During the second stage, In and Ga evaporation is terminated, and Cu and Se are evaporated while the temperature is increased to approximately 550 degrees C. During this stage, the film becomes Cu-rich, consisting of CIGS and Cu_XSe phases, and becomes partially liquid, which assists in diffusional kinetics.

In the third stage, the remaining In and Ga are evaporated in the presence of Se, bringing the final Cu/(In+Ga) ratio to 0.8 - 0.95, while the temperature is kept at 550 degrees C.

The overall result of the partial-liquid mixed phase during the second and third stages is to create very large CIGS grains that extend from the Mo back contact to the subsequent CdS buffer layer.

In the two-stage thermal evaporation process, Cu, In, Ga and Se are simultaneously evaporated, with the elemental species delivered to a substrate heated to approximately 550 degrees C.

During the first stage, Cu is delivered in excess of Ga and In (i.e., Cu/(In+Ga)>1), resulting in Cu-rich CIGS film growth. This step promotes the formation of the CIGS/Cu_XSe partially liquid, mixed phase.

In the second stage, the Cu evaporation rate is brought to zero, and the film reverts to a slightly Cu-deficient state with the Cu/(In+Ga) = 0.8 - 0.95. The resultant CIGS grain structure is very similar to what is obtained with the three-stage process described earlier.

Evaporation vessel

With both of these techniques, laboratory researchers are able to create CIGS solar cell devices with conversion efficiencies of over 15% and the record efficiency of 20%.

But while evaporation in the laboratory has resulted in excellent results, transition to manufacturing has been problematic. The primary challenges include the following:

■ *Temperature control.* Within the evaporation vessel, the temperature of the molten metal pool surface must be held very accurately. Minor fluctuations in temperature can result in large changes in the evaporation rate. For copper, a temperature change of only 20 degrees C - from 1,320 degrees C to 1,340 degrees C - results in almost a 50% increase in rate.

■ *High temperatures and material strength.* Heater design and the materials available to withstand the extreme temperatures of between 1,200 degrees C and 1,500 degrees C are limited. At the elevated temperatures, most high-temperature refractory metals typically used in small-area evaporation corrode and embrittle over very short time periods.

Furthermore, the presence of Se vapor that can react with the molten metal crucibles and surrounding thermal control shielding further makes material selection a challenge.

■ *Sensor technology capabilities.* Accurately controlling the temperature within a few degrees requires sensors to measure some physical property in the evaporation source. Again, exacerbated by the presence of Se, optical techniques have proven difficult.

Certain optical techniques work well for short runs in the laboratory, but over the long run, Se condensation inevitably occurs, and the sensor can no longer provide accurate data. That condition leaves contact thermocouples that have an error range that is sometimes greater that the temperature range of the molten metal pool to maintain good control.

Controlling atom trajectory

In principle, evaporation is a relatively simple process. A metal is heated to the point of melting and then further heated to the point that a vapor pressure of metal atoms above the molten metal pool is created. These vapor atoms either re-enter the molten pool or condense on nearby surfaces (in the case of CIGS, those surfaces include the vacuum chamber walls or the glass, metal-foil or polymer-film carrier substrate).

Several researchers have added to the body of literature of metal vapor pressures as a function of temperature. Successful evaporation of CIGS requires controlling the metal rate to achieve a uniform film across the desired area.

Open evaporation boats can be employed for a small area, but for larger areas, more metal would be deposited near the center of the molten pool than from the edges, because atoms leave the surface of a metal

Evaporation principles are described by low-pressure gas flow through an orifice. Within an evaporation system, there are two basic pressure regimes: free molecular flow (atom-to-atom collisions are rare)

facturing cost of each unit of operation - such as people, depreciation of equipment, facilities, material and indirect overhead - incrementally decreases.

To achieve throughput, there is a very compelling reason to attempt larger-area deposition; however, currently large-area deposition yields module efficiencies that are approximately one-half of the best laboratory devices.

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with a random trajectory. Statistically, more atoms will be condensed toward the center of the substrate than around the edges.

To control the flow and the trajectory of the atoms, restricting orifices or nozzles must be used between the molten metal surfaces.

Vapor emanating from the nozzle has a 3-D $\sin^2\theta$ vector distribution and, likewise, the indicant flux at the surface has a $\cos^n\theta$ where $n = 2$-3. Mathematical modeling can be conducted to create a series of overlapping vapor plumes to achieve a uniform film.

Knudsen equation

Important considerations include the nozzle-nozzle spacing, the nozzle diameter, the nozzle length and the number of nozzles. In many cases, a two-nozzle and three-nozzle source can achieve film uniformity.

within the vacuum chamber itself and transitional flow as the metal vapor moves from above the molten metal pool.

Flow regime can be determined by solving the Knudsen equation of $Kn = \lambda/\Gamma$ where Kn is the Knudsen number, λ is mean free path and Γ is the diameter of the orifice, or nozzle.

After determination of the Knudsen number flow, equations can be used to determine the flow rates as a function of the temperature of the molten metal pool surface.

In the PV industry, two key metrics define the economic viability of the final product: the area of PV created per unit of time, commonly referred to as system throughput, and the resulting performance of the PV. Both affect cost expressed in dollars per watt.

As performance increases, the watts per unit area improve, and the manu-

This discrepancy seems to be primarily due to the design and control of large-area deposition sources, and secondarily due to the introduction of currently unavoidable random defects.

There is a current trend in a few organizations to attempt to achieve improved throughput by very rapid deposition on small areas.

The objective of these processes is to achieve both an optimum combination of performance approaching laboratory results and throughput through rapid processing of wafer-size cells. Small-area deposition allows small, cylindrical, low-thermal mass sources to be employed and controlled. ✎

Robert G. Wendt is chief technical officer at XsunX Inc., a manufacturer and technology development company for thin-film photovoltaic modules. XsunX can be reached at (949) 330-8064 or info@xsunx.com