

**SERI/TP-211-3501
UC Category: 270
DE89009425**

Thin Film Photovoltaics

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May 1989

**Prepared for the 24th
Intersociety Energy Conversion
Engineering Conference,
Washington, D.C.,
6-11 August 1989**

Prepared under Task No. PV940301

**Solar Energy Research Institute
A Division of Midwest Research Institute**

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**Prepared for the
U.S. Department of Energy
Contract No. DE-AC02-83CH10093**

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Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A02

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ABSTRACT

Thin films are considered a potentially attractive technological approach to making cost-effective electricity by photovoltaics. Over the last twenty years, many have been investigated and some (cadmium telluride, copper indium diselenide, amorphous silicon) have become leading candidates for future large-scale commercialization. This paper surveys the past development of these key thin films and gives their status and future prospects. In all cases, significant progress toward cost-effective PV electricity has been made. If this progress continues, it appears that thin film PV could provide electricity that is competitive for summer daytime peaking power requirements by the middle of the 1990s; and electricity in a range that is competitive with fossil fuel costs (i.e., 6 cents/kilowatt-hour) should be available from PV around the turn of the century.

INTRODUCTION

Photovoltaics is considered by some to be a major option for producing energy on a large scale without pollution. However, implementation of this ambitious aim has been hampered by cost. Historically, photovoltaic electricity has cost orders-of-magnitude more than conventional electricity. In fact, this high cost has led some critics of photovoltaics to claim that it would never be practical. Given this background, one must consider all attempts to lower the cost of PV electricity to be of major significance.

One of the key technical ideas for substantially reducing the cost of photovoltaics is the idea of "thin films." Put simply, this means the use of thinner photovoltaic materials aimed at two major cost reductions:

- o Reduced materials costs
- o Reduced processing costs

Reduced materials costs come about because thin films are about 50 to 100 times thinner than previous solar cell options, e.g., crystalline silicon cells. Reduced processing costs result from the high-throughput methods adopted for making large-area-thin films. These can raise unit volumes by an order-of-magnitude over previous approaches.

Another advantage of thin film photovoltaics is the possibility of making on a continuous basis very large areas of interconnected cells--called PV modules. This is in contrast with previous silicon cells, which were relatively small and had to be individually wired together into practical sizes.

These basic ideas about the potential cost reductions associated with thin films have been around almost since the birth of practical solar cells in the 1960s. However, their practical incorporation into an effective PV technology has taken about twenty years.

In the 1960s and since, PV was used in space to power satellites. It was expensive (about \$100 per kilowatt-hour) but reliable and lightweight, qualities of great value for space applications. The idea of using PV on Earth for practical power generation was considered, but it was regarded as far fetched because of the immense cost reductions that were needed.

The few who held out hope for terrestrial PV had already formulated the thin film option as one possible avenue towards much lower costs. In fact, among the earliest practical PV cells (Shirland 1966) was a thin film cell made of a combination of two semiconductors: copper sulfide (Cu_2S) and cadmium sulfide (CdS). These cells were about 20 microns thick, in contrast to 'conventional' crystalline silicon cells, which were 300 micron-thick silicon wafers. The copper sulfide cells were the first thin film PV devices.

The $\text{CdS}/\text{Cu}_2\text{S}$ cells were the first attempt to actualize the potential of thin films. But their development was disappointing, ameliorated by the lessons learned along the way. Among these, copper sulfide cells were able to demonstrate some key progress needed to become useful: a reasonable efficiency of 10% for laboratory cells was reached and low-cost film fabrication processes were investigated (Bragagnolo et al. 1980). But they failed in one key aspect: stability. The Cu_2S material was itself structurally unstable. During operation, two effects were observed: the material's crystal structure changed (especially if it was exposed to the environment); and poorly bound copper atoms migrated and formed shunts. These instabilities caused substantial performance losses and eventually caused the abandonment of the Cu_2S technology (although some work continues in pockets in Europe and India).

Before the copper sulfide technology had been dropped, some companies had made the first large-area, thin film modules--about a square foot in size--and had begun thereby to understand the steps of designing and building these important thin film products. Demonstration of the practicality of thin-film modules was an important contribution of the copper sulfide technology.

By the time that Cu_2S was dropped (early 1980s), several other thin films had already made enough progress to step into its place. Three of them--amorphous silicon (a-Si), copper indium diselenide (CuInSe_2), and cadmium telluride (CdTe)--had already achieved approximately 10% efficiency in the laboratory for small-area cells. The achievement of 10% efficiency is considered the mark of a leading thin film candidate because cost calculations have shown that a thin film can be cost-competitive with conventional electricity when modules made from it reach 15% efficiency. The rest of this paper covers the subsequent developments in these three thin films (a-Si, CuInSe_2 , and CdTe) (Ullal et al. 1988).

There is one other important category of thin films which is being actively researched today: these can be called "crystalline thin films," and are based on silicon and gallium arsenide. Polycrystalline silicon films of under 50 microns thickness have been used to make efficient cells on a low-cost substrate such as ceramic. One such approach by Astrosystems Inc has resulted in reported efficiencies of 15.6%. This approach has the potential of achieving high-efficiencies while markedly reducing cost over previous crystalline silicon technologies. Another promising "crystalline" thin film approach uses single-crystal cells made of gallium arsenide (GaAs). Single-crystal cells have always been more efficient than polycrystalline cells; their cost has been the limiting factor. In the approach pioneered by Kopin Corporation, GaAs single-crystals are grown and then peeled from a reusable single-crystal GaAs substrate. This allows for a major cost reduction. These so-called "CLEFT" cells have had SERI-measured efficiencies of 21.5% (4 cm^2) and 22.3% (1 cm^2). The remaining issues of this technology concern the size of the reusable GaAs substrate and the frequency with which it can be reused; as well as handling CLEFT films in manufacture and integrating them into larger-area panels.

For the sake of brevity, this paper will not discuss these approaches further. Other ways of getting to low-cost PV--flat-plate silicon cells and high-efficiency concentrators, and hybrid thin film cascade cells--are also not covered. A multiplicity of promising approaches is one of the strengths of photovoltaics.

THE DOE GOALS

The Department of Energy (1987) has provided a context for the progress of thin films by roughly calculating the goals that a thin film needs to achieve to produce electricity on a system level that would cost the consumer about 6 cents per kilowatt-hour. It is well to fix these goals in mind when considering the progress of thin films, for they form the outline of the qualities that thin films need

to reach to become major global suppliers of electricity. The DOE goals are:

Performance: 15% sunlight-to-electricity conversion for modules (1000 cm^2 and larger);

Cost: On a module area basis, less than \$50 per square meter;

Durability: A thirty-year lifetime outdoors.

The DOE's calculations say that if these goals can be met, a PV system can be constructed (including all other costs such as land area, support structures, and power conditioners) that will provide the consumer with electricity at 6 cents per kilowatt-hour. Meanwhile, high-value power applications are available now. These markets will continue to expand as PV costs decrease and performance increases.

AMORPHOUS SILICON

The first commercially successful thin film was based on a semiconductor called amorphous silicon, or a-Si. Amorphous silicon, unlike crystalline silicon, has no crystalline or ordered atomic structure. It absorbs sunlight very strongly and has electronic properties that make it useful for thin film PV, as well as for large-area electronic applications such as flat-plate LCD screens.

Among the US pioneers in a-Si were researchers at RCA (later at Solarex; Newtown, PA), at Energy Conversion Devices (Troy, MI), and subsequently at Chronar (Princeton, NJ), and ARCO Solar (Camarillo, CA). Japanese companies like Sanyo, Fuji, Taiyo Yuden, and Kanekafuchi were also deeply involved in a-Si development. Although US researchers invented the a-Si technology, the Japanese a-Si corporations were responsible for an important evolution in thin-film PV, the initiation of a consumer market for small a-Si cells in 1980. These cells were used to power microelectronic devices such as calculators and watches.

The success of a-Si caused decision-makers in the Japanese and in the American national PV programs to fund government-industry 'initiatives' to develop a-Si modules of practical sizes for power production. These cost-shared government-industry partnerships, which began in the early 1980s, have since become recognized as an important strategic approach to developing new PV technologies.

Progress in the scale-up of a-Si devices to larger areas for practical use has been steady during the 1980s. After demonstrating 10%-efficient laboratory cells, larger, interconnected cells--called submodules--of 100 and then 1000 cm^2 were fabricated. Efficiencies of these have reached about 9%-10%. A semitransparent a-Si module has been made by ARCO Solar with efficiency of 9.4% for about 900 cm^2 . Very large modules of up to 1.2 m^2 have also been made (Chronar). The numerous processes needed to make the entire a-Si module have been incorporated

into reliable manufacturing lines that are almost fully automated. New products such as a-Si modules to power patio and sign lights have been introduced and have become relatively popular, bringing a welcome stream of revenue to these entrepreneurial companies.

A well-recognized light-induced stability problem in a-Si films has limited their acceptance in some critical PV applications. After a few months, a-Si modules deployed in the field stabilize at 70%-90% of their initial efficiencies. Manufacturers recognize this problem by pre-aging modules or under-rating the name-plate power that the consumer might expect from them. Some manufacturers now guarantee their long-term performance. For example, Solarex guarantees 80% of the initial rating of their newer modules for two years.

Much research has been done to understand and eliminate this light-induced loss. It appears that the instability is a fundamental one, basic to the nature of a-Si. Fortunately, several important modifications of a-Si devices have led to reduced losses from the light-induced effect. For instance, it was found that the losses were less if the a-Si layers were made thinner--approximately 0.2 microns versus 0.5-0.7 microns. However, these thinner a-Si layers are partially transparent to sunlight. They would normally allow a portion of the available light to pass through them without opportunity to convert it to electricity. This would result in a loss of efficiency. In order to improve the efficiency of thin a-Si devices, manufacturers are optimizing the light utilization within them by using highly reflective back contacts and textured, light-trapping front transparent contacts. Both of these allow the use of thinner layers without much loss of cell current.

Another way to minimize light losses in thinner, more stable cells is to adopt a different cell structure called a cascade cell. Cascade cells are conceptually quite simple. They are the stacking of one solar cell on top of another so that the sunlight that passes through the top cell can be used in the bottom cell. Single-junction a-Si cells have a practical efficiency limit of about 14%, while multijunctions may reach 18%-20%.

The use of cascade cells has resulted in the production by Energy Conversion Devices of a three-cell a-Si device with 13.3% sunlight-to-electricity conversion efficiency (Yang et al. 1988). This was the first practical example of the success of this innovative design and provided a model upon which future cascade cells films could be based. ECD reports a substantial reduction of initial instability to about 10%-15% (from 30%) in these thin-layer cells. ECD has made larger-area modules using a three-cell design and achieved 8.4% efficiency.

The key process used to make a-Si is a form of chemical vapor deposition called glow discharge. In this, gas feedstocks such as silane, diborane, and phosphine are broken down in a low-pressure plasma to supply the silicon and to provide the materials added to it to control its electronic properties.

Manufacturing issues include increasing the a-Si deposition rate from a nominal 3-5 angstroms/s to 15 angstroms/s and reducing high capital costs associated with extensive vacuum equipment. Also, the feedstock gases--as with some other thin films--are hazardous. The use of these compressed gases, which may be flammable, pyrophoric or toxic, presents risks that are well-documented and successfully handled in the electronics industry. The use or disposal of a-Si modules presents no known or anticipated risks to the consumer or environment.

With the existing a-Si technology, the major manufacturers expect substantial reduction in manufacturing costs when 10 MW/year and larger plants are in operation. Present pilot production lines are about 1 MW/year. Chronar Corporation's Eureka plant, rated at 10 MW/year, is the first step towards these expected economies-of-scale.

In 1988, some market studies reported that the volume of a-Si devices had surpassed that of crystalline silicon devices. This was a landmark achievement in the evolution of thin films.

COPPER INDIUM DISELENIDE

During the same period, another thin film material, copper indium diselenide (or CIS), made substantial progress and is now considered to be a leading-candidate thin-film PV material.

Scientists at Bell Laboratories (NJ) had success (1974-75) in making efficient (12%) CIS cells of very high-quality, single-crystal materials (Wagner et al. 1974). Single-crystals were too expensive to be of practical value, but these proof-of-concept results were significant enough to stimulate an effort in the late 1970s to develop other ways to use CIS for lower cost cells.

The University of Maine (Grindle et al. 1980) were able to make 5% efficient cells by thermally evaporating CIS on low-cost substrates. Further progress came from Boeing Aerospace Company (Seattle, WA) (Mickelsen and Chen 1980) supported by Federal DOE funding through the Solar Energy Research Institute. Boeing was able to make 10% efficient CIS cells by evaporation (Mickelsen and Chen 1983).

Boeing's success led to greatly increased interest in CIS. Among those who began work were the Solar Energy Research Institute (internally), the Institute of Energy Conversion (University of Delaware), and ARCO Solar (Camarillo, CA).

All of these were rapidly able to reproduce the Boeing success in cell efficiency by making evaporated cells in excess of 10% (Meakin 1985; Zweibel and Surek 1985). Meanwhile, ARCO Solar was able to develop proprietary processes, reported to be potentially low cost, for making most of the components of the CIS devices. This progress in manufacturability was a very significant contribution to the technology and subsequently led to ARCO Solar's successful scale-up of CIS modules.

ARCO Solar's scale-up of the CIS technology has recently born fruit (June 1988) with the fabrication of an 11.1% efficient 1000 cm² CIS module (Figure 1), the most efficient, at its size, among the thin films (Mitchell et al. 1989 and Ermer et al. 1989).

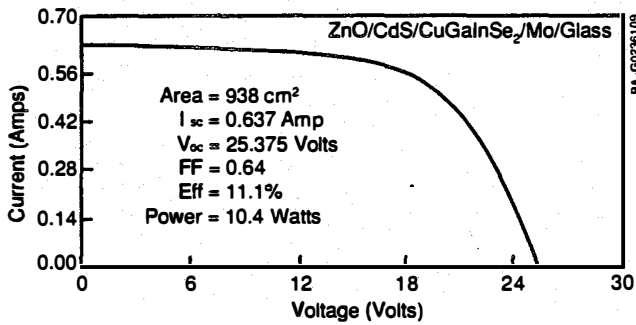


Figure 1. The highest efficiency thin-film submodule is an ARCO Solar CIS submodule that produces 10.4 Watts.

Subsequently (January 1989), they further increased module area to about 4000 cm² and achieved efficiencies in excess of 9% (Figure 2), also a thin film record at that size (Ermer et al. 1989). This module, which produced over 35.8 watts (before encapsulation), provided about 75% of the power of non-thin-film modules made of crystalline silicon--but with the advantage of the potentially lower cost of a thin film.

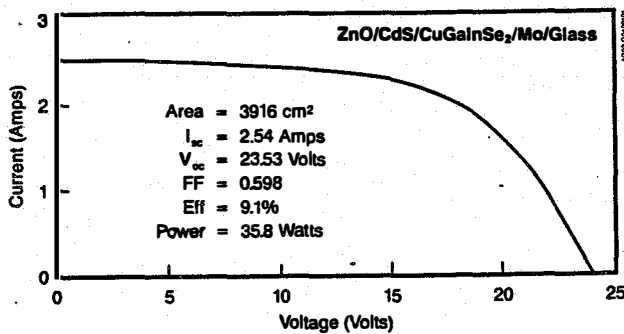


Figure 2. The near-four-foot-square ARCO Solar CIS panel produced over 35.8 Watts and a power output similar to existing non-thin-film PV modules.

Stability does not appear to be an issue based on the research conducted in CIS to-date. During early cell R&D at Boeing, some cells were exposed to light for almost 8000 hours without any degradation (Figure 3). This experience has since been confirmed for other CIS devices, including ARCO Solar's encapsulated modules. We at SERI have had them outdoors for over 4 months with no degradation (test duration to-date), the first independent confirmation of a stable thin film (Figure 4).

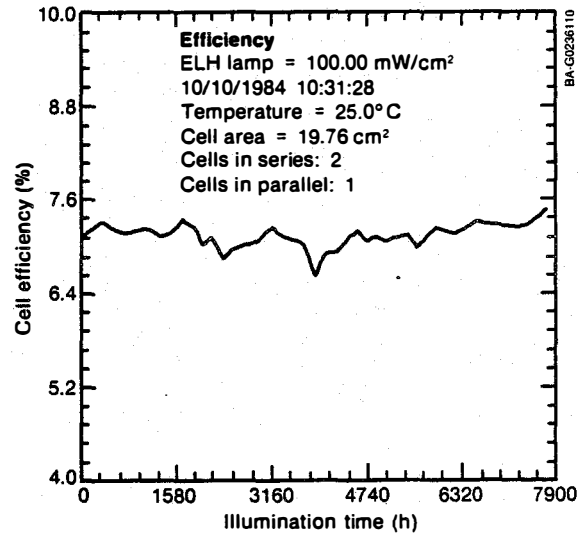


Figure 3. Boeing stability test of CuInSe₂ in a controlled environment showed no degradation after almost 8000 hours.

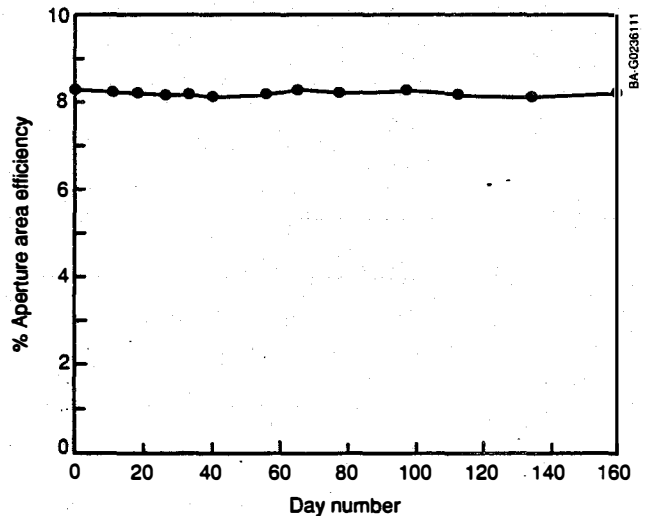


Figure 4. SERI outdoor test of an encapsulated ARCO Solar CIS module gives initial confirmation of the stability of CIS devices.

ARCO Solar has made several innovative changes in the structure of their CIS cells in order to achieve higher efficiencies (Mitchell et al. 1989). Figure 5 shows a typical ARCO Solar[®] CIS cell structure. It incorporates an innovative, highly transparent set of top layers (zinc oxide, ZnO; and very thin cadmium sulfide, CdS). These improved cell currents (and efficiencies) by about 20% over previous designs. Another ARCO innovation was the use of small amounts of gallium to replace indium in its CIS layer. This also improved efficiencies by about 20% over previous

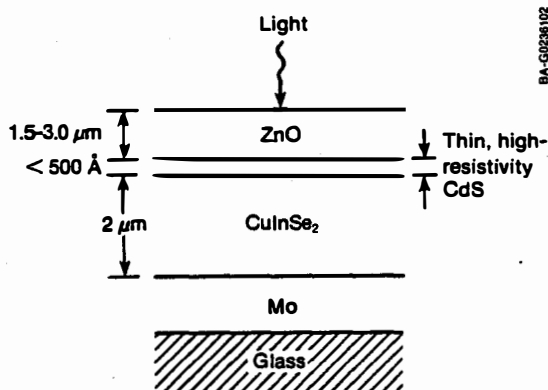


Figure 5. The basic structure of CIS devices includes thin CdS to allow greater ultraviolet response.

designs. The result has been the achievement of extremely high efficiencies (14.1%; Figure 6), confirming the likelihood that CIS will eventually achieve the DOE 15% module efficiency goal.

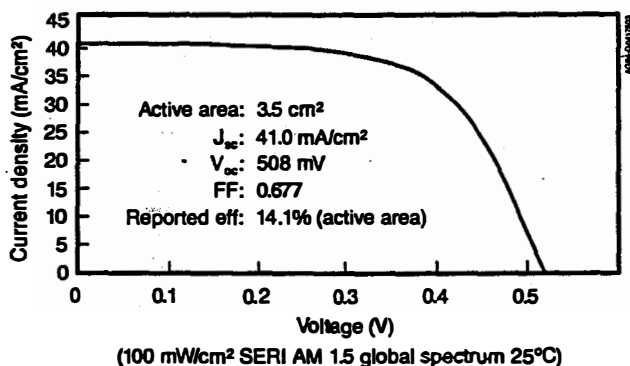


Figure 6. Small-area CIS cells have achieved very high efficiencies and should eventually surpass the efficiencies needed to make the DOE goal of 15% for modules.

Others followed ARCO Solar into CIS, including International Solar Electric Technology (ISET) and Chronar. ISET recently demonstrated a 10.9% efficient CIS cell. The CIS was made by a low-cost, 'two-stage' method. On top of a molybdenum-coated glass, copper and then indium are evaporated, much as is done in the glass-coating industry. Then this Cu-In sandwich is exposed to a selenium-bearing gas that breaks down and leaves behind Se, forming very high quality CuInSe₂. Other layers are also needed to complete the cell, and potentially low-cost processes for making them are being developed at ISET. An example is a thin cadmium sulfide layer deposited on top of the CIS by a process called dip-coating. (ARCO Solar also uses thin CdS in their very high-efficiency CIS devices.) In the ISET process, a saturated solution precipitates the CdS on the CIS in a very thin (300 angstroms), uniform layer.

Industry estimates the potential cost of CIS modules can be under \$100 per square meter with initial annual production volumes of about 10 megawatts. For modules of 10% efficiency, this would translate to electricity in the range of \$0.12/kWh (DOE 1987). Similar industry estimates are that with production of 30 or more megawatts, economies of scale should reduce costs to under \$50 per square meter, attaining the DOE module cost goal.

CIS has a high likelihood of meeting *all* the relevant DOE goals (15% efficiency, \$50/m² cost, 30-year life) for thin films. In full production, single-junction CIS modules should provide 6 cent/kWh electricity.

Two issues have been identified as possible problems for the CIS technology if it is used on a large scale. One is that a key material component of CIS, indium, is rather rare. If CIS production reaches a reasonable level--a billion watts annually--it would put serious pressure on the indium marketplace (Zweibel et al. 1986). To avoid this eventuality, we are working with indium producers to assure ongoing capacity increases to meet the new demand. Since indium is about as plentiful as silver in the Earth's crust (and silver is produced at several hundred thousand metric tons annually--orders of magnitude more than would be needed for PV), this problem is not considered one of availability but of matching the capacity and price of the producers with the growing needs of the CIS manufacturers.

Another identifiable concern is with the manufacture of CIS via selenization. As now constituted, selenization is done with an extremely toxic gas, hydrogen selenide (H₂Se). Although manufacturers are confident of safely controlling this toxic gas during production, we see advantages in eventually replacing it with a less toxic feedstock.

CADMIUM TELLURIDE (CdTe)

A 'dark horse' in the development of cost-effective thin films is cadmium telluride (CdTe). Like CIS, it is a polycrystalline semiconductor. It was actually under development before either CIS or a-Si and made some progress in the 1970s and early 1980s before plateauing. Recently progress has again been accelerating.

Several companies reported achieving 10% CdTe cell efficiency in the early 1980s, including groups at Kodak (Rochester, NY), Monosolar (Inglewood, CA), and ARCO Solar (Tyan and Perez-Albuern 1982; Basol 1984; Mitchell et al. 1988; Zweibel and Hermann 1985). But Kodak and ARCO Solar eventually abandoned CdTe, and Monosolar was bought by SOHIO (Cleveland, OH) and then by British Petroleum (Middlesex, England)--which has since become one of the leaders in the field.

Other early participants were Ametek Inc (Harleysville, PA) and Southern Methodist University (Chu 1988). Ametek (like Monosolar) used an innovative, potentially low-cost method of making the CdTe--electrodeposition. In this method, cadmium and tellurium are deposited from an electrolyte onto a suitable cathode, which is actually a part of the device (glass/tin oxide/CdS). Electrodeposition can be

used to make quality CdTe films, as demonstrated by the fact that Ametek (Meyers 1988) has made 11% efficient CdTe devices by this method (the highest SERI-verified efficiency for CdTe).

In about 1984 another company--with previous thin film Cu_2S experience--began work in CdTe. Photon Energy of El Paso (Texas) chose to skip small-area cell fabrication and go directly to the manufacture of product-sized modules (Jordan and Albright 1988). With SERI funding, they succeeded in 1988 by making a record (for CdTe) 7.3%-efficient square-foot module. They have also made prototype four-square-foot CdTe modules. Photon Energy has very aggressive near-term aims to enter the power-production market. They have proprietary methods, reported to be low-cost, of making the CdTe devices. Their costs estimates suggest that they may potentially be among lowest cost module manufacturers. They do not appear to require the same levels (i.e., 10 MW) of manufacturing scale-up to achieve economies-of-scale. In fact, they claim low cost (\$1-\$2/W modules) for production of about 3 MW/year.

Unfortunately, the CdTe technology is not free of stability concerns. These are associated with the contacting of the CdTe (Zweibel and Hermann 1985). In the past, metal contact to CdTe has been arduous and often unstable. Severe chemical treatments had been adopted to accomplish this difficult contacting, but these treatments themselves became a cause of instability.

To avoid this problem, Ametek Inc (Meyers 1988) developed a CdTe device structure in which it was unnecessary to contact the CdTe directly (Figure 7). Instead, the CdTe was sandwiched between two other semiconductor layers, which themselves were contacted. Ametek's cells of this design have since been tested under illumination for more than 3000 hours without degradation.

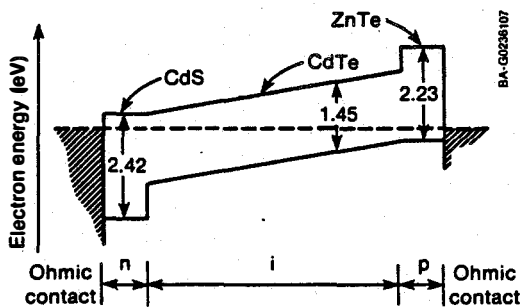


Figure 7. The Ametek cell structure avoids the necessity of contacting the CdTe. Instead, contact is made to two other semiconductors that surround the CdTe.

We have also tested Photon Energy CdTe panels outdoors at SERI without degradation for over two months (Figure 8). We are hopeful because of the Ametek and Photon Energy results, but further testing is needed to assure that the contact/CdTe problem has been resolved.

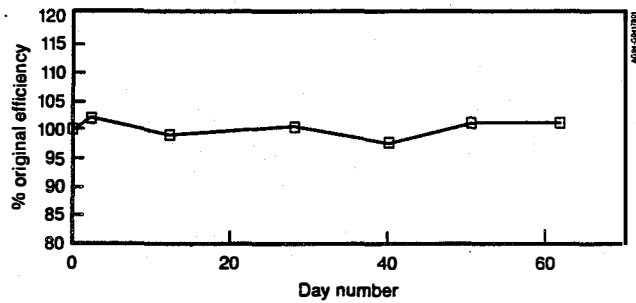


Figure 8. We have tested outdoors encapsulated CdTe devices made by Photon Energy. For the first two months, they showed no degradation.

Although CdTe cells and modules are at present less efficient than those of CIS, there is no theoretical reason to expect that this will continue when the CdTe technology reaches its full potential (Sites 1988). In addition, module manufacturing appears to be quite amenable to low cost. Thus the uncertainty about CdTe stability remains as the most critical issue relating to the CdTe technology.

One other issue exists to potentially cloud the future of CdTe: the presence of Cd itself. This metal is among those considered toxic by world and US environmental agencies. Thin film CdTe modules have minimal amounts of Cd--as little as 6 grams per square meter. Manufacturers believe that Cd can be successfully handled in the workplace. But another issue may be product disposal. Can CdTe panels be disposed of in uncontrolled waste dumps?

Once fabricated, the CdTe itself is quite a stable, nonreactive material. It is unlikely to break down. The Cd should remain fixed in the panel and not enter and pollute groundwater. We are presently undertaking tests to assess this hypothesis.

SUMMARY AND CONCLUSIONS

Thin films have made great progress in this decade toward the goals of cost-competitiveness established by the Department of Energy. Progress in the efficiency of large-area modules (1000 cm^2) has been especially marked (Figure 9). Square-foot CIS modules of over 11% efficiency are more than two-thirds of the way to the DOE goal (15%). Low cost is being incorporated into the manufacturing lines now being constructed to make thin films on a large enough scale to achieve economies-of-scale. Thin films are making good progress toward achieving long-term stability. The penetration of thin films into the market is already significant (viz a-Si) and is expected to grow even more rapidly in the 1990s.

The recent progress of CIS and CdTe has led the DOE and SERI to reassess them. SERI/DOE now considers them to be leading-candidate thin films along with a-Si. Crystalline thin films (silicon and gallium arsenide) are also supported

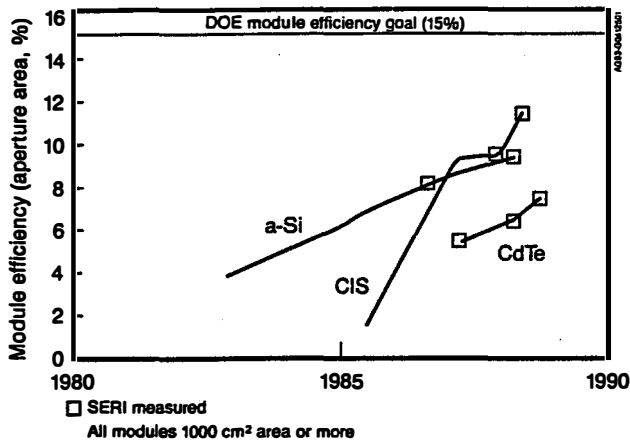


Figure 9. Progress has been rapid and steady in scale-up of new thin films to product-sized (1000 cm²) modules.

by the program. To support progress in CIS and CdTe, we have released a competitive initiative (RFP RX-9-19019) for major cost-shared industrial contracts to enhance the technical infrastructure supporting CIS and CdTe and to accelerate their progress toward the DOE goals. A third a-Si government/industry initiative is also anticipated to continue module development, with a focus on stability and enhanced efficiencies.

An opportunity for cost-competitive PV electricity seems to be on the horizon. PV modules that produce electricity at about \$0.12/kWh are expected when industry achieves sufficient scale-up and manufacturing capacity of current technologies. Great confidence exists that the long-term DOE goals for \$0.06/kWh electricity will be attained if current technical momentum continues--at which point we would expect PV to have an impact on global electricity production.

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