Toward Cd-free CIS modules

Stangl to offer a new, less toxic system for buffer deposition developed at Berlin-based institute


Christian-Herbert Fischer

Inventor of ILGAR: HZB senior scientist Christian-Herbert Fischer and his group designed a process for depositing Cd-free buffer layers for CIS modules.

Standard chalcopyrite-based solar cells are equipped with a thin cadmium-sulfide buffer layer. Even if this layer is just a few nanometers thick, it modifies the pn junction of the solar cells in a way that pushes efficiencies up to 5 percent higher. But there is a strong drive to move away from cadmium-containing compounds to less toxic alternatives. One such process was developed by the Helmholtz Center Berlin. And next year, Stangl, a leading supplier of equipment for buffer-layer deposition, will offer equipment based on this new spraying method.

A chalcopyrite solar cell, more commonly known as a CIGS or CIS cell, is a three- to five-element compound made of copper, indium, gallium, selenium and sulfur. Researchers in Germany are now developing a tool to improve the manufacturing of chalcopyrite solar cells with a cadmium-free process just as a handful of companies hope to introduce the first truly commercial volumes of CIGS cells into the marketplace.

Standard CIGS solar cells are formed by five layers deposited one after the other onto a glass substrate. A molybdenum layer, which serves as a back contact, is followed by a hole-conductor (p-type) CIGS film that absorbs the light. The heterojunction is formed by depositing a very thin – 10 to 50 nm – negative-conducting (n-type) buffer layer and a zinc-oxide (ZnO) bi-layer. This includes an intrinsic (i-) and a heavily doped n-ZnO, and is also used as the transparent front contact, in the case of monolithic integration.

Both record cells and most commercial photovoltaic modules use a cadmium sulfide (CdS) buffer layer. This layer is essential, as increased efficiencies of up to 5 percent absolute can be achieved. In laboratory scale, CdS is grown by chemical bath deposition (CBD). Standard recipes contain cadmium salt, thiourea as a sulfur source and ammonia in an aqueous solution. The thiourea hydrolyzes, and cadmium and sulfur ions recombine to form cadmium sulfide. The substrate is immersed in a cold solution, which is then heated at temperatures between 60 and 80 °C. Even if the chemical bath deposition of CdS is very reproducible and yields good cell performance on any chalcopyrite absorber in the laboratory, there are a lot of drawbacks concerning industrial up-scaling.

Of course, large amounts of the carcinogen thiourea and hazardous cadmium are undesirable. On top of that, according to buffer expert Christian-Herbert Fischer, a senior scientist at Helmholtz Center Berlin (HZB), »Often just a small window for process parameters, like pH-value, concentration, temperature and reaction time allows useful results. Additionally, thiourea from various suppliers and even different batches from the same supplier can lead to CdS layers with different material properties.« Fischer is the inventor of a novel deposition technique: the Ion Layer Gas Reaction (ILGAR), an alternative chemical low-cost aerosol-assisted deposition at atmospheric pressure (AACVD). The Spray-ILGAR method for the indium sulfide (In_2S_3) buffer layer deposition is a two-step chemical process based on simple reactions (see graphic). In this case, the precursor solution, a mixture of ethanol (EtOH) and indium chloride ($InCl_3$), is converted into an aerosol using an ultrasonic source. The generation of ultrasonic spray mist has several advantages compared to gas pressure sprayers: no plugging of a nozzle, smaller drop size – especially for frequencies in the MHz range – and a narrower size distribution leading to high-layer homogeneity. The mist is pushed forward by an inert carrier gas, such like nitrogen (N_2).

In the first step, the alcoholic $InCl_3$ solution is sprayed onto the substrate. The In_2S_3 buffer layer is formed by sulfurization in a hydrogen sulfide (H_2S) atmosphere. Both steps take place at a low substrate temperature of about 200 °C. In order to avoid degradation of the CIGS absorber, temperatures below 250 °C have to be chosen.

»The processed In_2S_3 layers contain small amounts of chloride – less than 5 percent,« says co-inventor Nicholas Allsop. The spray and reaction cycle is repeated until the desired thickness of the In_2S_3 buffer layer is reached. »Just 44 ml of indium solution is needed for depositing a 20 nm thick buffer layer onto a 60 × 100 cm large substrate. Our aim is to deposit a 20 nm thick In_2S_3 buffer layer using a maximum of three cycles,« adds Allsop.

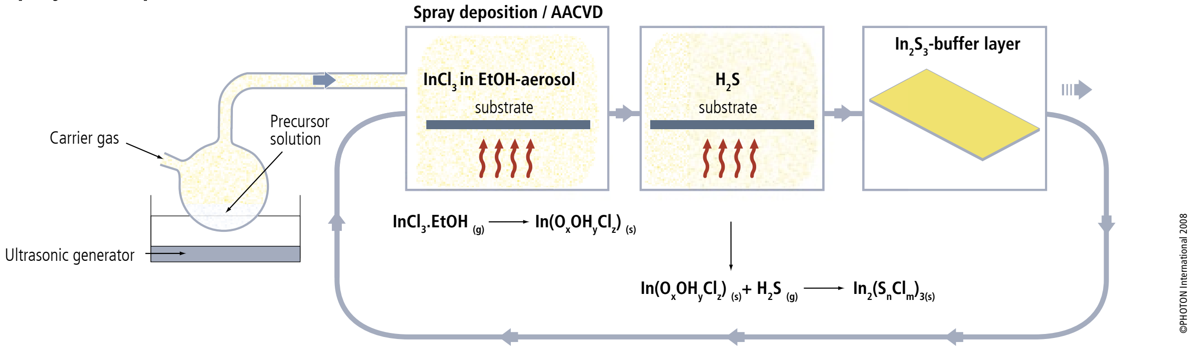
On the other hand, CBD requires dipping of commercial substrates of 60 × 100 cm or 110 × 130 cm into huge amounts of solution. Additionally, although the CdS layer is needed just on one side of the substrate, it is deposited onto both sides of the glass, meaning that the back side of the glass has to be cleaned. Another problem associated with CBD methods is the comparatively low material yield of less than 10 percent.

Germany-based Stangl Semiconductor GmbH is the only known supplier of equipment for buffer-layer deposition. At the end of the 1990s, the company designed a patented wobbling process in order to achieve single-sided wet chemical CdS coating using just one-twentieth of the solution needed for buffer deposition using chemical baths. In this case, a lid forms a liquid-tight seal with the edges of the substrate. Therefore, just one side of the substrate is covered with CdS-solution in order to minimize the volume needed for homogeneous deposition of the buffer layer. The substrate is mechanically agitated by a rocking mechanism. Nevertheless, expensive deionized water (di-H_2O) plants for rinsing and drying steps are still needed, resulting in 10 to 15 minute durations, depending on the process. Still, Stangl's fully-automated »dry-in/dry-out« system from the Tenuis line also offers a Cd-yield of less than 10 percent. The base equipment includes eight wobbling systems and is priced between €1.3 and €3 million ($1.9 and $4.3 million) depending on the substrate size and throughput.

However, according to Stangl's product manager, Jens Eckstein, »As the size of the substrates used in thin-film production increases – from 60 × 100 cm to 110 × 140 cm – and the tact time decreases, there is an increasing need for new methods of buffer-layer production.«

Since the ILGAR technique achieves similar efficiencies compared to cadmium sulfide buffer layers on various CIGS absorbers, it is a promising alternative. Additionally, explains Allsop, »At least a 30-percent deposition yield of indium is achieved.« And throughput is no issue any-

Spray-ILGAR process



more, he says, since a line speed of 1 m per minute has been estimated, and by adding hydrochloric acid (HCl) to the waste, the $InCl_3$ precursor can be recovered.

Beside three times better material yield and easy recovery of the residuals compared to the existing Cd-based technology for buffer deposition, a further advantage of ILGAR is the deposition of mixed layers containing, for example, zinc sulfide and indium sulfide ($ZnS:In_2S_3$). The deposition of mixed layers is made possible by the use of different precursors for the sub-layers. A CBD process cannot offer that possibility. But ILGAR can do more than that: »i-ZnO deposition is also possible using ILGAR,« claims HZB's senior scientist Sophie Gledhill. If this layer can be deposited in the same way as the buffer layer, the interruption time by changing handling between wet and dry processes can be avoided. This is very important because until now this layer has been deposited using a sputtering technique. Therefore, the substrate had to be unloaded from the vacuum system in order to apply the P2 laser scribe (see PI 8/2008, p. 258), before finishing the cell with the n-ZnO layer. But this is only the next step – for now, the process is ready to start replacing the CdS window.

And Stangl is obviously convinced that ILGAR is the right process for such a move: it has signed an exclusive license for building manufacturing equipment for the ILGAR process, which it plans to start offering for series module production by the end of 2009. A price for the system is not yet available. Currently, only a prototype exists. However, Stangl's Jens Eckstein is certain, »By using the ILGAR method, investment costs amounting to millions will be avoided since you get rid of di-H_2O.«

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