

Development Situation and Study Trend of Cu-III-VI Compound Semiconductor Solar Cell

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As environmental and energy resource concerns have increased, greater stress has been placed on development of renewable energy resources such as photovoltaic electric generators. A polycrystalline thin film of copper indium diselenide (CuInSe_2 , or CIS) compound semiconductor has a great attractive as a potential material for the terrestrial photovoltaic generation.

Let's us look around the development situation and study trend of CIS solar cell.

It has extremely high absorptivity that allows 99 % of the available incident light to be absorbed in the first micron of the material. But that is not the only reason that copper indium diselenide is attractive for PV devices. It also has shown very good stability in outdoor tests, an important criterion for commercialization. Recent outdoor tests show no degradation in this material after many years.

Laboratory cells of CIS recently exceeded 18.8 % (1999/02) efficiency by NREL. This means that the best CIS cell has exceeded the best efficiency of a polycrystalline silicon cell (18.6 %). This progress bodes well for meeting the year 2001 cell-efficiency goal of 20 %. And $3,651 \text{ cm}^2$ submodules achieved an efficiency of 11.8 % (1998/09), generating more than 36 W of power by Simen Solar Industry. After two decades of R&D, CIS has been introduced to the market, its modules consistently reaching stable efficiencies

Table 1. Highest Efficiency of Solar Cell by Material

Material	Efficiency (%)	Area(cm ²)	Research organization
Single <u>Si</u> Solar Cell	24.0	4.0	Australia UNSW
	Module	22.3	787
Poly <u>Si</u> Solar Cell	18.6	1.0	United Georgia Tech
	Module	15.3	1027
a- <u>Si</u> Solar Cell	11.2	0.25	United Solar
	Module	8.9	1200
<u>CuInSe₂</u> Solar Cell	18.8	0.414	United NREL
	Module	11.8	3651
<u>CdTe</u> Solar Cell	16.4	0.25	United NREL
	Module	10.5	830

Table 2. Development Situation of CIS Solar Cell

	Material	Efficiency (%)	Report Organization
Cell	Cu(In,Ga)Se ₂	18.8	NREL
	Cu(In,Ga)Se ₂	17.6	EUROCIS
	Cu(In,Ga)Se ₂	17.6	Matsushita
Module	Cu(In,Ga)Se ₂	11.8	United Siemens Solar
	Cu(In,Ga)Se ₂	7.7	EPV
	Cu(In,Ga)(S,Se) ₂	14.1	Showa Shell
	Cu(In,Ga)Se ₂	13.9	IPE, ZSW

greater than 11 %-beating the goal set in the last five year plan by more than a year. So, At least one major company expects to comercialize CIS soon.

Researchers are investigating ways in which to push efficiencies even higher, by exploring the chemistry and physics of the junction formation, and by examining concepts to allow more of the high energy part of the solar spectrum to reach the absorber layer. They are also trying to drop costs and facilitate the transition to the commercial stage by increasing the yield of CIS modules.

The layers of materials in CIS cells can be made by several different processes that were developed in the computer related thin film industry. All of these methods are well established commercially in various industries.

1) One of the most popular preparation methods for the CIS layer is evaporation. Small amounts of each of the elements are electrically heated to a point where the atoms vaporize. They then condense on a cooled substrate to form a CIS layer.

2) Another common method is sputtering. High-energy ions bombard the surface, driving off atoms of the target material. These then condense on a substrate to form a thin layer.

3) Another technique used successfully to deposit Copper Indium Diselenide on a substrate is spray pyrolysis. In this method, solutions of the salts of the necessary elements are sprayed onto a hot substrate. They react under the elevated temperatures to form the required CIS layer, while the solvent evaporates.

4) Electrodeposition can also be used to form the CIS layer in the same way gold is plated onto jewelry. Passing electricity through a solution containing ions of the required elements causes them to be deposited out of solution onto an electrode, which acts as substrate.

Table 3. Fabrication Methods of CIS Solar Cell

Process	Growth Mechanism
Coevaporation	Vapour-solid growth
Advanced coevaporation	Vapour liquid solid growth
Sequential deposition	Diffusion, liquid-solid growth
Selenization (Se)	Liquid-solid growth, diffusion
Selenization (H ₂ Se)	Reaction-diffusion intermetallics
Selenization (RTP)	Diffusion-reaction
Sputtering	Gas phase-solid
Annealing of stacked element layers	Solid state diffusion
Screen Printing	Solid state diffusion with flux
Electrodeposition	Ions from liquid-solid
MOCVD	Metalorganic precursors
Atomic layer epitaxy on CaF ₂	Vapour-solid growth

5) CIS layers can also be made by using one of these methods to deposit only the copper and the indium. This is followed by a treatment with hydrogen selenide gas to add the selenium. This approach is considered the most likely to lead to commercial CIS

products.

The most common material for the window layer in CIS devices is cadmium sulfide(CdS); sometimes zinc is added to improve the transparency. Adding small amounts of gallium to the absorbing CIS layer boosts the band gap of CIS, which improves the voltage and therefore the efficiency of the device. For the last couple of years, university and industry groups have focused their work on copper indium gallium diselenide (CuInGaSe₂ or "CIGS") films and devices. Ga alloying made it much easier to produce cells with higher open-circuit voltages, although short-circuit current densities have frequently suffered with the alloying. Most groups obtained their own champion cell results with absorber layers having an effective band gap of 1.1 to 1.2 eV. This corresponds to a Ga/(Ga+In) atomic ratio of 25 % to 30 %. In many instances, the Ga content of the absorbers is graded, either accidentally (the Ga tends to accumulate near the rear or Mo contact of the absorber) or deliberately, by introducing a Ga profile. Several Ga profiles, as well as absorbers with more or less Ga grading, have allowed researchers to produce cells with high efficiencies. In addition, current density enhancement, Mo back-electrode and ZnO junction buffer(CdS)-less of CIGS have been also researched to improve the solar cell efficiency.

The strength of CIS is also its problem. It is efficient because it is complex, but costs/manufacturability are impacted by complexity. Copper indium diselenide is really CIGS or even CIGSS (with sulfur), and layers of these complex compounds are made more complex by gradations designed for better cell performance. Fortunately, and against all intuition, some of the added compositional complexity has actually led to greater flexibility in processing. Several groups report that adding gallium widens the window of compositional variation within which excellent cells can be made. This issue, the complexity of high-efficiency CIGSS cells, will have to be addressed by the manufacturers. Some of the work to explicate CIGS growth mechanisms should be of help.

CIS cells have a band gap of 1.0 eV. Vaibly by themselves, they can also be used with a higher bandgap material in a multijunction device. One company is exploring the commercial possibilities of a multijunction device employing amorphous silicon of 1.7 eV on top of CIS. Laboratory multijunction devices have achieved 16 % efficiency and

submodule of 12 % efficiency. CIS is a versatile material being explored for use a bottom cell in tandem with top cells of other materials, such as CdTe and GaAs, both of which have band gaps of approximately 1.43 or 1.44 eV. In fact, recently an experimental multijunction device that used GaAs for the top cell and CIS for the bottom cell achieved an efficiency of 25.8 %. As like CIS/CuGaSe(CGS) tandem device using Cu-III-VI compounds each other also have been studied these days.

Some researchers are investigating the use of nanoparticle-based materials and process technologies as precursors to improved materials employed in thin film devices based on cadmium telluride, cadmium sulfide, tin oxide, and copper indium gallium diselenide. When combined with ink-based deposition technologies (spray or screen printing), nanoparticles may be able to produce films with very high quality yet at relatively low cost. The unique properties of nanoparticles may also enable us to use substantially lower sintering temperatures and produce some unique device configurations.

Thin film devices based on CIS are the best performing and most durable. The modules are stable and the standard against which all other thin film modules are measured. Why CIS modules are not yet commercially available? Process scale-up to high-yield, large-area manufacturing has been difficult. CIS does not draw on the traditional knowledge associated with mainstream semiconductors such as silicon or gallium.

Nevertheless, good stability and proven high efficiency make CIS a strong thin film. Manufacturability issues that run the gamut from fundamental properties through actually settling on a viable process make commercialization still problematic. In the long term, the technology is as promising as any, and it is likely that the existing manufacturability issues will, one by one, give way to technological solutions.

Thank you for joining me.