NREL
Advances in Research at the
National Renewable Energy Laboratory

Research Brief

Growing a Better Crystal

NREL's Powerful Characterization Tools Applied to Heat Exchanger Method

PIX #03590, Photo courtesy of Crystal Systems

Crystal Systems' heat exchanger furnace uses a single-crystal process to produce record-setting, high-quality multicrystalline silicon at costs comparable to those of other multicrystalline growth processes. Under a cooperative agreement, NREL will use its expertise to help perfect this highly promising technology.

Crystal Systems, Inc. (CSI) of Salem, Massachusetts, is a small company with a big potential to reduce the cost and improve the quality of solar cells. Under a 2-year cooperative agreement, CSI is now getting theoretical and analytical help from the National Renewable Energy Laboratory (NREL) to perfect its highly promising technology. Producing and selling crystal products and also furnaces to grow crystals, the 25-year-old company specializes in the heat exchanger method (HEM)—a crystal growth technique that uses precise temperature control to grow large, high-quality crystals in a crucible with the capability of annealing in the crucible prior to cooling. The 23-employee firm originally developed HEM for producing industrial sapphire crystals for optical, laser, and other uses.

The Challenge

Single-crystal and multicrystalline silicon wafers account for the great majority of the solar cells made today—65% and 31%, respectively, on a peak power basis in 1993. Multicrystalline silicon has numerous individual grains rather than one single, large grain. It is generally presumed not to be as good a material for solar cells, but it can be made by faster, less expensive methods.

When CSI sought to expand use of HEM to also produce square single-crystal silicon for making solar cells—"2 days at 1450°C instead of 2 weeks at 2100°C for sapphire crystal: piece of cake"—they encountered good news and bad news. The bad news was that a portion of each ingot was multicrystalline. The good news from Salem, however, was that solar cells made from that multicrystalline portion of the ingot performed nearly as well as single-crystal cells did. (The Georgia Institute of Technology has made 18.2%-efficient cells—a world record for multicrystalline silicon—from HEM multicrystalline wafers, and Sandia National Laboratories has made modules with efficiencies greater than 15% .)

So, rather than perfecting HEM for single-crystal silicon—even though it did produce much larger boules (silicon crystals as grown, before being cut into wafers) than other single-crystal growth methods—CSI chose to concentrate on development of HEM for making completely

Other Silicon-Crystal Growth Processes

Czochralski (CZ) Method—A seed of crystalline silicon is dipped to touch the surface of molten silicon in a crucible and is then slowly raised. Silicon solidifies—in the crystal pattern of the seed—as it is pulled from the crucible to form part of the growing boule. The CZ method dominates commercial growth of single-crystal silicon and produces laboratory cells with efficiencies as high as 20%.

Float-Zone (FZ) Method—A rod of silicon is placed atop a crystalline-silicon seed, and a movable heating coil encircling the rod is slowly raised from the seed upward. As the coil is raised, it melts the silicon, which then solidifies in the pattern of the crystal seed below it as the coil moves farther upward. FZ silicon has produced cells with a laboratory efficiency as high as 24%. Commercial applications for FZ silicon, however, have so far been restricted largely to high-efficiency cells (such as for satellites or concentrator systems). One limiting factor for FZ technology is the need for the feed rod of silicon to be smooth, uniform in diameter, and free of cracks. This precludes the use of most electronics industry seconds—used by many of the other silicon growth processes in photovoltaic applications—therefore requiring more expensive silicon meltstock and keeping costs high.

Casting/Directional Solidification—Molten silicon is either poured into a heated mold or melted in a crucible and allowed to slowly cool and solidify as multicrystalline silicon. Simple casting, however, has only relatively modest temperature control for producing quality cells. Most current casting operations have therefore added more complex temperature controls, and some have produced cells with a laboratory efficiency as high as 17.8%—the old record broken by the 18.2%-efficient cells made from HEM wafers. Cast silicon is usually made in square shapes that are better for packing solar cells into modules. (Both CZ and FZ single-crystal ingots are round.)

Ribbon/Sheet Growth—Several variations pull flat "ribbons" or sheets of multicrystalline silicon (one is single-crystal) from a crucible. The ribbons or sheets can then be cut directly into semiconductor wafers for solar cells, without the waste and expense of sawing ingots. Laboratory cell efficiencies reach 15%. The main drawback seems to be relatively slow production rates.

Thin Layer—Because of the potential for inexpensive production processes, there is considerable interest in thin films of amorphous silicon and various nonsilicon semiconductors for solar cells. It may also be possible to grow thin layers of crystalline silicon, and various researchers are investigating this option.

multicrystalline silicon ingots with a high degree of uniformity in structure and properties. Single-crystal growth builds on a pattern started by a crystal "seed," generally a very slow process that must be monitored carefully. But most multicrystalline silicon is essentially made by allowing molten silicon to cool and solidify in a mold (see sidebar above on other crystal growth methods). To compete in the "faster growth" market of multicrystalline silicon while using a single-crystal growth technique, the cost of HEM needed to be reduced.

The Response

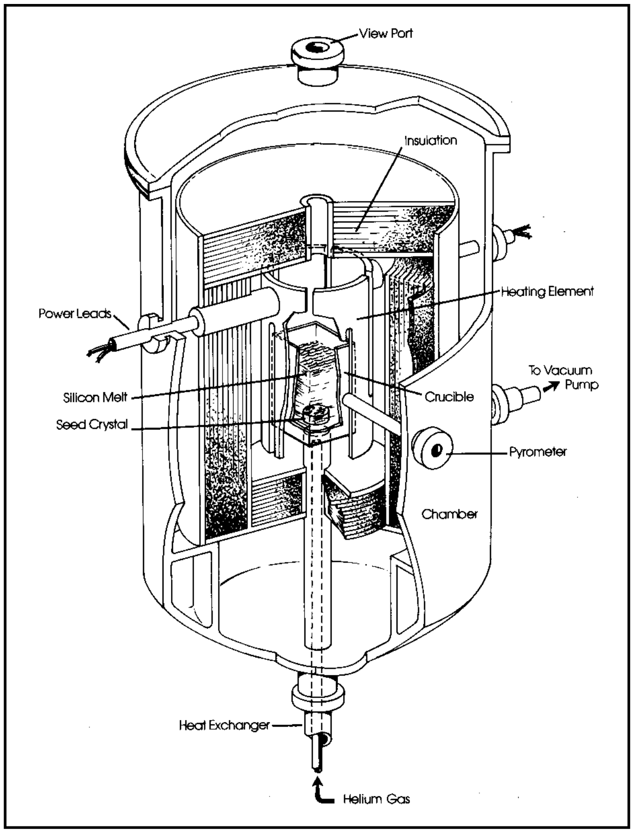
The basic features of an HEM furnace are a square-based crucible surrounded by a heating element with a helium heat exchanger connected to the bottom of the crucible. To grow a single-crystal ingot, a seed crystal is placed in the bottom of the crucible, and the silicon feedstock is placed on top of it to fill the crucible. The chamber is evacuated and the furnace heated to melt the silicon, but the seed is prevented from melting by the flow of cold helium gas through the heat exchanger. The gas flow is gradually increased, lowering the temperature of the heat exchanger, causing silicon to gradually solidify and the crystal to grow outward from the original seed. The temperature of the molten feedstock is controlled by the heating element; however, the temperature of the solid crystal is independently controlled by the heat exchanger. This dual control of both heating and cooling allows much more precise control of the position and movement of the solid-liquid interface of the crystal-formation process than is possible with most other casting or directional solidification processes.

Another key feature of CSI's original HEM design for silicon was the use of a highly pure silica crucible (to prevent contamination of the crystal). The crucible was heat-treated to develop a graded density that caused the crucible to delaminate during cooldown, thus preventing the ingot from cracking. Without this delamination, crystals would crack during cooldown because bonds form between the silicon crystal and the silica crucible, and the two materials have different thermal expansion coefficients.

To reduce costs of this single-crystal technology to compete with multicrystalline growth methods, CSI made several changes. First of all, because CSI was now looking at multicrystalline growth, the troublesome seeding step was no longer needed (but growth would still be directional from the bottom up). This also allowed for heat extraction through the entire bottom of the crucible instead of just the center where the seed was, so the solidification process could be speeded up. CSI also took further advantage of one of HEM's strong points by increasing the already large ingot size from 33 cm on a side for 40 kg, to 44 cm for 80 kg, and even to 55 cm for 155 kg. With the height remaining about the same, the process handles as much as four times as much material with only a marginal cost increase.

To improve the reliability of the process, CSI switched from custom-made, single-use crucibles to standard, commercially available silica crucibles. The challenge was coating the crucibles to prevent bonding and to avoid contamination by forming an effective barrier to the transport of impurities from crucible to silicon. CSI developed a coating that worked quite well and proved its reliability by producing 80- to 155-kg ingots. To further reduce costs and increase reliability, CSI incorporated all of its various improvements to the process into a fully automated furnace now available for sale. Sophisticated software allows the computer controller operating the furnace to continuously monitor all parameters needed to run the furnace. Labor is needed only to load and unload the furnace. All the operating parameters of the furnace can be displayed on a single screen, or the operator can easily select more detail on particular ones.

For even greater cost reduction, however, a reusable crucible was needed. Ceramics, with their high heat tolerance, seemed to be the answer, but they are expensive and not as pure as silica, so contamination was a concern. Crystal Systems responded to the challenge and came up with an appropriate ceramic and a variation of its silica-crucible coating that worked quite well. This work is still in development, but CSI has now reused its ceramic crucible as many as 16 times. The potential for low-cost production is now very great.



Schematic diagram of the HEM furnace (courtesy of Crystal Systems)

The heat exchanger method's dual control of both heating (heating element surrounding the crucible) and cooling (helium gas heat exchanger underneath the crucible) allows much more precise control of the position and movement of the solid-liquid interface of the crystal-formation process than is possible with most other casting or directional solidification processes.

The New Challenge

CSI wanted to implement reusable crucibles and other cost-reducing process modifications without sacrificing quality, and to further improve the quality of the product. To do this, however, CSI scientists found themselves needing a highly precise understanding of the physics of their crystal formation process. So they turned to NREL, with its sophisticated arsenal of characterization tools and techniques for photovoltaic (PV) materials.

Under a January 1995 cooperative research and development agreement (CRADA), NREL is analyzing CSI silicon ingots for crystalline defects and impurities, analyzing PV cells made from CSI wafers, and evaluating gettering and hydrogenation for optimization of cell performance. Characterization tools being used include transmission electron microscopy, scanning defect mapping, infrared characterization of inclusions and precipitates, minority-carrier diffusion length mapping, deep level transient spectroscopy, Fourier transform infrared spectroscopy, small-area solar array current-voltage measurements, secondary ion mass spectroscopy, and Auger analyses. The principal objective of this array of analyses is to understand:

- The interaction of CSI's crucibles with the silicon melt and the resulting effect on the crystallization process and product properties
- The ways in which defects are generated or impurities are incorporated in HEM-grown material. (Even though defect levels are quite low, they are often concentrated in localized areas that do not perform well. Understanding why these defects form will aid in achieving high efficiency for large-area cells.)
- The optimal HEM thermal profiles for growing and annealing multicrystalline silicon
- The effectiveness of gettering on HEM multicrystalline silicon
- The effectiveness of various cell fabrication methods for HEM multicrystalline silicon.

Initial work under the CRADA has already shown that impurities in HEM-grown multicrystalline silicon tend to move to and precipitate at the grain boundaries and other defect clusters in the silicon. It is much harder to remove impurities with gettering or other processes if the impurities are in defect clusters. This performance-limiting mechanism may also be true for silicon made by all processes. To effectively remove impurities, it is therefore crucial to deal with defect clusters. NREL and CSI are working on ways to remove impurities from defect clusters.

Capable of greater than 18% efficiency, solar cells made from HEM multicrystalline silicon perform nearly as well as the best ones made from single-crystal silicon. In fact, most of the difference is because texturing—chemical treatment to create small pyramidal structures on a cell's top surface—does not improve light capture for multicrystalline material in the same way as it does for single-crystal material. Texture captures more energy for the cell because light that reflects off the cell is more likely to strike the cell again. However, because multicrystalline material is oriented in multiple directions, less of this internally reflected light is useful than it is for single-oriented, single-crystal material. Both NREL and CSI scientists are working to develop an appropriate etch or other antireflection texture for HEM-produced and other multicrystalline silicon.

NREL Analysis Will Make Process Even Better

Using HEM processing, CSI can produce very large ingots of high-quality multicrystalline silicon. Cost and processing time both increase only marginally with ingot size for HEM because the heat exchanger is enlarged to match the ingot cross section, but the height remains about the same. Thus, by producing large ingots with an automated process, CSI can use its high-quality "single-crystal process" to produce multicrystalline silicon with consistently high quality and uniformity of properties at a cost competitive with other less carefully controlled multicrystalline processes. HEM processing offers:

- Simple-to-operate equipment
- Low labor costs because it is largely automated
- Low energy costs because the heat zone is well insulated
- High yields because the ingots are large
- High-quality product.

To transfer this technology to solar cell manufacturers or other multicrystalline silicon users, CSI sells a fully automated furnace that will produce a consistently high-quality product. Incorporation of reusable crucibles should bring expendable materials costs down considerably. The analysis and research conducted under the CRADA between NREL and CSI should greatly facilitate the use of reusable crucibles while maintaining high quality. Better understanding of the basic physics of the HEM process may also identify a variety of other ways to reduce costs or improve quality. Record-setting HEM is ready to make a big impact on the multicrystalline silicon solar cell industry.

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Produced by the Communications and MIS Branch for the Photovoltaics Division
NREL/MK-336-8359 1/96

The National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393,
a national laboratory of the U.S. Department of Energy (DOE), managed for DOE by Midwest Research Institute

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