T. F. Ciszek
G. H. Schwuttke
K. H. Yang

Solar-Grade Silicon by Directional Solidification in Carbon Crucibles

Directional solidification of silicon in carbon crucibles was achieved by using two variations of the Bridgman-Stockbarger method. One was a static technique wherein liquid silicon in a carbon crucible was positioned in a temperature gradient of about 35°C/cm, with the highest temperature at the top of the crucible. Solidification was achieved by lowering the system temperature at a rate of 4–5°C/min. The second technique entailed lowering a silicon-loaded carbon crucible through a fixed-rf coil at a rate of 0.55 cm/min. Crack-free silicon was produced by both methods. The equilibrium grain structure was initiated by nucleation at the crucible walls, with surviving grains tending to grow in alignment with the temperature gradient to produce an axially columnar grain structure of mainly ⟨110⟩ orientation. The average grain diameter was 0.11 cm; a typical length was 0.7 cm. Solar cells made with this material gave an AM1 conversion efficiency of 11.5%.

Introduction

Large-scale implementation of photovoltaic electric power generation in the U.S. as a long-term goal is aimed at displacing U.S. petroleum-consuming electric power. Such a displacement, as estimated by the Department of Energy, could save approximately two million barrels of oil per day.

To meet such an objective, photovoltaic power generation must be capable of producing 40 GW of electricity on a continuous basis. Assuming that solar power is available approximately 20% of the day, 40 GW of continuous photovoltaic power would require 200 GW of solar array capacity, including a proper storage system.

Successful implementation of flat-plate photovoltaic power generation on such a large scale would require a substantial price reduction at the materials level. The Low-Cost Solar Array Project, conducted by the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, with funding from the Department of Energy, has the objective to demonstrate the practicality of processes for producing polycrystalline silicon suitable for terrestrial solar cells at a volume of 500 peak MW per year at a market price of less than $10/kg (1975 dollars) in 1986. Parallel to the polycrystalline silicon program, efforts are being pursued to reduce the cost of sheet silicon. Several promising low-cost silicon-sheet technologies are presently being developed. The photovoltaic sheet silicon being developed is structurally less perfect than that required for high-performance integrated circuits. The most promising growth techniques for low-cost solar-array silicon material are listed in Table 1.

In this context, silicon growth techniques based on directional solidification deserve attention. It has been shown by B. Authier [1] that polycrystalline silicon produced in this fashion can produce solar cells with AM1 efficiencies of 10–12%.

Directional solidification, or Bridgman/Stockbarger crystal growth, is an effective and simple technique for the growth of many metal and alkali halide crystals

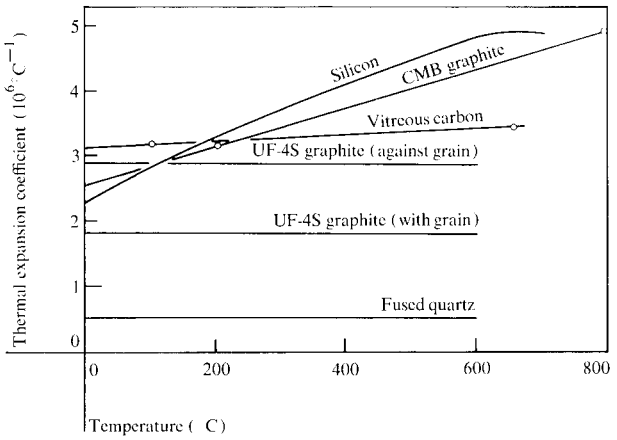

Figure 1 Thermal expansion coefficients of silicon, fused quartz, and several forms of carbon in the temperature range from 0 to 800°C.

[2]. The growth rates attainable are comparable to those achieved by more complex techniques such as Czochralski growth and float-zoning. Thus, directional solidification is an economically attractive approach for large-scale applications of silicon crystals, such as terrestrial photovoltaics.

Historically, silicon has been a material that presented great difficulty in growing crystals by the directional so-

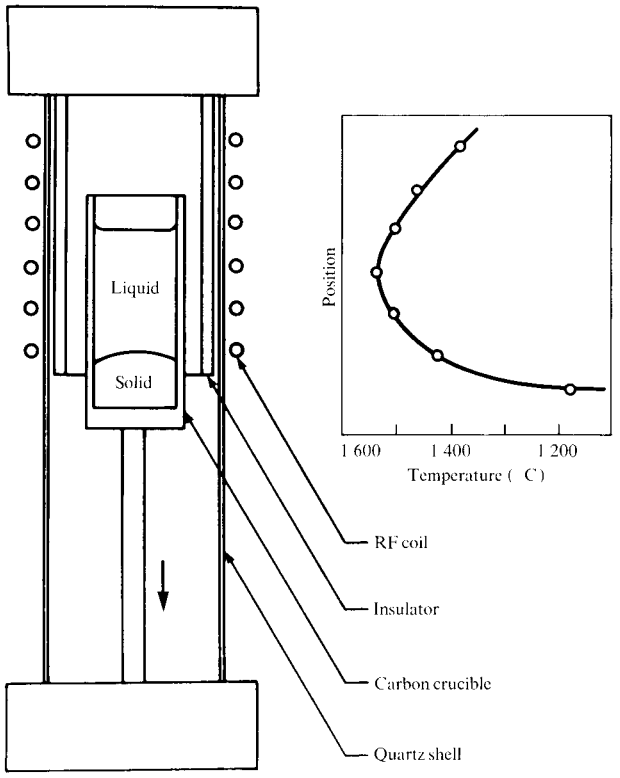

Figure 2 Schematic diagram of the apparatus and temperature profile used for the directional solidification by the moving-crucible method.

Table 1 Silicon growth techniques.

	Cylindrical		*Ribbon*		*Cast in mold*	
	Czochralski	*Float zone*	*Web*	*Capillary*	*Poured*	*Directionally solidified*
Rate of growth (mm/min)	2	4	30	30	?	5
Maximum width (mm)	150	100	35	95	100	100
Throughput (g/min)	80	170	0.7	2	—	90
Crystal structure	single		twinned		multigrained	
Operator skill	high	very high	very high	high	low	low
Sawing/surface preparation	yes	yes	no	no	yes	yes
Highest demonstrated AM1 solar cell efficiency (%)	18	18	12	12	12	12
Typical AM1 solar cell efficiency (%)	15	15	10	10	10	10

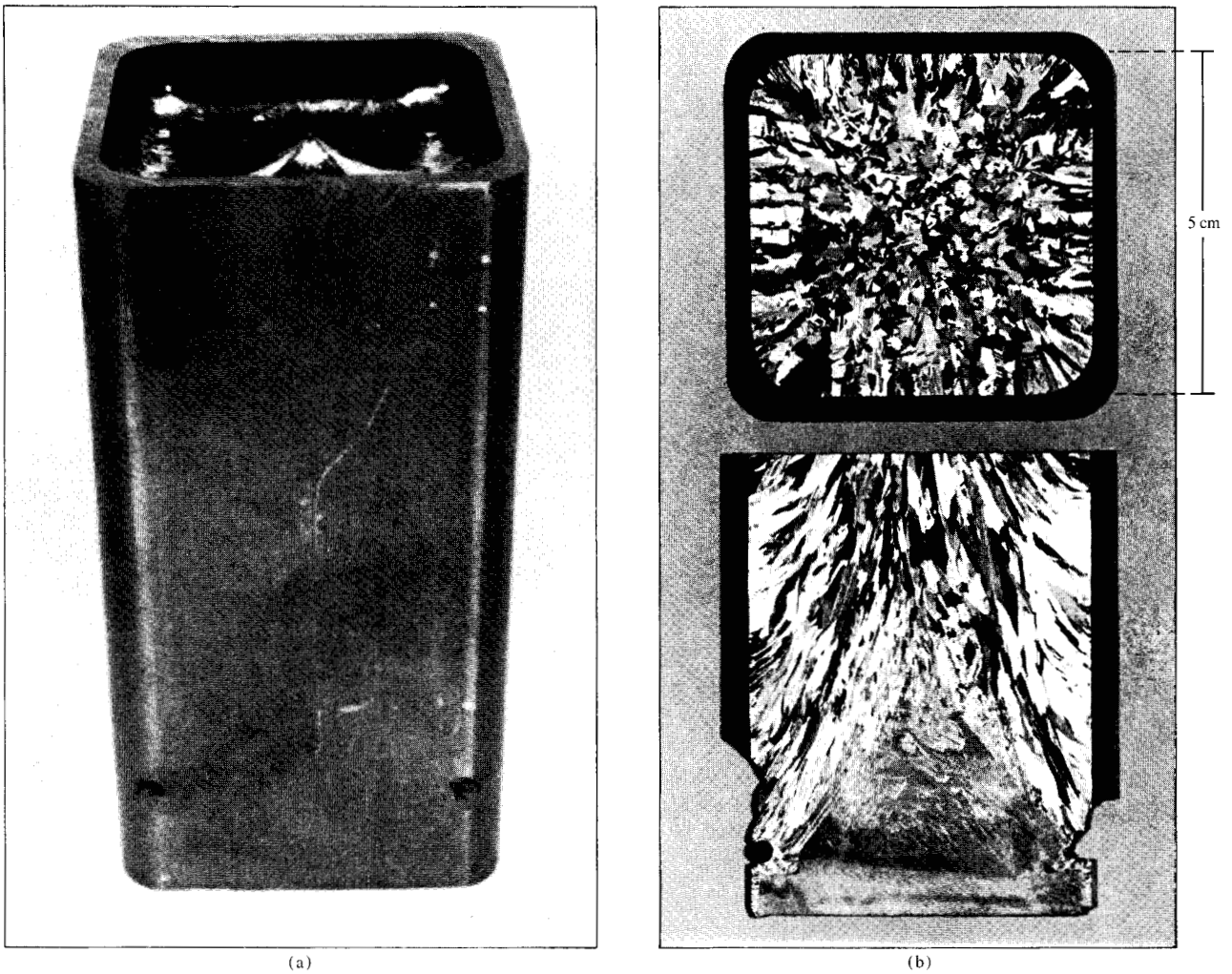

Figure 3 (a) CMB graphite crucible filled with directionally solidified silicon; (b) cross section and partial longitudinal section of solidified silicon.

lidification method. The primary problem with silicon relates to cracking of the crucible or container walls during the solidification process, which involves cooling the material from the melting point of silicon (1415°C) to room temperature [2].

The container used for directional solidification should be inert and the material to be grown should contract upon freezing, or at least not stick to the crucible walls. Silicon in traditionally fused quartz crucibles does neither. The silicon adheres to the container walls and both the container and the silicon crack due to differential thermal expansion during cooling. Authier [1] overcomes this cracking problem by pouring (casting) the silicon melt into a suitable mold. The sidewalls of the mold are kept at a temperature of several hundred degrees Celsius. Thus, wetting of the silicon melt at the container walls is prevented. At the same time a temperature gradient between the bottom and top of the melt in the container is maintained during cooling. This leads to directional solidification. This technique has grown large blocks (10 cm by 10 cm) of polycrystalline silicon without cracking.

In this paper, the use of carbon containers for directional solidification of silicon is explored. It is shown that crack-free growth of silicon is attainable with two different types of carbon. The ingots produced are typically multicrystalline with a structure very similar to that reported for cast silicon by Authier [1], by Fischer and Pschunder [3] and by Hunt, Dosaj, and McCormick [4]. The AM0 solar cell efficiencies reported by them for photovoltaic cells made of multigrained cast silicon are in the range of 8–10.5%. In the present work, an AM1 efficiency of 11.5% or an AM0 efficiency of 9.8% is obtained.

Experimental procedure

• *Carbon container properties*

General considerations for the compatibility of various graphites with liquid silicon were reported by Ciszek [5]. It was shown that graphite is a durable substrate in contact with liquid silicon, provided that the density is greater than about 1.75 gm/cm^3 and that the grain size is less than about 50 μm. The degree of carbon contamination of the silicon (about 20 ppm) is similar to the level of oxygen contamination when silicon is grown from conventional SiO_2 crucibles; however, unlike oxygen, carbon is not electrically active in silicon. Vitreous carbon, because of its impervious structure, is also durable in contact with liquid silicon.

In addition to structure and composition, another important characteristic of crucibles used for the directional solidification of silicon is the coefficient of thermal expansion (CTE). Silicon is capable of plastic deformation from the melting point (1415°C) down to about 650°C. Below that temperature, silicon responds to an increasing applied stress by deforming elastically until the fracture stress (cracking point) is reached. In the temperature range from 650 to 20°C, the thermal expansion coefficient monotonically and almost linearly decreases from 5 × 10^{-6}/°C to 2.4 × 10^{-6}/°C (see Fig. 1). Thus, when silicon is solidified and then cooled below 650°C in a quartz crucible, the silicon shrinks at a much higher rate than the crucible (the thermal expansion coefficient of fused quartz is 0.55 × 10^{-6}/°C in the temperature range from 15 to 1000°C). Since the silicon sticks to the quartz, cracking results as the silicon fracture stress is exceeded.

Graphites are available with a wide range of thermal expansion coefficients (1.1 to 8.3 × 10^{-6}/°C), some being isotropic and some anisotropic. To avoid cracking of the silicon charge and/or the crucible, the graphite or carbon crucible should have a thermal expansion coefficient in the range of 650°C to about 20°C that either matches the thermal expansion coefficient of silicon or, on the average, produces about the same dimensional change. An example of a graphite that has a reasonably close CTE to that of silicon is Union Carbide's [6] grade CMB graphite. According to the manufacturer, the CTE is isotropic, with values of 5.0 × 10^{-6}/°C at 800°C and 3.2 × 10^{-6}/°C at 200°C (see Fig. 1). The maximum grain size is 76 μm and the density is 1.76 g/cm^3. As shown later, this grade of graphite was successfully used for directional solidification despite the marginal grain size. Another graphite, UF-4S [6], with a similar density (1.79 gm/cm^3) but a larger maximum grain size (203 μm) and a lower, anisotropic CTE (1.8 × 10^{-6}/°C measured in the direction of the grain, and 2.9 × 10^{-6}/°C measured against the grain direction over the range of 0–600°C) was not successful as a crucible material. The thermal expansion coefficient of vitreous carbon [7] ranges from 3.5 × 10^{-6}/°C to 3.2 × 10^{-6}/°C at 100°C and has about the same average dimensional change as silicon in this range (at 650°C the silicon shrinks more than the carbon with decreasing temperature, while near room temperature the silicon shrinks less than the carbon with decreasing temperature). This material has also been used successfully as a crucible.

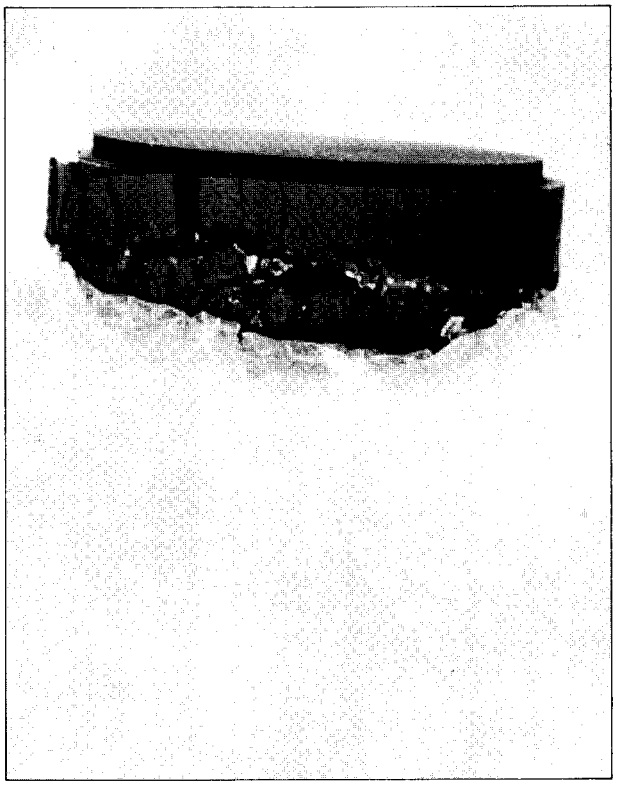

Figure 4 Graphite UF-4S crucible failure by swelling and cracking. The upper part of the crucible is lodged within an opaque quartz cylindrical insulator.

• *Solidification techniques*

Two techniques were used to solidify silicon in carbon crucibles. In the first, the crucible was lowered through a fixed-induction (rf) heating coil as shown in Fig. 2. The coil was on the exterior of a 94-mm-diameter clear-quartz tube. The ends of the tube were water-cooled and sealed to allow the establishment of an argon ambient within the tube. An opaque quartz insulator was fixed within the tube and the solid-liquid interface was approximately at the level of the bottom of this insulator. Directional solidification occurred as the crucible was lowered at a controlled rate.

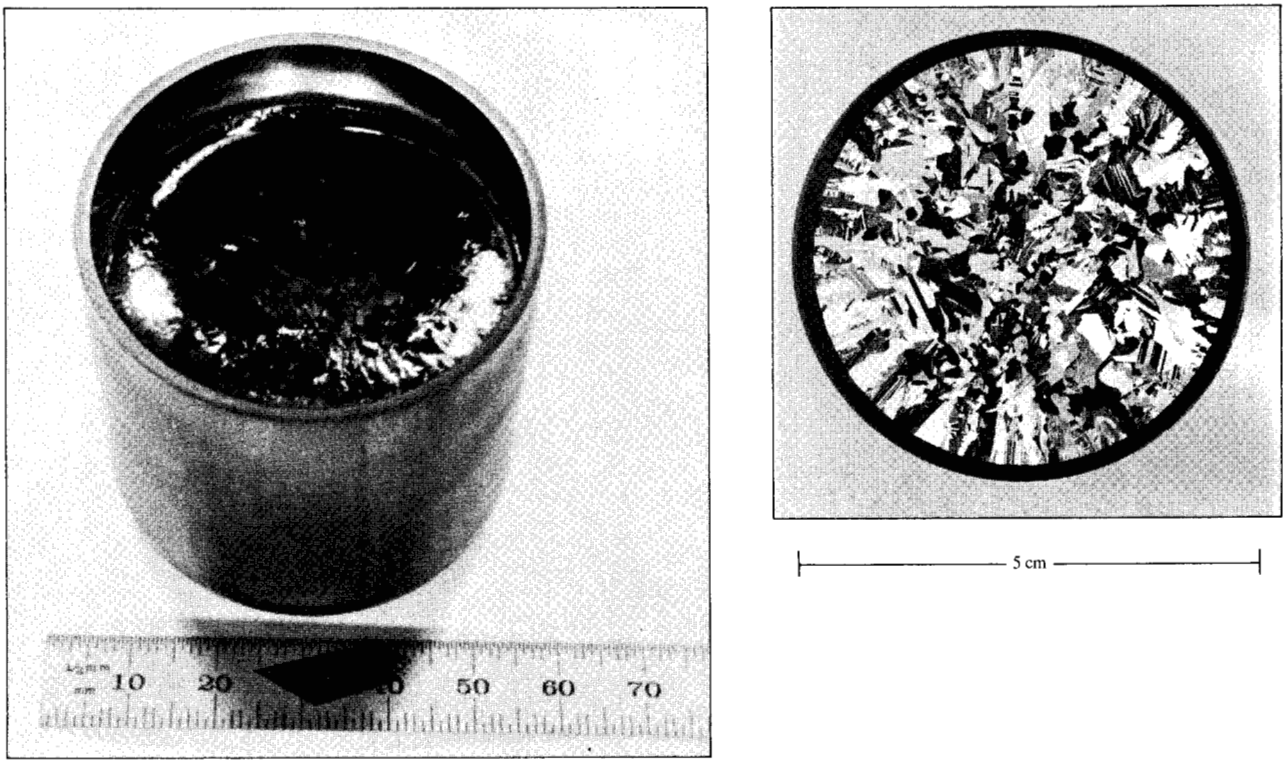

Figure 5 (a) Vitreous carbon crucible filled with directionally solidified silicon; (b) cross section of solidified silicon.

In one experiment, a CMB graphite crucible was used. It had a 50-mm × 50-mm square cross section and a 3-mm wall thickness, and was 130 mm deep. A 50-mm × 50-mm ⟨100⟩ seed crystal was held at the bottom of the crucible with 3-mm-diameter graphite pins and the crucible was filled with 580 g of silicon. The crucible was positioned within the coil to melt the silicon and part of the seed. It was then lowered at a rate of 5.5 mm/min. The CMB crucible and its directionally solidified contents are depicted in Fig. 3(a). A cross section and a partial longitudinal section of the resultant solidified material are shown in Fig. 3(b). It can be seen that the structure is dominated by grain nucleation at the crucible walls. Surviving grains tend toward an axial alignment and soon obliviate single-crystal propagation from the seed.

A similar experiment with a 70-mm-diameter round UF-4S graphite crucible resulted in cracking and swelling of the crucible as shown in Fig. 4.

The second solidification technique was a static one. A 139-g polycrystalline charge of silicon was placed in a 50-mm-diameter by 50-mm-high vitreous carbon crucible, along with sufficient boron to produce an average resistivity of 2 ohm-cm. Graphite rf susceptors and heat shields were arranged to establish a vertically increasing temperature gradient of about 35°C/cm, the top of the crucible being the hottest region. The system was first heated to melt the silicon and then heated to a temperature of 1680°C at the top melt surface. Since the melt was about 3 cm deep, the temperature at the bottom of the crucible was approximately 1575°C. The molten silicon was held at this temperature for 15 minutes. The system temperature was subsequently decreased at a rate of 2.5°C/min, while maintaining the vertical gradient, until the entire charge had solidified (about 2 h). The cooling rate was then increased to 20°C/min until the silicon temperature was 1000°C, at which time the power was turned off. Upon removal from the furnace, the solidified silicon was found to be intact and free of cracks. This is shown in Fig. 5(a). A cross section of the silicon is shown in Fig. 5(b). The grain structure is similar to that seen with the CMB crucible.

Results

• *Grain size*

The method and assumptions of Smith and Guttman [8] were used to calculate the mean grain diameter D from measurements of the mean number of intercepts of test lines with grain boundaries per unit length of the test line N_L ($D = 3/2N_L$).

Table 2 Grain dimensions for silicon crystallized by two variations of the Bridgman/Stockbarger method.

	Stationary crucible (vitreous carbon) temperature reduction	*Moving crucible (CMB graphite) approximately constant temperature*
Growth speed (mm/min)	0.7	5.5
Average grain diameter (mm)	1.08	1.09
Standard deviation (mm)	0.16	0.28
Maximum grain diameter (mm)	7	11
Minimum grain diameter (mm)	0.05	0.07
Typical grain length (mm)	—	7

Measurements were made at 2-mm intervals from the center to near the edge of the round specimen shown in Fig. 5(b) by using 10-mm-long test lines perpendicular to the radius. For the square specimen shown in Fig. 3(b) measurements were made at 4-mm intervals across the width of the sample, again by using 10-mm-long test lines. The resultant mean grain sizes for the two solidification techniques were nearly the same (1.08 mm for the static method with a vitreous carbon crucible and 1.09 mm for the moving-CMB crucible) even though the growth rates were different by a factor of 7.8 (see Table 2). For the longitudinal section shown in Fig. 3(b) (moving-CMB crucible), the lengths of thirteen randomly selected grains were measured and an average value of 7 mm with a standard deviation of 0.28 mm was obtained.

• *Grain orientation and structure*

Grain orientation was determined by an x-ray diffraction technique. In this technique, the x-ray beam scans the wafer surface at an angle θ. The angle θ is changed through wafer rotation. The reflected x-ray intensity is picked up by a counter positioned at an angle 2θ relative to the incident x-ray beam. The reflected x-ray intensity is recorded as a function of the scan angle 2θ. Figure 6 shows two strong intensity peaks at position $2\theta = 47.3^\circ$ and 47.4° for silicon grown in the UF-4S carbon containers. For the copper radiation used, the Bragg angle θ_B for the 220 reflection is 23.65° for $K\alpha_1$ and 23.71° for $K\alpha_2$. Therefore, the two peaks at $2\theta_B$ indicate that all grains have a $\langle 110 \rangle$ surface orientation. For wafers grown with the CMB graphite container, x-ray data indicate that most grains also have $\langle 110 \rangle$ orientation, but some have $\langle 111 \rangle$ orientation. Transmission electron microscopy (TEM) was used to determine the degree of grain perfection and the type of grain boundaries; see Figs. 7(a–c). The grain

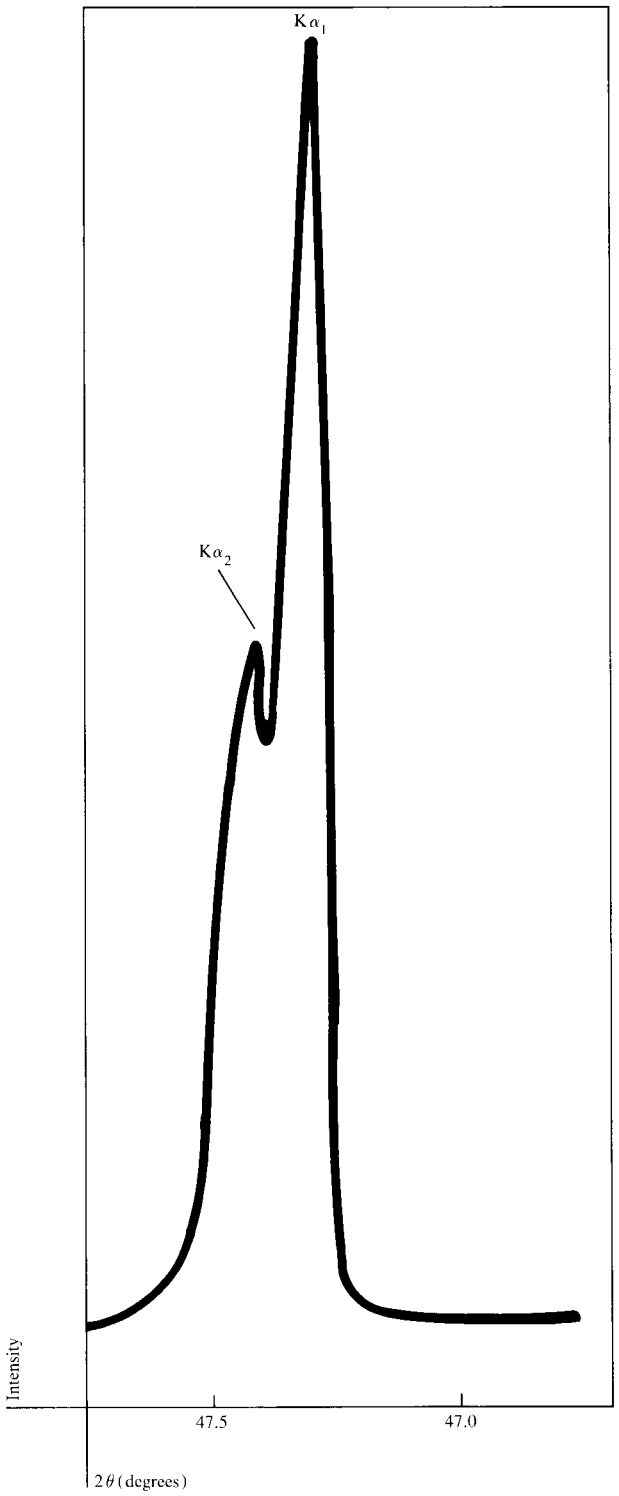

Figure 6 Diffraction curve for directionally solidified silicon grown in the UF-4S carbon container.

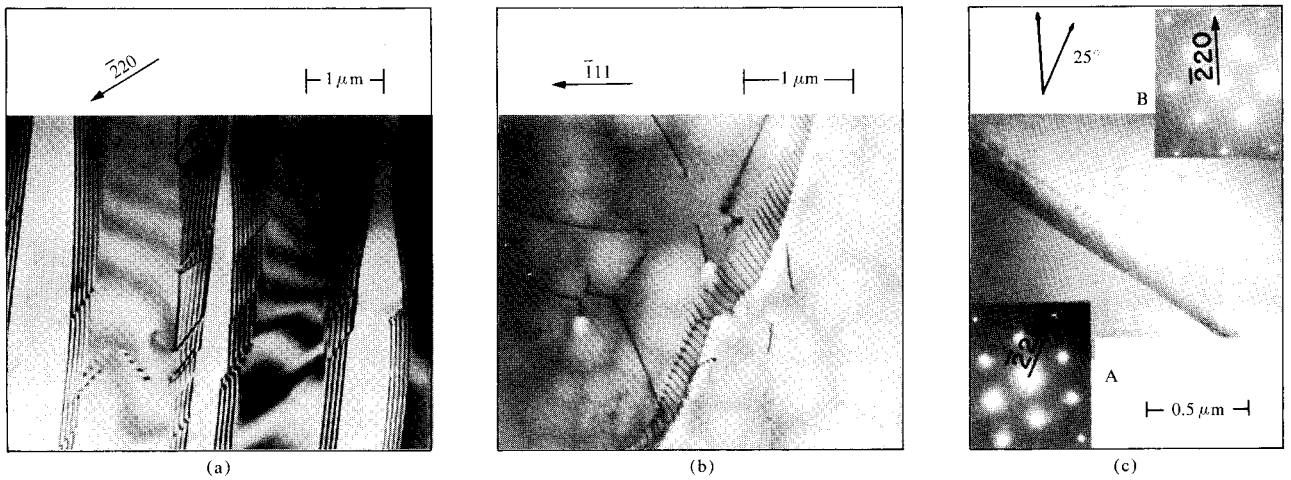

Figure 7 Transmission electron micrographs of (a) typical twin boundary (note dislocations in the boundary); (b) small-angle grain boundary; and (c) twist boundary (rotation is about 25° around the ⟨110⟩ orientation; note dislocations in the boundary).

growth is columnar. The dislocation density in single grains is variable, the maximum being $10^6/cm^2$. An average dislocation density of 10^3 to $10^4/cm^2$ is representative of the whole grain structure. The Burgers vector of the dislocation is of the (a/2)⟨110⟩ type. Twin boundaries occur quite frequently in single grains and such twin boundaries contain dislocations. Grain boundaries are of the small- and large-angle type; the small-angle boundaries consist of closely-spaced dislocations. The misorientation between such grains is estimated from Kikuchi patterns and is approximately one degree. The large-angle boundaries are twist boundaries. The grains maintain their ⟨110⟩ orientation; misorientation between grains is the result of a relative rotation of the grains around their ⟨110⟩ orientation. The electron diffraction patterns obtained from each grain indicate that the rotation in this example is 25 degrees. Such boundaries also have a high dislocation density.

• *Solar cell performance*

Solar cell data for a device made from 2-ohm-cm material that had been directionally solidified in a vitreous carbon crucible is shown in Fig. 8. The cell area was 4 cm^2. Under AM0 illumination, a short-circuit current of 130 mA and an open-circuit voltage of 0.55 V was obtained with a curve fill factor of 0.744. The efficiency was 9.8% at AM0 and 11.5% at AM1. The measurements were made with an antireflective coating on the cell.

Summary and conclusions

Crack-free silicon can be directionally solidified in vitreous carbon and in CMB graphite containers. An important parameter in achieving crack-free growth is the degree to which the thermal expansion coefficient of the container matches that of the silicon over the temperature range from 20 to 700°C. It is estimated that acceptable limits for the average thermal expansion coefficient are 3 to 4.4 × 10^{-6}/°C.

Grain nucleation at the crucible walls dominated attempts to seed the growth at the crucible bottom. The structure is composed of predominantly ⟨110⟩ axially oriented grains with an average diameter slightly in excess of 1 mm. Grain size does not vary significantly with the growth rate in the range from 0.7 to 5.5 mm/min. Grain boundaries range from twins containing dislocations to large- and small-angle boundaries composed of dislocation arrays. The typical dislocation density within a grain is 10^3 to $10^4/cm^2$ with a Burgers vector of type (a/2)⟨110⟩ as determined by TEM examination.

Solar cells made from directionally solidified (in graphite containers) silicon produced maximum AM1 efficiencies of 11.5%, and typical AM1 efficiencies of 10%. These values are comparable to those achieved by multigrain ribbon-growth techniques such as ribbon-to-ribbon float zoning [9], capillary-action-shaping-technique (CAST) growth [10], and edge-defined film-fed growth [11]. Advantages of the directional solidification method over ribbon growth for low-cost silicon are the technological simplicity and higher throughput (by a factor of 50) during the crystallization process. The major disadvantage is the requirement for post-growth wafering of the bulk material, which results in material losses.

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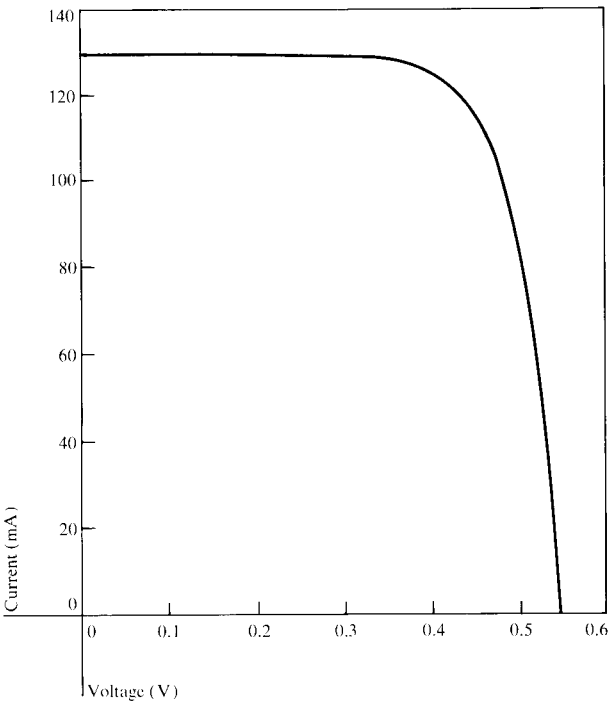

Figure 8 Solar cell current *vs* voltage curve and cell data for silicon directionally solidified in a vitreous carbon crucible.

T. F. Ciszek is located at the Solar Energy Research Institute, Photovoltaics Branch, Golden, Colorado 80401. G. H. Schwuttke and K. H. Yang are located at the IBM Data Systems Division laboratory, East Fishkill (Hopewell Junction), New York 12533.