US DOE NREL
THIN FILM PV PARTNERSHIP

NREL World Record Thin-Film Cell Efficiency

R&D Partner

Thin-film photovoltaic (PV) cells are being developed because they have the potential to be made from pennies' worth of active material. But for two decades, they have been viewed as performing too poorly—in terms of converting sunlight to electricity—to be of value. Now, building on a tradition of shared progress with the thin-film community, the National Renewable Energy Laboratory (NREL) has fabricated thin-film solar cells in which sunlight-to-electricity efficiencies rival the best of conventional, more costly PV cells (Figure 1). NREL's 17.7%-efficient cell made in 1996 is within one percentage point of the best polycrystalline silicon cell efficiency (18%)—a parity of performance once thought impossible.

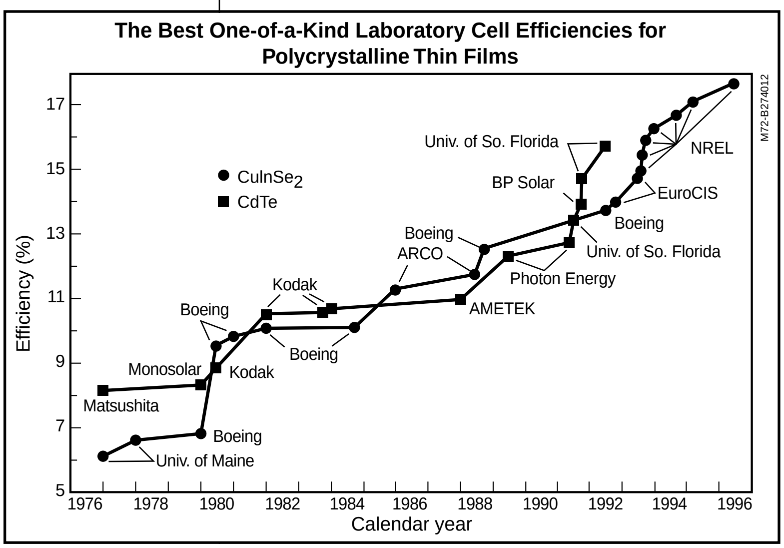

Figure 1. The best one-of-a-kind laboratory cell efficiencies for thin films now approach the best efficiencies produced by classic polycrystalline silicon cells, and are the basis for expecting thin films to reach the performance goals needed for truly low cost.

Achieving this goal is more than symbolic. It indicates that thin films, with active semiconductor layers thinner than a human hair, have an excellent chance of someday achieving performance and cost goals that would make PV a source of more than 10% of the electricity used on this planet. For example, combining the cost potential of thin films (estimated to be about $50/m^2) and the efficiency of thin-film modules, and projecting from current laboratory cell progress (i.e., modules over 15% efficient), a module would cost of about 30 cents/watt (W) (= $50/m^2/150 W/m^2). This is ten times less than PV's current price (about $4/W). System costs for thin-film-based PV (with all other costs included) could be between $1 and $1.5/W (compared to today's $6–$10/W). This "price break" would result in opening PV markets orders of magnitude larger than today's markets (e.g., daytime peak and intermediate power shaving in developed countries, and rural electrification in developing countries).

Background

NREL's progress in thin-film cell efficiency builds on the work of several excellent research groups. In the early 1980s, Boeing (Seattle, WA), pioneered a new kind of PV cell based on copper indium diselenide ($CuInSe_2$). Later simply called CIS (even when gallium and sulfur are added), this compound displayed some very attractive qualities: sunlight absorption that was the strongest of any PV material (absorbing over 90% of available light within 0.2 microns), and the capability of producing high-efficiency cells in initial experiments at the University of Maine and Bell Labs. Boeing researchers, funded by the U.S. Department of Energy (DOE)-sponsored Thin-Film Program at NREL, pushed the efficiency of CIS-based cells above 10% in 1980, making CIS the first thin film to surpass this milestone. Others, including NREL, began work in CIS at about that time. During much of the 1980s, efficiencies plateaued as researchers tried to transfer these cell achievements to larger areas appropriate for commercialization. Meanwhile, new insights were gained, and new groups, such as a European consortium of universities called EuroCIS, began to have an impact. Building on the Boeing work, EuroCIS and NREL made significant efficiency advances. EuroCIS reached almost 15% in 1993. Then NREL made rapid, almost unheard of progress, surpassing 15% by 1994 and reaching 17.7% in 1996.

The NREL Process

The NREL process for making CIS films builds on two principles: simplification and flexibility for potential manufacturing ease, and insights into material growth to achieve these desired simplifications. A key aspect was being aware that combining Cu, In, Ga, and Se can result in a variety of end products (combinations of elements, binaries with Se, and off-stoichiometric ternaries and multiternaries). NREL devoted much research to understanding the proper combination of compositions, gradients, and temperatures needed to make quality films. A set of approaches emerged that allows us to tailor both the process and the device designs for simplicity and high efficiency.

Fabricating device-quality CIS films requires a Cu-rich layer to produce good morphology, and a Cu-poor surface layer to make a high-performance junction. The first need can be achieved by adding extra copper. By raising the temperature at which films are completed to about 550°C, the Cu-rich precursor can be melted. Adding In (usually with Se) then results in the desired surface layer. In some cases, NREL discovered a simplified version of this process that allowed relatively poor starter films to be

Pictorial Description (Start ---> Finish)	Chemical Reaction Path	Manufacturing Issues
(1) **17.1%** - Concurrent delivery of the metals in the presence of Se (2-stage)		
Start: $(In,Ga)_ySe$ / Cu-rich $Cu(In,Ga)Se_2$ / Mo / soda-lime --> Finish: Graded $Cu(In,Ga)Se_2$ / Mo / soda-lime	• Cu + (In,Ga) + Se $\xrightarrow{500°C}$ $Cu(In,Ga)Se_2 + Cu_xSe$ • CIGS : Cu_xSe + (In,Ga) + Se $\xrightarrow{550°C}$ **$Cu(In,Ga)Se_2$**	• Stage 1 Cu-rich precursor can be easily synthesized • Stage 2 conversion does not require Cu
(2) **16.8%** - Sequential delivery of Metals in the presence of Se (3-stage)		
Start: Cu_xSe / $(In,Ga)_ySe$ / Mo / soda-lime --> Finish: Graded $Cu(In,Ga)Se_2$ / Mo / soda-lime	• $(In,Ga)\ Se_x + Cu_xSe$ + Se $\xrightarrow{500°C}$ $Cu(In,Ga)Se_2 : Cu_xSe$ • CIGS : Cu_xSe + (In,Ga) + Se $\xrightarrow{550°C}$ **$Cu(In,Ga)Se_2$**	• Separates Cu & (In,Ga) delivery • Simplifies in-situ process control • Conducive to large-area deposition technology
(3) **15.1%** - In-line / Variable Flux Process (1-stage)		
Start: Variable (Cu, In, Ga, Se) Flux / Mo / soda-lime --> Finish: Graded $Cu(In,Ga)Se_2$ / Mo / soda-lime	• <u>Cu</u> + (In,Ga) + Se $\xrightarrow{500°C}$ $Cu(In,Ga)Se_2 : Cu_xSe$ • CIGS : Cu_xSe + Cu + <u>(In,Ga)</u> + Se $\xrightarrow{550°C}$ **$Cu(In,Ga)Se_2$**	• Designed for in-line, continuous large-area deposition • Process design flexibility
(4) **12.6%** - Sequential delivery of metals without Se followed by compound formation in Se vapor (2-3 stages)		
Start: Cu+Ga / Cu+In / Mo / soda-lime + Se (g) --> Finish: Graded $Cu(In,Ga)Se_2$ / Mo / soda-lime	• Cu,In + Cu,Ga --> $Cu_xIn + Cu_yGa$ + Cu + In + **Se** $\xrightarrow{300°C}$ $Cu_xSe + (In,Ga)_ySe$ + **Se** $\xrightarrow{450°C}$ **$Cu(In,Ga)Se_2$**	• Separates deposition processes from thermal/chemical processes • Utilizes established large-area metal deposition technology

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Figure 2. NREL's progress builds on an in-depth understanding of how $Cu(In,Ga)Se_2$ can be made by a variety of routes.

deposited at low temperatures, followed by only one critical, high-temperature step. Fourteen-percent-efficient cells have now been made by such an approach using electrodeposited precursors. Several of the NREL approaches, which build on how CIS forms, are outlined in Figure 2.

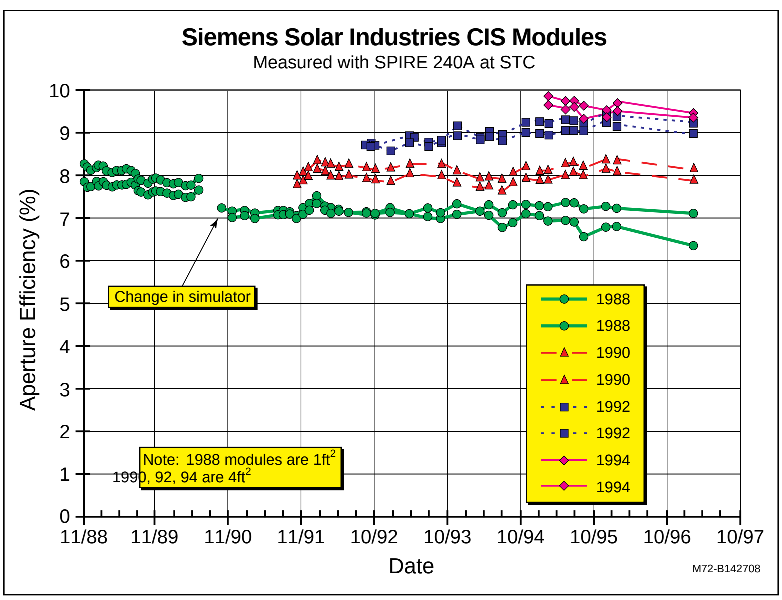

Figure 3. ARCO Solar's (now Siemens Solar Industries) CIS modules are remarkable for their stability over the past 8 years and are the benchmark for all other thin films.

Overcoming Obstacles to Commercialization

Thin-film devices based on CIS are the best performing and most durable. Figure 3 shows data from an 8-year outdoor test of early ARCO Solar (now Siemens Solar Industries) CIS modules. The modules are stable and the standard against which all other thin-film modules are measured. Yet CIS modules are not yet commercially available. Why not? 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 arsenide. Thus, one of NREL's research goals is to extend the knowledge of CIS materials and processes in parallel with progress in cell performance. Through NREL's sophisticated approaches to making high-efficiency CIS, researchers know why and how various elemental and compound constituents (Cu, In, Ga, Se, S, and their binary alloys) combine to form quality CIS. Researchers know at what temperature reactions occur and which steps can or cannot precede others (due to undesirable alloying or reaction chemistries). NREL has ventured into the realms of high efficiency (like a latter-day Columbus) while charting the unknown scientific waters so that future manufacturers can use these maps to bring commercial success.

Parallel to advancing the technology, NREL has sought new ways of helping the CIS community in the United States. Early on, NREL scientists visited Solarex, Siemens Solar, ISET, the University of Delaware, and EPV to demonstrate our technology. These extended, usually "hands-on" visits resulted in both immediate and longer-term progress.

NREL has patented its CIS technology and is seeking favorable commercialization avenues. All U.S. CIS companies are discussing with NREL the future of NREL patents and licenses. Several licenses and a number of working agreements have been signed. Others are being negotiated.

A major vehicle for ongoing CIS technology transfer and progress is the Thin-Film Partnership and its teamed research. NREL researchers are team leaders and strong participants in the Partnership's National CIS Research and Development (R&D) Team. NREL's CIS technical skill, combined with its intense commitment to NREL's mission—the success of PV on a global scale—makes the CIS Team an exciting arena for further progress.

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