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SILICON ON CERAMIC PROCESS

Silicon Sheet Growth for the Large-Area Silicon Sheet Task of the Low-Cost
Solar Array Project

Annual Report No. 4, September 29, 1978—September 30, 1979

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Solar Energy

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Period Covered: 9/29/78 - 9/30/79

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SUMMARY

The objective of this research program is to investigate the technical and economic feasibility of producing solar-cell-quality sheet silicon by coating one surface of carbonized ceramic substrates with a thin layer of large-grain polycrystalline silicon from the melt. The effort is divided into several areas of investigation in order to most efficiently meet the goals of the program. These areas include: 1) dip-coating; 2) continuous coating; 3) material characterization; 4) cell fabrication; and 5) theoretical analysis. The work in the continuous coating technology development area was funded directly by Honeywell from 1 January 1978 to 30 September 1979, but is included within this report for completeness. During the past year, significant progress was made in all areas of the program.

The production dip-coating activity was initiated to: 1) provide material for solar cell fabrication at Honeywell; 2) provide material for evaluation by JPL; and 3) evaluate coating compatibility of different slot configurations and substrate compositions. This coating was carried out on the machine which began operation during 1976. This activity has demonstrated that the silicon-on-ceramic (SOC) process can be controlled reproducibly, and can be a high-yield process. Sixty-nine dip-coating runs were conducted resulting in over 1000 usable substrates. Several factors limiting yield have been identified and eliminated. The lessons learned in the dip-coating process are expected to be directly applicable to the silicon coating by inverted meniscus (SCIM) process.

The new dip-coating facility was modified during this time period. The design of this coater is similar to the production dip-coater but includes means of convective cooling. This coater was dedicated to the study of how the linear coating speed of SOC material could be increased without sacrificing material structural quality. Results to date indicate 200- μ m-thick layers can be dip-coated on slotted substrates using helium cooling through cooling shoes at a rate of 0.2 cm/sec.

During the first portion of this report period, we were still unable to produce useful layers in the continuous (SCIM) coater. This was due to the fact that meniscus stability could not be obtained with the coater in the horizontal position. A new heater configuration, plus increasing the angle at which the meniscus contacted the substrate, produced the first SCIM-coated SOC layers. The largest one to date has an area of 225 cm². Minority carrier diffusion length (L_n) measurements indicate this material is very similar to dip-coated material produced at the same coating speed (0.06 cm/sec). This is an important result indicating the technical viability of an SOC continuous-coating process.

The light-beam-induced current (LBIC) technique has been extended to permit L_n measurements on unprocessed material, non-antireflection (AR)-coated junctions, and antireflection-coated junctions. Significant increases in L_n have been measured in large-grain areas of SOC material after processing, although no deliberate gettering process has been used.

Theoretical analyses of the effect of grain boundary recombination on short-circuit current density, J_{sc} , has led to the definition of: 1) an effective diffusion length, $L(x)$, which describes solar cell behavior in the vicinity of a grain boundary, and 2) an effective surface recombination velocity at the grain boundary. The total loss of J_{sc} due to a grain boundary can be expressed as an effective width of the grain boundary. The effective width is highly dependent on the wavelength of the impinging light.

The best SOC solar cell fabricated to date has a total-area conversion efficiency of 10.0 percent (AM1, AR) for an area of 4.1 cm^2 . Cell performance was investigated as a function of silicon thickness and base doping concentration. Results indicate that the efficiency increases by about 20 percent as the silicon thickness increases from 100 to 200 μm . The optimum base doping concentration is slightly greater than $1 \times 10^{16} / \text{cm}^3$.

We have undertaken a theoretical analysis of thermal conditions for growth of sheet silicon from the melt. Two apparently distinct growth modes are possible. In the so-called "symmetric" mode, which we believe includes all our experimental growth to date, the liquid-solid interface is roughly perpendicular to the pulling direction. Thermal analysis predicts that sheet thickness, t , falls rapidly with increasing pull speed, v . For ceramic-supported growth, the relation $t \sim v^{-x}$ holds, where the exponent x is greater than 2. The other mode, wedge-shaped or "asymmetric" growth, is characterized by a greatly elongated LSI which is nearly parallel to the pulling direction. This mode offers high throughput potential because the liquid-solid interface presents a much larger area for heat transfer. However, the thermal environment ordinarily used for symmetric growth does not appear to be compatible with wedge-shaped growth. Analysis indicates that heat should be applied to one surface of the solidified sheet over a region extending from the end of the solidification wedge to a point roughly an inch downstream.

INTRODUCTION

This research program began on 21 October 1975. Its ongoing purpose is to investigate the technical and economic feasibility of producing solar-cell-quality sheet silicon by coating inexpensive ceramic substrates with a thin layer of polycrystalline silicon. The coating methods to be developed are directed toward a minimum-cost process for producing solar cells with a terrestrial conversion efficiency of 11 percent or greater.

By applying a graphite coating to one face of a ceramic substrate, molten silicon can be caused to wet only that graphite-coated face and produce uniform, thin layers of large-grain polycrystalline silicon; thus, only a minimal quantity of silicon is consumed. A dip-coating method for putting silicon on ceramic has been shown to produce solar-cell-quality sheet silicon. A continuous-coating process also being investigated has excellent scale-up potential which offers an outstanding, cost-effective way to manufacture large-area solar cells. The dip-coating investigation has shown that, as the substrate is pulled from the molten silicon, crystallization continues to occur from previously grown silicon. Therefore, as the substrate length is increased (as would be the case in a scaled-up process), the expectancy for larger crystallites increases.

A variety of ceramic materials have been dip-coated with silicon. The investigation has shown that mullite substrates containing an excess of SiO_2 best match the thermal expansion coefficient of silicon and hence produce the best SOC layers. With such substrates, smooth and uniform silicon layers 25 cm^2 in area have been achieved with single-crystal grains as large as 4 mm in width and several cm in length. Crystal length is limited by the length of the substrate. The thickness of the coating and the size of the crystalline grains are controlled by the temperature of the melt and the rate at which the substrate is withdrawn from the melt.

The solar-cell potential of this SOC sheet silicon is promising. To date, solar cells with areas from 1 to 10 cm^2 have been fabricated from material with an as-grown surface. Conversion efficiencies of about 10 percent with an AR coating have been achieved. Such cells typically have open-circuit voltages and short-circuit current densities of 0.55V and 23 mA/cm^2 , respectively.

The SOC solar cell is unique in that its total area is limited only by device design considerations. Because it is on an insulating substrate, special consideration must be given to electrical contact to the base region. One method which offers considerable promise is to place small slots in the substrate perpendicular to the crystalline growth

direction and contact the base region by metallizing the silicon that is exposed through the slots on the back side of the substrate. Smooth, continuous coatings have been obtained on substrates which were slotted in the green state prior to high-temperature firing. The best slotted-cell results to date indicate a 10.0 percent conversion efficiency (AR-coated) on a 4-cm² (total area) cell.

Development efforts are continuing in such areas as improvement in growth rate, reduction of progressive melt contamination, and optimization of electrical contacts to the base layer of the cell. The investigation has shown that mullite substrates, to a limited extent, dissolve in molten silicon. The impurities from the substrate are believed to adversely affect solar-cell conversion efficiency. A method for reducing substrate dissolution is to reduce the contact area the substrate makes with the silicon melt. Therefore, a silicon coating facility (referred to as SCIM or Silicon Coating by Inverted Meniscus) has been constructed which is designed to coat large (10 cm x 100 cm) substrates in a continuous manner. It is expected that this facility not only will improve the growth rate, but also will minimize the silicon melt contact with the substrate. This should reduce the rate at which the melt becomes contaminated. The facility will also permit a study of possible continued grain growth by accommodating the use of longer substrates. It should also reveal problems that are likely to be encountered in a scale-up process. This machine has succeeded in demonstrating coatings exhibiting unidirectional solidification (desirable and occurring in dip coating) on substrates 18 inches long and 2 inches wide. Material characteristics indicate this material is similar in structure and purity to material obtained from our dip-coating facilities.

TECHNICAL DISCUSSION

SHEET SILICON GROWTH (J. D. Zook, J. D. Heaps, B. Koepke, L. D. Nelson, D. J. Sauve, O. J. Harris, and H. Burke)

Dip-Coating Production (J. D. Zook and O. V. Harris)

During 1979, the three main objectives of the dip-coating production effort were to:

- 1) Provide material for solar-cell fabrication at Honeywell.
- 2) Provide material for evaluation by JPL (much of this material was used at OCLI and at Spectrolab to fabricate solar cells).
- 3) Evaluate coating compatibility of different slot configurations and substrate compositions.

A continuing goal was to identify problems or potential problems associated with yield in the supported growth of silicon.

The production was carried out on the original dip-coating system which began operation in 1976. A standard dip-coating procedure was followed, as discussed in Quarterly Report No. 10. While minor variations in procedure were made during runs, the standard procedure is still as outlined there.

During the year, 69 dip-coating runs were made. Previous quarterly reports contain tables summarizing the runs. The runs for third quarter 1979 are summarized in Table 1. Runs 202 through 213 were conducted to supply material to JPL. As a matter of policy, we retain several samples from each run for our own cell-processing effort.

During the year, several problems were identified and solved. For example, a persistent growth of particles at the edge of the melt was observed. The particles were identified as SiC and their origin was definitely established as due to an air leak in the packing seal of the argon valve. The O_2 reacted with the heater to form CO which in turn reacted with the melt to form SiC. Details are given in Quarterly Report No. 11.

Table 1. Dip-Coating Production - Third Quarter 1979

Run No.	Dopant Level (boron)	Growth Speed (cm/sec)	Number Dipped	Comments
194	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.070	9	New slot configuration.
195	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.070	13	
196	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.070	0	Water supply failure; system shut down.
197	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.070	10	
198	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.070	9	
199	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.070	13	Good yield.
200	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.070	12	Good yield.
201	$1.4 \times 10^{16} \text{ cm}^{-3}$	0.060	13	
202	1.0×10^{16}	0.06	17	Some SiO ₂ ; new "standard doping."
203	1.0×10^{16}	0.06	10	
204	1.0×10^{16}	0.06	11	New crucible holder.
205	1.0×10^{16}	0.06	12	Two carbon substrates dipped.
206	1.0×10^{16}	0.06	12	
207	1.0×10^{16}	0.06	13	
208	1.0×10^{16}	0.06	12	Tendency to form dendrites.
209	1.0×10^{16}	0.06	12	y = 100%.
210	1.0×10^{16}	0.06	12	
211	1.0×10^{16}	0.06	12	
212	1.0×10^{16}	0.06	12	
213	1.0×10^{16}	0.06	8	Run terminated because a substrate broke.
214	1.0×10^{16}	0.06	16	13 Dag coated, 1 carbon substrate were dipped.

Another problem was the formation of dendrites. These can be eliminated by raising the crucible temperature a few degrees, but some variability exists. There is some evidence that dendrite formation is reduced if the substrates are well-baked-out before dip-coating. The usual bakeout has been for an hour at 140°C, which has eliminated

substrate breakage of dye-checked substrates. However, an overnight bakeout seems preferable to eliminate dendrites. A possible mechanism relating dendrite formation to substrate bakeout is not known.

Dip-coating of other substrates was also carried out. Poco Carbon substrates give very nice dip-coated layers but the melt temperature must be 5 to 10°C cooler than for mullite substrates. Several types of mullite produced by Coors were also evaluated. Type "O" and type "N" were judged to be equal to the type "K" substrates used normally.

Low-cost vitreous carbon substrates produced by Tylan were also dipped and evaluated by JPL.* The carbon was observed to remain at the interface. A continuous layer of SiC was formed with thickness dependent on contact time. At the top of the sample where the contact time was the least, the SiC layer was on the order of a micron thick. At the bottom of the substrates, there were a significant number of SiC particles. On the basis of these observations, it is speculated that the SiC particles observed at the silicon-ceramic interface can be formed as the result of precipitation from the melt and also as a result of breakup of thicker layers of SiC. The SiC layers appear to develop fairly rapidly, but, even in the case of the thinnest layers of vitreous carbon, the carbon is only partially converted to SiC. The shortest contact times to date have been on the order of 30 seconds. It is not clear how much SiC formation will occur in the SCIM-coating process, with significantly lower contact times. Hopefully, the layer will be sufficiently thin to permit electrical contact to the carbon.

In summary, the dip-coating production effort demonstrated during the year that the SOC process can be controlled reproducibly, and can be a high-yield process. Several of the factors limiting yield were identified and eliminated. The lessons learned in the dip-coating process are expected to be directly applicable to SCIM coating.

Experimental Dip Coater (B. Koepke, D. Zook, D. Suave)

Introduction--During the past year, a new dip-coating facility was established at Honeywell's Corporate Material Sciences Center (CMSC). The primary goal of this facility is to determine the conditions under which the throughput of the supported growth of silicon sheet on a ceramic substrate can be optimized. A reasonable throughput is considered to be 100- μ m-thick layers grown at a speed of 0.25 cm/sec.

The design of the new dip-coater closely resembles that of the existing coater, with a few major exceptions as discussed in more detail below. Basically, the new coater is

---

* Evaluation was done by T. O'Donell, of JPL.

larger and has more access ports to accommodate the extra heating and/or cooling equipment necessary to grow at higher rates. The main experimental approach used to increase growth rates is to remove the latent heat of solidification by forced convective and radiative cooling through the use of cooling shoes placed in the vicinity of the liquid-solid interface. As will be discussed below, when this is done an afterheater must also be used to prevent fracture of the coated substrate during cooling.

Description of Equipment--

Dip Coater--The experimental dip-coater is shown in Figure 1. The older dip-coater is seen in the background of the figure. There are four access ports in the central portion of the chamber. Two are aligned at 11 degrees and two are aligned at 30 degrees to the geometrical center of the parting plane between the upper and lower chambers. There are four access ports in the top of the chamber that also point to the center of the parting plane and are inclined at an angle of 60 degrees. During a run, the melt surface is typically level with the parting plane.

Figure 1. Photograph of Experimental Dip Coater

The heater assembly is shown in Figure 2. A silicon charge is shown inside a fused-silica crucible in a graphite crucible holder. The crucible holder in turn is situated inside a graphite resistance heater which is surrounded by a heat shield consisting of

two concentric graphite cylinders spaced with graphite wool. The heat shield, heater, and crucible holder can be independently positioned. The glass tube on the right of the heater is used to blow argon gas over the melt surface during some runs to minimize SiO formation on the silicon coating when cooling shoes are not used. The heater is a picket-fence design considered to be more rugged than the thin-wall heater used in the other coater.

Figure 2. Photograph of Heater Assembly in Experimental Dip Coater

Cooling Shoes--The position of front and back cooling shoes with respect to the substrate and heater assembly is shown in Figure 3. The cooling shoes are machined from nickel and contain passages for both water cooling and gas flow. The cooling and gas flow in a cooling shoe is shown in Figure 4. At present, the gas exits through holes drilled in the end of the shoe. This is not an acceptable situation because the nonuniform cooling on the silicon results in coatings with vertical striations. Examples will be shown later. On the other hand, nonuniform gas coverage clearly shows the effects of gas cooling on the growth pattern during dip-coating. Future modifications of the cooling shoes will provide more even gas coverage over the surface of the substrate.

Afterheater--When forced convective cooling is provided at the liquid-solid interface during dip-coating, the thermal shock is almost always sufficient to fracture the substrate particularly at higher pull rates. To minimize thermal stresses in the coated substrate

Figure 3. Photograph Showing Front and Back Cooling Shoes in Place in Experimental Dip Coater

Figure 4. Schematic Showing Water and Gas Flow in Cooling Shoes

an afterheater must be used. Early attempts with "passive" afterheaters (i.e., those heated only by conduction or radiation from the melt zone) were not satisfactory and an independently powered graphite resistance afterheater was finally installed. The heater is a thin-wall, cylindrical, split-resistance element similar to those used early in the program as crucible heaters. The heater is powered by unregulated a-c current through two transformers in series. The relationship of the crucible, cooling shoes, and afterheater is shown in Figure 5. The cooling shoes are inclined at an angle of 20 degrees to the melt surface. The arrows on the sketch indicate the direction of gas flow in each shoe. Note that in the shoe facing the uncoated side of the substrate the holes are drilled parallel to the axis of the shoe, while the holes in the other shoe are drilled perpendicular to the substrate surface. This arrangement allows the back side of the substrate to be cooled slightly below the liquid-solid interface, while the front side is cooled above the interface. It could be pointed out at this time that typically the gas flow rate on the back side of the substrate is four times that through the front shoe.

Figure 5. Schematic Showing Relationship of Afterheater, Cooling Shoes, and Crucible Assembly in New Dip Coater

Procedures--In a typical run, a substrate is lowered to just above the melt surface and held 2 minutes to approach thermal equilibrium. It is then inserted into the melt, held for a 30-second soak and withdrawn. The immersion and pull rates are always the same. The gas cooling is turned on after pulling begins.

The main variables examined to date have been melt temperature and gas flow rate. In early runs, the melt temperature was fixed at that temperature yielding thick, smooth coatings at 0.05 cm/sec with no cooling. We realize now that the melt temperature must be optimized each time any variable is changed.

Gas flow has not been studied a great deal and, at present, the flow rate settings must be considered arbitrary.

Results--In the paragraphs that follow, only results indicating the general progress of this effort over the past year will be presented. A detailed discussion of every run would be cumbersome and would not add much to the report. The results will be discussed chronologically in terms of quarterly efforts.

First Quarter (9/30/78 - 12/31/78)--By the end of this quarter, the experimental coater was operating and cooling shoes had been installed through side ports in the upper half of the chamber at 30 degrees to the melt surface. At that time, only one shoe was drilled for gas flow. Throughout these and subsequent runs the cooling shoes have been positioned in such a way that the gas jets are about 10 mm from the substrate surface and about 6 to 10 mm above the melt surface. We note that in this position the gas jets on the uncoated side of the substrate are directed at or slightly below the liquid-solid interface.

During the first quarter, substrates were pulled at 0.15 and 0.2 cm/sec with argon gas flowing through the front shoe. Unslotted Coors K-mod substrates were coated. The thickness data obtained during this period are shown in Figure 6. The bars indicate data taken on substrates coated without external cooling. The dotted lines show the spread in all the data taken in the other dipper and published as Figure 10 in Annual Report No. 3. The data taken in the new dipper follow the relation $V^{2.3}t = \text{constant}$, where V is the growth velocity and t is the coating thickness. Data taken with external cooling on the front side of the substrates are shown as triangles. The square represents a goal of 100 μm at 0.3 cm/sec.

Figure 7 is a photograph of a substrate coated at 0.2 cm/sec with gas cooling on the coating side. Most of the silicon had solidified dendritically, indicating the melt temperature was too low and/or the melt below the liquid-solid interface was being undercooled by the

Figure 6. Coating Thickness, t , versus Pull Rate, V , for Coatings Pulled in New Dip Coater During First Quarter (9/30/78 to 12/31/78). The triangle represent data taken with external coating applied.

Figure 7. Photograph of Solid Substrate Dip Coated at 0.2 cm/sec With Argon Gas Cooling on Coated Side

gas. It is notable that a portion of the coating was smooth. In this and subsequent samples, if a portion of the coating is smooth, the thickness of that region is measured and logged as data.

Second Quarter (1/1/79 - 3/30/79)--During this quarter, most of the work centered around improving the operation of the dip-coater. The cooling shoes were mounted on the bottom of the chamber and were modified to allow two-dimensional positioning in the chamber. No runs were made during this period.

Third Quarter (4/2/79 - 6/29/79)--During this quarter, 10 runs were made in an effort to grow at high throughputs. Typically, 10 to 12 substrates are coated during a run. Runs were made in which the front, back, and both sides of the substrate were cooled with argon gas. Important observations made during these runs are discussed next.

At 0.1 cm/sec, smooth coatings with thicknesses of 125 μm were obtained on unslotted substrates. The coatings had horizontal variations in thickness corresponding to the position of the gas jets in the cooling shoes and were always thicker directly under the jets. An example of a 125- μm coating on a solid substrate is shown in Figure 8. In this case, gas was only directed at the coated side of the substrate and was turned on after one-third of the substrate had been coated. Before the gas was turned on, a smooth, 50- μm -thick coating formed. After the gas was turned on, a coating (with

Figure 8. Photograph of Substrate at 0.1 cm/sec With Argon Gas Directed Only at the Front Side of the Substrate. The vertical stripes correspond to where the gas jets impinged on the coating. The cooling was turned on after one-third of the substrate had been coated.

vertical stripes) formed that was partially dendritic and 125 μm thick in the thicker portions of the smooth coating.

Another run was made, with gas directed only at the coated side, in which the pull rate was steadily increased from 0.05 to 0.2 cm/sec. The coatings were typically 20 percent dendritic and exhibited nominal thicknesses of 100 μm at 0.1 cm/sec, 50 μm at 0.125 cm/sec, and 15 μm at 0.2 cm/sec. In each dip the gas was turned on after one-third of the substrate had been coated at 0.05 cm/sec. In every case, the smooth coating remained smooth and increased in thickness. We conclude from these runs that forced convective cooling can increase the thickness of silicon sheet produced by supported growth techniques.

During the middle of this period, a problem with cracking of slotted substrates during dip-coating arose and it was realized an afterheater was required. A "passive" afterheater heated by conduction and convection from the melt was positioned above the melt, while power supplies for the "active" afterheater discussed earlier were requisitioned.

The best results to date were obtained with the graphite "passive" afterheater in place and cooling directed only at the back side of the substrate. Under these conditions, a slotted substrate was coated to a thickness of 125 μm at 0.15 cm/sec. A photograph of this sample is shown in Figure 9. The vertical stripes corresponding to the positions of the individual gas jets are clearly visible.

Figure 9. Photograph of a Slotted Substrate Coated at 0.15 cm/sec With a "Passive" Graphite Afterheater in Place and Argon Gas Cooling Directed Only at the Backside of the Substrate. The vertical stripes correspond to where the gas jets impinged on the substrates. The thicker regions have a thickness of 125 μm .

Fourth Quarter (6/30/79 - 9/29/79)--At the beginning of this quarter, an a-c-powered graphite resistance afterheater was installed and the dip-coating geometry became that shown in Figure 5. A series of runs was made with argon gas flowing through the cooling shoes onto unslotted substrates. In all cases, uneven, vertically striped coatings were obtained. In some cases, the coatings were partially dendritic. The thickest portions of the smooth regions were measured and are shown plotted (as crosses) as a function of growth speed in Figure 10.

Figure 10. Summary of Data Obtained With the Experimental Dip Quarter Using an "Active" Afterheater and Helium Gas Cooling. The open circles are taken on substrates coated without gas cooling, and the line is a summary of data taken on the other dip coater under the same experimental conditions.

The line drawn on the far left side of Figure 10 represents a large amount of data taken on the other dipper without afterheaters or cooling shoes. The data follow the relationship, $V^{2.9}t = 0.059$. The circles are data taken in the experimental coater without cooling shoes or an afterheater. The agreement between the two coatiers is good. The crosses are the data taken with argon flowing through the cooling shoes. The argon data lie on a line roughly parallel to the other and displaced toward higher V and t . Note that with argon cooling, a smooth coating thickness of 300 μm was achieved at a growth speed of 0.1 cm/sec but all coatings produced at 0.2 cm/sec were less than 100 μm thick.

A series of runs was then made with helium flowing through the cooling shoes in an effort to get thicker coatings (the thermal conductivity of helium is approximately eight times that of argon). These results are shown as the squares plotted in Figure 10. The appearance of the coatings produced under helium was the same as observed previously (i.e., vertical striations corresponding to individual gas jets plus some dendritic regions). The major difference is that the coatings grown under helium are thicker. Coatings exhibiting smooth regions with thicknesses of 200 and 300 μm have been grown at 0.2 cm/sec. An example of a sample with a 200- μm -thick coating produced on a slotted substrate at 0.2 cm/sec is shown in Figure 11. The smooth portion of the coating has thicknesses ranging from 25 to 200 μm . Smooth coatings were also grown at 0.25 and 0.3 cm/sec under helium and the data are plotted in Figure 10. These data must be considered preliminary because the melt temperatures have not been optimized for the higher-speed growth. As indicated in Figure 10, a goal of 100 μm thick at a growth speed of 0.25 cm/sec appears to be feasible with the present equipment.

(a) Front Side

(b) Back Side

Figure 11. Photograph of a Slotted Substrate Coated at 0.2 cm/sec With Helium Gas Directed at (a) the Front and (b) the Back Sides of the Substrate. The thicker regions are 200 μm thick.

Future Studies--Future experiments with the experimental coater will concentrate on producing coatings at high growth speeds suitable for solar-cell manufacture. The cooling shoes are being modified to allow an even flow of gas to be directed at the substrate surface during growth. This will eliminate the vertical striations on the coating. Growth conditions will be optimized for coating production of 0.25 cm/sec. The position of the cooling shoes and direction of gas flow with respect to the position of the liquid-solid interface will be studied. Finally, a systematic study of the relationship of coating thickness to growth speed will be carried out with helium gas cooling.

Continuous Coating Process (J.D. Heaps, L.D. Nelson and H. Burke)
[Honeywell Funded 1/1/78 - 9/30/79]

At the outset of this reporting period, we were still unable to produce silicon coatings greater than 2 inches in length due to a molten silicon spillover problem. This problem is illustrated in Figure 12. As the substrate passes over the trough, molten silicon wets the substrate and is drawn downstream of the trough before solidification occurs (see t_1). As the substrate continues its motion, this molten layer of silicon thickens (see t_2 through t_6) until it eventually spills over and annihilates the trough heating element located below.

Figure 12. Illustration of Molten Silicon Spillover Problem in Relation to Coating Length, L

We reasoned that if we could create a steeper temperature gradient immediately downstream of the trough, that solidification would occur nearer the trough, thereby reducing the chance of spillover. To obtain this steeper gradient, two changes were made:

- 1) A new-type trough-heater assembly was installed in the coater. This heater was fabricated in such a way that the graphite trough holder itself was an active resistive element of the assembly (see Figure 13). The rectangular legs of this heating assembly served the final substrate heating requirement. The power density of each leg was graduated in such a way (see Figure 14) that the substrate temperature never exceeded the melting point of silicon. Contrary to the original approach (see Figure 15), the heating zone now terminated abruptly at the downstream edge of the trough.
- 2) As shown in Figure 14, the upper substrate heater was shortened, thereby shifting the peak temperature in an upstream direction.

Figure 13. Photograph of New Trough/Substrate Heater (Also Showing Quartz Crucible/Trough Piece)

Figure 14. Growth Chamber Cross Section Showing Shorter Upper Substrate Heater

Figure 15. Growth Chamber Cross Section Showing Adjustable Substrate Guide and Substrate Cooling Gas Ports

Following the above modifications, the liquid-solid interface, if desired, could now be shifted until solidification occurred at the edge of the trough. This is the dip-coating equivalent of having the surface of the melt freeze around the substrate as it is being withdrawn from the melt. The temperature of this shorter heater was now a critical coating parameter. If too hot, solidification, as usual, occurred too far downstream. If not hot enough, the substrate would freeze to the melt. In spite of the fact that the solidification position could now be controlled, the spillover problem remained for all positions of the liquid-solid interface that were tried.

A decision was made early in March to incline the coater to selected angles above horizontal. By doing so, gravity would act to contain the molten silicon. To accomplish this, the coater was extensively modified. The two most significant changes were:

- 1) A motor-driven mechanism was added which permitted tilting the coater at various angles above horizontal.
- 2) New crucible and trough heaters were added which provided superior thermal independence and temperature uniformity than was previously attainable.

Once accomplished, several successful coating runs were made with the coater tilted at a small angle. Smooth, shiny silicon layers were coated on 5-cm x 55-cm x 0.1-cm mullite substrates (K-modification) at a coating velocity of 0.06 cm/sec. The best one of these silicon-coated substrates is shown in Figure 16. As shown, this substrate was for the most part uniformly coated over an area of 225 cm² and has a nominal thickness of approximately 100 μ m. The layer consisted of large columnar silicon grains virtually identical to those achieved by dip-coating under similar growth conditions. Minority carrier diffusion length (L_n) measurements made on these coatings indicate an L_n value which is also similar to dip-coated silicon. Due to a small, but still existing thermal gradient along the trough, the layers varied in thickness from one side of the substrate to the other side.

The above results are of considerable significance, since they demonstrate that by passing the substrate at an angle over the silicon-filled trough, the long-sought-after meniscus stability necessary to SCIM coating has been achieved. The above results also clearly demonstrate that the overall sheet silicon area of any single coating is limited only by the physical dimensions of the substrate. It was made clear, however, that temperature uniformity along the trough is of utmost importance. The above results further demonstrate that because of the similar nature of the SCIM-coated layers, all of our past development efforts on dip-coated layers should be applicable to the SCIM-coated layers as well.

Figure 16. Photograph of SOC Sheet Silicon Showing Dip-Coated and SCIM-Coated Substrates

As shown by Figure 17, the liquid-solid interface appears to occur along a straight line approximately 8 mm downstream of the trough. This observation was based on the fact that the temperature of the back surface of the substrate is elevated where the substrate is in contact with molten silicon. The location of this interface with respect to the melt is not unlike that of dip-coating which produces a condition which is conducive to meniscus stability.

On 24 July, our Technology Center's water supply failed. A few laboratory facilities dependent on this water for cooling purposes were damaged. Among those most seriously damaged was the SCIM coater. It was necessary to completely disassemble the equipment to perform the needed repairs. Since a modification of the substrate transport mechanism had been discussed for some time, and since an improvement in temperature uniformity along the trough was also needed, we felt this was an appropriate time to implement these changes, while the damaged parts were being repaired.

Near the end of this reporting period, the SCIM coater was again on line, but time did not permit any further coating runs. This modified mechanism uses a series of graphite rollers to convey the substrate to, through, and away from the coating chamber. The rollers are spaced 6 inches apart, with the bottom roller driving and the top roller

acting as a gravity-weighted idler. Rollers contained within the preheater, coating chamber, and postheater are driven by 99.8 percent alumina shafts. Figure 18 is a cross-sectional view of a portion of the coating chamber showing its latest features, including the rollers contained within. The improved trough heater shown in this drawing is 9 inches in length. This is approximately 50 percent longer than the prior heater, and the central portion of the heater over which the substrate passes is expected to be very uniform in temperature. The temperature uniformity can also be adjusted by trimming the heated rectangular element located directly below the trough heater.

Figure 17. Silicon Meniscus with Tilted Substrate as Observed Through the Viewing Port of the SCIM Coater

During the fourth quarter of 1979, the addition of this new transport mechanism should increase our experimental output. The optimum coating angle, θ , will be determined and various asymmetric growth configurations will be experimentally examined.

Design for SCIM coater No. 2 will be completed and construction of this second coating unit will be underway.

Figure 18. Most Recent Configuration of Growth Chamber Section Showing a Portion of the Graphite Roller Transport Mechanism

So far, the best SOC solar cell has a total-area conversion efficiency of 10.04 percent (AM1, AR) for an area of 4.08 cm^2 . The dark and light I-V characteristics of this cell are given in Figures 19 and 20. Additional information on this cell is presented in Tables 2 and 3, along with corresponding information on 55 other recent SOC cells. In Table 2, the following data are listed: cell number, base doping concentration, dip speed, specific series resistance, base sheet resistance, and total-area conversion efficiencies, for conditions before and after AR coating. Table 3 presents data on: short-circuit current, I_{sc} ; open-circuit voltage, V_{oc} ; fill factor, FF; short-circuit current density, J_{sc} ; and conversion efficiency, η . The SOC cells listed in Tables 2 and 3 were fabricated during the last 3 months. The characteristics of the other SOC cells fabricated this year are given in Quarterly Reports 10, 11, and 12.

Recently, cell performance was investigated as a function of silicon thickness and of base doping concentration. In addition, the dark and light I-V characteristics were used for determining values of shunt resistance (R_{SH}), of series resistance (R_s), and of diffusion length (L_n). The results of these investigations are discussed in the three sections that follow.

Silicon Thickness

To determine the effect of silicon thickness on cell performance, we fabricated a number of photodiodes on unslotted substrates. The values of silicon thickness were in the range from $5 \text{ }\mu\text{m}$ to $200 \text{ }\mu\text{m}$. Unslotted substrates were used because it is difficult to grow thin ($<50 \text{ }\mu\text{m}$) layers on slotted substrates. The primary characteristics of the various photodiodes are listed in Table 4. For each substrate, five to 20 photodiodes were fabricated and the average values of V_{oc} , FF, J_{sc} , and n were recorded.

Figure 21 shows silicon thickness as a function of growth speed for the eight SOC substrates reported in Table 4. The solid line indicates that the data can be approximately represented by an equation of the following form:

$$v^{2.91} T = 0.0586$$

where v is the growth speed in cm/sec and T is the silicon thickness in μm .

Figure 19. Light I-V Characteristics for Cell No. 187-2-201

Figure 20. Dark I-V Characteristics for Cell No. 187-2-201

Table 2. Conversion Efficiencies of Recent Slotted-Substrate Cells

item	Cell Number	P-type Doping (atoms/cc)	Dip Speed (cm/sec)	RA Product (ohms-sq cm)	Base Sheet Resistance	Total Area Conversion Efficiencies	
						Before AR (%)	After AR (%)
1	181 - 2-102	9.3e+015	0.06	1.9	84	6.06	
2	181 - 2-201	9.3e+015	0.06	1.5	84	6.26	
3	181 - 4-101	9.3e+015	0.07	1.4	167	6.03	
4	181 - 4-202	9.3e+015	0.07	1.3	167	5.62	
5	181 - 6-101	9.3e+015	0.06	0.9	119	6.87	9.52
6	181 - 6-202	9.3e+015	0.06	1.2	119	6.23	8.99
7	181 -22-101	9.3e+015	0.06	1.0	87	6.03	8.63
8	181 -22-202	9.3e+015	0.06	0.8	87	6.42	9.08
9	182 - 5-101	4.7e+016	0.08	0.9	48	4.66	7.49
10	182 - 5-202	4.7e+016	0.08	0.6	48	6.72	9.59
11	182 - 6-101	4.7e+016	0.06	1.0	24	6.91	9.53
12	182 - 6-202	4.7e+016	0.06	0.7	24	6.65	9.67
13	182 - 7-101	4.7e+016	0.07	0.9	30	6.69	9.32
14	182 - 7-202	4.7e+016	0.07	0.6	30	6.86	9.59
15	184 -15-101	2.3e+015	0.08	2.3	271	5.74	7.88
16	184 -15-202	2.3e+015	0.08	2.3	271	3.81	5.68
17	184 -16-102	2.3e+015	0.06	2.1	217	6.32	8.52
18	184 -20-101	2.3e+015	0.07	2.5	168	5.73	7.78
19	184 -20-202	2.3e+015	0.07	2.2	168	5.45	7.94
20	185 - 1-102	2.3e+015	0.06	1.6	311	6.38	8.54
21	185 - 1-201	2.3e+015	0.06	2.0	311	5.53	6.36
22	185 - 2-102	2.3e+015	0.06	1.7	374	6.45	8.80
23	185 - 2-201	2.3e+015	0.06	2.0	374	6.29	8.36
24	185 - 5-101	2.3e+015	0.06	1.4	348	6.30	8.72
25	185 - 5-202	2.3e+015	0.06	1.5	348	6.03	7.05
26	185 - 7-102	2.3e+015	0.08	1.5	331	5.96	8.29
27	185 - 8-101	2.3e+015	0.06	1.7	305	5.90	8.22
28	185 - 8-202	2.3e+015	0.06	1.3	305	6.19	8.63
29	185 - 9-102	2.3e+015	0.07	1.5	290	6.15	8.58
30	185 - 9-201	2.3e+015	0.07	1.8	290	6.12	8.13
31	185 -16-101	2.3e+015	0.08	1.9	255	5.75	
32	185 -16-202	2.3e+015	0.08	1.6	255	5.80	
33	185 -17-102	2.3e+015	0.06	2.6	223	5.60	8.58
34	185 -17-201	2.3e+015	0.06	1.7	223	5.45	7.53
35	185 -18-102	2.3e+015	0.07	2.1	162	5.18	
36	185 -18-201	2.3e+015	0.07	2.3	162	5.58	
37	185 -20-102	2.3e+015	0.06	1.0	137	6.50	8.86
38	185 -20-201	2.3e+015	0.06	1.2	137	6.32	8.50
39	185 -24-101	2.3e+015	0.07	1.8	180	5.92	
40	185 -24-202	2.3e+015	0.07	1.4	180	5.90	
41	187 - 2-102	2.3e+016	0.06	0.6	48	7.12	10.03
42	187 - 2-201	2.3e+016	0.06	0.8	48	7.12	10.04
43	187 - 7-101	2.3e+016	0.06	0.8	54	5.92	8.29
44	187 - 7-202	2.3e+016	0.06	1.0	54	6.17	8.72
45	187 - 9-102	2.3e+016	0.06	0.8	57	4.82	7.53
46	187 - 9-201	2.3e+016	0.06	0.7	57	5.11	7.80
47	188 - 2-101	2.3e+015	0.06	1.8	358	5.94	8.09
48	188 - 2-202	2.3e+015	0.06	1.6	358	5.32	7.04
49	191 - 9-101	9.3e+015	0.07	8.3	119	5.33	7.38
50	191 - 9-202	9.3e+015	0.07	4.0	119	5.75	7.96
51	191 -22-102	9.3e+015	0.07	1.1	67	6.58	9.28
52	191 -22-201	9.3e+015	0.07	1.2	67	4.96	7.85
53	191 -30-102	9.3e+015	0.07	1.5	54	6.31	8.81
54	191 -30-201	9.3e+015	0.07	1.2	54	6.27	9.05
55	192 - 1-103	9.3e+015	0.07	1.2	173	6.07	9.07
56	192 -11-103	9.3e+015	0.07	1.6	145	5.22	

Table 3. Characteristics of Recent Slotted SOC Cells
and Their Corresponding Single-Crystal
Control Cells

item	Cell Number	Isc (mA)	Voc (V)	Fill Factor	Total-Area	
					Jsc (mA/sqcm)	Eff. (%)
1	181 - 2-102-0	72.60	0.530	0.642	17.79	6.06
2	181 - 2-201-0	69.90	0.526	0.695	17.13	6.26
3	181 - 4-101-0	70.40	0.526	0.664	17.25	6.03
4	181 - 4-202-0	64.70	0.527	0.673	15.86	5.62
5	181 - 6-101-0	73.10	0.528	0.726	17.92	6.87
5	181 - 6-101-1	99.20	0.538	0.728	24.31	9.52 (AR)
6	181 - 6-202-0	70.00	0.526	0.690	17.16	6.23
6	181 - 6-202-1	99.10	0.542	0.683	24.29	8.99 (AR)
7	181 -22-101-0	67.90	0.526	0.689	16.64	6.03
7	181 -22-101-1	94.40	0.536	0.696	23.14	8.63 (AR)
8	181 -22-202-0	67.30	0.532	0.732	16.50	6.42
8	181 -22-202-1	94.00	0.543	0.726	23.04	9.08 (AR)
9	182 - 5-101-0	65.00	0.539	0.543	15.93	4.66
9	182 - 5-101-1	93.80	0.557	0.585	22.99	7.49 (AR)
10	182 - 5-202-0	64.20	0.558	0.765	15.74	6.72
10	182 - 5-202-1	91.80	0.573	0.744	22.50	9.59 (AR)
11	182 - 6-101-0	66.40	0.561	0.757	16.28	6.91
11	182 - 6-101-1	95.90	0.575	0.705	23.51	9.53 (AR)
12	182 - 6-202-0	63.20	0.559	0.768	15.49	6.65
12	182 - 6-202-1	95.60	0.573	0.722	23.43	9.67 (AR)
13	182 - 7-101-0	67.80	0.553	0.728	16.62	6.69
13	182 - 7-101-1	93.30	0.562	0.725	22.87	9.32 (AR)
14	182 - 7-202-0	65.30	0.560	0.765	16.00	6.86
14	182 - 7-202-1	92.70	0.565	0.747	22.72	9.59 (AR)
15	184 -15-101-0	70.10	0.498	0.671	17.18	5.74
15	184 -15-101-1	95.30	0.516	0.653	23.36	7.88 (AR)
16	184 -15-202-0	64.20	0.479	0.506	15.74	3.81
16	184 -15-202-1	87.70	0.499	0.529	21.50	5.68 (AR)
17	184 -16-102-0	74.00	0.512	0.680	18.14	6.32
17	184 -16-102-1	102.90	0.524	0.645	25.22	8.52 (AR)
18	184 -20-101-0	67.40	0.506	0.686	16.52	5.73
18	184 -20-101-1	90.40	0.523	0.671	22.10	7.78 (AR)
17	184 -20-202-0	64.10	0.505	0.687	15.71	5.45
19	184 -20-202-1	92.10	0.525	0.670	22.57	7.94 (AR)
20	185 - 1-102-0	74.20	0.503	0.698	18.19	6.38
20	105 - 1-102-1	100.80	0.518	0.667	24.71	8.54 (AR)

Table 3. Characteristics of Recent Slotted SOC Cells
and Their Corresponding Single-Crystal
Control Cells (Continued)

item	Cell Number	Isc (mA)	Voc (V)	Fill Factor	Total-Area	
					Jsc (mA/sqcm)	Eff. (%)
21	185 - 1-201-0	69.90	0.501	0.644	17.13	5.53
21	185 - 1-201-1	96.00	0.520	0.520	23.53	6.36 (AR)
22	185 - 2-102-0	73.60	0.504	0.709	18.04	6.45
22	185 - 2-102-1	105.00	0.511	0.675	25.74	8.88 (AR)
23	185 - 2-201-0	74.10	0.512	0.676	18.16	6.29
23	185 - 2-201-1	103.40	0.519	0.636	25.34	8.36 (AR)
24	185 - 5-101-0	73.20	0.499	0.704	17.94	6.30
24	185 - 5-101-1	101.30	0.514	0.683	24.83	8.72 (AR)
25	185 - 5-202-0	72.40	0.497	0.684	17.74	6.03
25	185 - 5-202-1	98.30	0.514	0.569	24.09	7.05 (AR)
26	185 - 7-102-0	70.30	0.505	0.685	17.23	5.96
26	185 - 7-102-1	97.90	0.519	0.666	24.00	8.29 (AR)
27	185 - 8-101-0	72.20	0.505	0.660	17.70	5.90
27	185 - 8-101-1	100.60	0.519	0.642	24.66	8.22 (AR)
28	185 - 8-202-0	72.00	0.501	0.700	17.65	6.19
28	185 - 8-202-1	99.10	0.518	0.686	24.29	8.63 (AR)
29	185 - 9-102-0	71.20	0.502	0.702	17.45	6.15
29	185 - 9-102-1	99.80	0.513	0.683	24.46	8.58 (AR)
30	185 - 9-201-0	74.30	0.507	0.663	18.21	6.12
30	185 - 9-201-1	101.90	0.517	0.629	24.98	8.13 (AR)
31	185 -16-101-0	67.30	0.504	0.692	16.50	5.75
32	185 -16-202-0	66.00	0.509	0.705	16.10	5.80
33	185 -17-102-0	71.80	0.509	0.625	17.60	5.60
33	185 -17-102-1	100.20	0.531	0.658	24.56	8.58 (AR)
34	185 -17-201-0	67.90	0.506	0.647	16.64	5.45
34	185 -17-201-1	94.60	0.524	0.620	23.19	7.53 (AR)
35	185 -18-102-0	70.30	0.508	0.592	17.23	5.18
36	185 -18-201-0	68.90	0.508	0.650	16.89	5.58
37	185 -20-102-0	70.20	0.513	0.736	17.21	6.50
37	185 -20-102-1	96.60	0.526	0.711	23.68	8.86 (AR)
38	185 -20-201-0	69.40	0.516	0.720	17.01	6.32
38	185 -20-201-1	94.10	0.528	0.698	23.06	8.50 (AR)
39	185 -24-101-0	67.60	0.505	0.707	16.57	5.92
40	185 -24-202-0	66.50	0.508	0.712	16.30	5.90

Table 3. Characteristics of Recent Slotted SOC Cells
and Their Corresponding Single-Crystal
Control Cells (Continued)

item	Cell Number	Isc (mA)	Voc (V)	Fill Factor	Total-Area	
					Jsc (mA/sqcm)	Eff. (%)
41	187 - 2-102-0	69.80	0.547	0.761	17.11	7.12
41	187 - 2-102-1	98.60	0.551	0.753	24.17	10.03 (AR)
42	187 - 2-201-0	69.40	0.562	0.758	17.01	7.12
42	187 - 2-201-1	98.90	0.556	0.745	24.24	10.04 (AR)
43	187 - 7-101-0	63.30	0.537	0.711	16.52	5.92
43	187 - 7-101-1	86.70	0.548	0.712	21.25	8.29 (AR)
44	187 - 7-202-0	64.20	0.540	0.726	15.74	6.17
44	187 - 7-202-1	90.40	0.552	0.713	22.16	8.72 (AR)
45	187 - 9-102-0	61.90	0.526	0.604	15.17	4.82
45	187 - 9-102-1	92.40	0.538	0.618	22.65	7.53 (AR)
46	187 - 9-201-0	61.20	0.531	0.642	15.00	5.11
46	187 - 9-201-1	91.10	0.543	0.643	22.33	7.00 (AR)
47	188 - 2-101-0	73.80	0.504	0.651	18.09	5.94
47	188 - 2-101-1	102.10	0.514	0.629	25.02	8.09 (AR)
48	188 - 2-202-0	68.50	0.495	0.640	16.79	5.32
48	188 - 2-202-1	89.50	0.507	0.633	21.94	7.04 (AR)
49	191 - 9-101-0	69.60	0.522	0.599	17.06	5.33
49	191 - 9-101-1	94.90	0.535	0.593	23.26	7.38 (AR)
50	191 - 9-202-0	69.10	0.524	0.648	16.94	5.75
50	191 - 9-202-1	96.70	0.537	0.625	23.70	7.96 (AR)
51	191 -22-102-0	68.50	0.530	0.740	16.79	6.58
51	191 -22-102-1	96.30	0.541	0.727	23.60	9.28 (AR)
52	191 -22-201-0	65.80	0.523	0.580	16.13	4.96
52	191 -22-201-1	89.90	0.534	0.637	22.03	7.85 (AR)
53	191 -30-102-0	67.10	0.529	0.724	16.45	6.31
53	191 -30-102-1	93.30	0.547	0.704	22.87	8.81 (AR)
54	191 -30-201-0	65.70	0.530	0.735	16.10	6.27
54	191 -30-201-1	93.50	0.550	0.718	22.92	9.05 (AR)
55	192 - 1-103-0	159.60	0.519	0.733	15.96	6.07
55	192 - 1-103-1	235.00	0.533	0.724	23.50	9.07 (AR)
56	192 -11-103-0	148.40	0.512	0.687	14.84	5.22
(Single-Crystal)						
57	072A- 0-101-0	84.60	0.545	0.747	20.74	8.44
58	072A- 0-202-0	86.60	0.545	0.740	21.22	8.56
59	077A- 0-102-0	87.20	0.531	0.739	21.37	8.39

Table 3. Characteristics of Recent Slotted SOC Cells and Their Corresponding Single-Crystal Control Cells (Concluded)

item	Cell Number	I _{sc} (mA)	V _{oc} (V)	Fill Factor	Total-Area J _{sc} (mA/cm ²)	Eff. (%)
60	R10 - 0-102-0	89.20	0.553	0.684	21.86	8.27
61	R11 - 0-102-0	86.30	0.566	0.765	21.15	9.16
62	R11 - 0-201-0	84.50	0.564	0.763	20.71	8.91
63	R12A- 0 102 0	86.50	0.567	0.760	21.20	9.14
64	R12B- 0-102-0	85.80	0.560	0.750	21.03	8.83
65	R14B- 0-102-0	85.30	0.538	0.732	20.91	8.23
66	R8 - 0-102-0	86.10	0.556	0.762	21.10	8.94
66	R9B - 0-102-0	89.00	0.560	0.758	21.81	9.26

Table 4. Characteristics of Photodiodes Fabricated on Unslotted SOC Material Grown at Various Speeds

Substrate No.	No. of Photodiodes	Doping Concentration (cm ⁻³)	Growth Speed (cm/sec)	Thickness (μm)	V _{oc} (V)	Fill Factor	Active-Area	
							J _{sc} (mA/cm ²)	η (%)
189-2	13	2.3 x 10 ¹⁶	0.059	190	0.53	0.75	19.7	7.76
190-11	14	9.3 x 10 ¹⁵	0.069	100	0.51	0.69	18.6	6.58
190-3	12	9.3 x 10 ¹⁵	0.071	130	0.52	0.71	19.8	7.28
190-12	14	9.3 x 10 ¹⁵	0.081	95	0.51	0.69	18.6	6.51
190-5	9	9.3 x 10 ¹⁵	0.1	70	0.50	0.68	19.6	6.69
189-5	13	2.3 x 10 ¹⁶	0.103	60	0.51	0.69	17.5	6.21
190-14	14	9.3 x 10 ¹⁵	0.135	20	0.48	0.65	14.3	4.41
190-10	X	9.3 x 10 ¹⁵	0.195	6	(No junction formed)			
Single-crystal								
R15	4	4Ω-cm	X	400	0.52	0.68	24.0	8.54
R17	7	4Ω-cm	X	400	0.51	0.71	24.2	8.80

Figure 21. Silicon Thickness as a Function of Growth Speed for the Eight Substrates Reported in Table 4

Figure 22 presents the same data as given in Table 4. As the silicon thickness decreases, V_{oc} , FF, J_{sc} , and η all decrease. The active-area efficiency, η , is 7.8 percent for a thickness of 190 μm , 6.6 percent for 100 μm , and 4.4 percent for 20 μm . All efficiency values are for photodiodes without an AR coating. The results given in Figure 22 indicate that the efficiency decreases by about 20 percent as the silicon thickness decreases from 200 μm to 100 μm .

Base Doping Concentration

In Quarterly Report No. 12, we reported that the optimum base doping concentration was $10^{16}/\text{cm}^3$. The primary results of that quarter are indicated by dotted lines in Figure 23. Note that the dotted curve in Figure 23(d) has a maximum value when the base doping concentration, N_{BG} , is about $10^{16}/\text{cm}^3$.

Figure 22. Photodiode Characteristics as a Function of Silicon Thickness. The photodiodes were fabricated on unslotted SOC materials grown at various speeds.

(a)

(b)

(c)

(d)

Figure 23. Performance of Slotted SOC Cells as a Function of Base Doping Concentration, for Cells with AR Coating. Dashed lines correspond to results given in Quarterly Report No. 12. Solid lines correspond to new results.

The solid curves in Figure 23 represent more recent results which indicate that cell performance can be improved if N_{BG} is greater than $10^{16}/\text{cm}^3$. The recent results differ from the previous results primarily at the low and high base doping concentrations. That is, several new SOC cells were fabricated with concentrations of 2.3×10^{15} and $4.6 \times 10^{16}/\text{cm}^3$. It is assumed that the recent results are more accurate than the previous results although sufficient information does not exist as yet to prove this assumption. Thus, in the remainder of this subsection, we will refer only to the solid curves in Figure 23.

Figure 23(a) shows that the open-circuit voltage, V_{oc} , increases linearly as a function of $\log N_{BG}$. For a given value of N_{BG} , the center of the vertical line indicates the average value of V_{oc} and the length of the line is 2σ , where σ is the standard deviation. Thus, for a base doping concentration of $2.3 \times 10^{16}/\text{cm}^3$, the average value was 0.536 v, with a standard deviation of 0.005 v. For the low and high values of N_{BG} , two vertical lines are given. The lower line corresponds to the results of Quarterly Report No. 12 and the upper line to the recent results. The upper lines are sometimes slightly displaced to the right or left so that the various vertical lines do not overlap. The solid line for V_{oc} indicates approximately how the average value of V_{oc} should vary as a function of N_{BG} , based on the recent measurement.

As has been stated, Figure 23(a) shows that V_{oc} increases linearly as a function of $\log N_{BG}$. This result is consistent with conventional solar cell theory. Figure 23(b) shows that the fill factor, FF, also increases linearly as a function of $\log N_{BG}$. The increase is due primarily to a corresponding decrease in series resistance. Figure 23(c) shows that, as N_{BG} increases, the short-circuit current density is relatively constant until $N_{BG} = 10^{16}/\text{cm}^3$ and then decreases for higher values of N_{BG} . Finally, Figure 23(d) shows that the conversion efficiency, η , increases as N_{BG} increases. As has been stated, this result is based on insufficient information. There certainly must be a maximum value for η and we will continue to fabricate additional SOC cells to determine the optimum base doping concentration, which is apparently greater than $10^{16}/\text{cm}^3$.

Dark and Light I-V Characteristics

The dark I-V characteristics of the 23 cells fabricated during the month of October were measured and values were calculated for the various parameters in the following equation (which was discussed in Quarterly Report No. 11):

$$J = J_{01} \exp \left[\frac{q(V - J R_s A)}{kT} - 1 \right] + J_{02} \left[\exp \frac{q(V - J R_s A)}{nkT} - 1 \right] + \frac{V - J R_s A}{R_{SH}} \quad (2)$$

Table 5 lists the calculated values of R_{SH} , n , J_{02} , $R_s A$, and J_{01} . From the table, the following conclusions can be made regarding recent SOC solar cells:

- 1) Shunt resistance values are typically greater than 10K ohms, indicating that shunting resistance is not a problem with SOC cells.
- 2) For shunt resistance values greater than 10K ohms, n is approximately 1.7 for many cells.
- 3) Specific series resistance values are typically in the range from $0.7 \Omega\text{-cm}^2$ to $1.7 \Omega\text{-cm}^2$. These values are higher than values for typical single crystals, but this does not represent a major limitation of the SOC material, as discussed in Quarterly Report No. 11.
- 4) For a base doping concentration of $2.3 \times 10^{15}/\text{cm}^3$, J_{01} is approximately $4 \times 10^{-8} \text{ mA/cm}^2$. Note that, in Table 5, the first six cells have a base doping concentration of $2.3 \times 10^{16}/\text{cm}^3$, and the remaining cells have the just noted concentration of $2.3 \times 10^{15}/\text{cm}^3$.

The value of J_{01} can be used to estimate the minority-carrier diffusion length, L_n , using the following equation:

$$J_{01} = q \frac{D_n n_i^2}{L_n N_A} \quad (3)$$

where D_n is the diffusion constant, n_i is the intrinsic carrier concentration (approximately $1.5 \times 10^{10}/\text{cm}^{-3}$), and N_A is the base doping concentration. In single-crystal silicon, $D_n = 26 \text{ cm}^2/\text{sec}$ for $N_A = 2.3 \times 10^{15}/\text{cm}^2$. To estimate L_n for SOC material, we will assume that $D_n = 13 \text{ cm}^2/\text{sec}$ for SOC material, which is one-half the single-crystal value. Thus, the calculated diffusion length for the best 16 SOC cells in Table 5 is approximately $50 \mu\text{m}$, assuming that Equation (3) is valid for SOC material.

Table 5. Calculated Values for Recent SOC Cells

Item	Cell No.	A (cm ²)	R _{SH} (k Ω)	n	J ₀₂ (mA/cm ²)	R _S A (Ω -cm ²)	J ₀₁ (mA/cm ²)
1	187-2-102	4.08	820	1.8	3.7×10^{-5}	0.9	1.0×10^{-8}
2	187-2-201	4.08	150	2.3	2.4×10^{-4}	0.9	1.4×10^{-8}
3	187-7-101	4.08	31	2.3	1.0×10^{-3}	0.8	1.3×10^{-8}
4	187-7-202	4.08	5.7	2.6	9.2×10^{-4}	1.0	1.6×10^{-8}
5	187-9-102	4.08	--	--	--	--	--
6	187-9-201	4.08	--	--	--	--	--
7	185-7-102	4.08	4.7	2.6	3.3×10^{-3}	0.9	2.5×10^{-8}
8	185-9-102	4.08	1000	1.7	7.0×10^{-5}	1.1	4.4×10^{-8}
9	185-9-201	4.08	29	2.0	2.6×10^{-4}	1.4	4.9×10^{-8}
10	185-1-102	4.08	230	1.7	6.8×10^{-5}	1.2	4.4×10^{-8}
11	185-1-201	4.08	180	1.7	4.8×10^{-5}	1.6	4.3×10^{-8}
12	185-2-102	4.08	49	2.1	2.9×10^{-4}	1.4	5.2×10^{-8}
13	185-2-201	4.08	140	1.8	6.2×10^{-5}	1.6	3.7×10^{-8}
14	185-5-101	4.08	150	1.9	1.7×10^{-4}	0.9	3.8×10^{-8}
15	185-5-202	4.08	370	1.7	6.4×10^{-5}	0.9	3.1×10^{-8}
16	185-8-101	4.08	66	2.0	2.1×10^{-4}	1.3	4.6×10^{-8}
17	185-8-202	4.08	3.1	3.9	8.1×10^{-3}	1.0	6.8×10^{-8}
18	185-17-102	4.08	70	3.9	1.8×10^{-4}	3.0	3.5×10^{-8}
19	185-17-201	4.08	0.4	2.1	4.9×10^{-4}	1.5	4.6×10^{-8}
20	185-20-102	4.08	∞	1.7	4.3×10^{-5}	0.7	3.1×10^{-8}
21	185-20-201	4.08	125	1.7	4.4×10^{-5}	1.0	3.1×10^{-8}
22	188-2-101	4.08	590	1.6	2.6×10^{-5}	1.5	3.9×10^{-8}
23	188-2-202	4.08	0.4	2.3	1.1×10^{-3}	1.5	5.9×10^{-8}

MATERIAL EVALUATION (D. Zook and R. Hegel)

During the past year, the LBIC (light-beam-induced current) technique has been further developed, and has been used to evaluate SOC material quality. The technique has been used to evaluate unprocessed material, cells before AR coating, cells that have been AR coated, and cells that show appreciable shunting resistance. We have found that LBIC can be useful in identifying difference in short-circuit current due to cell processing. Several people have requested a description of the experimental setup, and we have therefore included a description of the LBIC technique below.

The LBIC Technique

A number of papers have addressed the problem of lifetime and diffusion length measurement in solar cell material.^{1, 2} It is desirable to use a measurement technique that can be used on fabricated cells, whether AR-coated or not, as well as on unprocessed, "as-grown" material, which can later be fabricated into solar cells. Recent emphasis has been on the scanning electron microscope (SEM) in the electron-beam-induced current (EBIC) mode.³ EBIC techniques have the virtue that they can provide very high-resolution images of structural defects which act as recombination centers. However, quantitative unambiguous measurements of diffusion length are made difficult by surface recombination and/or electron-beam-induced inversion layers on p-type silicon, unless special samples are prepared.

Light-spot scanning (LSS) techniques can also provide high-resolution images if a laser is used as the light source.⁴ Although the HeNe laser gives high resolution when the laser energy (approximately 0.1 mV), is focussed on a small area (approximately 10 μm), the intensity is very high $\left[0.1 \text{ mW}/(10 \mu\text{m})^2 = 10^5 \text{ mW}/\text{cm}^2\right]$, giving very high injection levels (>1000 suns). Thus, laser scan measurements are not necessarily relevant to normal solar-cell operation. Light-spot scanning without a laser has been performed at low resolution (25 μm to 2 mm). In fact, a light-beam scan was used to demonstrate the first reported p-n junction by Goucher, et al.⁵ It has also been used to evaluate large areas of material for low-cost solar cells.⁶ The present technique has a resolution similar to a laser system, and can be used over the entire response spectrum.

In the present technique, a high-pressure short-arc xenon lamp is used with a single-pass monochromator. As discussed below, the xenon spectrum has a number of readily identified peaks with well-known wavelengths that have intensities in the order of one sun (i. e., the generated current density is on the order of 30 mA/cm^2 at the focussed spot.) The peaks are in a convenient range for determining the diffusion length, L , in silicon.

A schematic diagram of the experimental setup is shown in Figure 24. The xenon lamp is focussed on the entrance slit of the monochromator, and the exit slit is focussed on a pinhole aperture which can be varied by rotating a wheel to a different pinhole. The pinhole is focussed by a 15X, F/0.28 reflecting objective. Such an objective has the advantage that the focussing is independent of wavelength so that the sample can be focussed in the visible and then scanned in the infrared. Focussing and viewing the sample is done with a beam splitter and viewing eyepiece. The beam splitter is an uncoated pellicle which transmits about 95 percent of the light. A fiber-optic illuminator provides viewing light and can be used as a white-light bias.

The scanning is done with a d-c motor drive and a variable-speed control. It was found helpful to also have a small motor drive for the other axis of the x-y stage for focussing. This arrangement avoids the application of torque to the stage which can vary during the scan. The sample and the reflective objective are on mounts that have 2 degrees of tilt adjustment. The entire system beyond the monochromator was mounted on a short optical bench and enclosed in a light-tight box.

The absolute spectral response measurements are made by inserting a calibrated reference diode in front of the sample and comparing d-c currents. It is important to have a highly uniform and accurately calibrated reference cell. The linearity and uniformity of the reference cell can be readily evaluated by moving it in and out of focus and scanning the beam across it, while monitoring the current through it. The cell we used for this work was found to give the same current reading to within a few percent under all conditions, as long as all the light strikes the cell. We conclude that our reference cell is not only highly uniform but also linear, since the light intensity can change by seven orders of magnitude as the spot goes from the focussed condition (5 μm diameter) to a size of 2 cm^2 .

A typical scan of an SOC p-n junction diode is shown in Figure 25. Scans of the short-circuit current at four wavelengths are shown which can be compared with the photograph and sketch at the top of the figure. For the purposes of discussion, a "grain boundary" is defined as the boundary between two regions ("grains"), where each grain can have a number of parallel boundaries. The seven grain boundaries labeled in Figure 25(a) are associated with the deepest minima in the scans. Actually grain boundaries numbered 3 and 5 each appear to have subsidiary minima associated with them. Also, there are additional, lesser minima for which no corresponding structure is visible in the photograph. However, to a first approximation, the photocurrent is constant within grains and shows deep minima at grain boundaries.

Figure 24. Schematic Diagram of LBIC System

Figure 25. Typical LBIC Scan Showing (a) Trace of Photograph of Diode, and (b), (c), (d), and (e) LBIC Scans at Four Different Wavelengths

Electrolyte Technique

A number of investigators have reported the properties of an electrolyte acting as a Schottky-barrier contact to a semiconductor.⁴ Generally, these studies have used n-type semiconductors because of problems with oxidation or corrosion with p-type semiconductors. In the latter case, however, the purpose of the electrolyte is to provide an optically transparent contact to p-type silicon. We have found that an aqueous solution of EuCl_3 (0.1N in 0.1N HCl) can be used satisfactorily in a voltage-biased mode. Figure 26 shows schematically the arrangement used for testing. Since the electrolyte and the fused silica window are between the sample and the objective, the large working distance of the reflecting objective is essential. Figure 27 shows the current-voltage relationship observed for photocurrents in the microampere range. Because of the leakage current in the cell, it is necessary to use chopped light and signal detection with a lock-in amplifier. A typical scan of a large-grain area of SOC material is shown in Figure 28. Generally, the spectral response is very similar to that of a p-n junction.

Determination of Effective Diffusion Length

A number of authors have discussed the use of the long-wavelength spectral quantum efficiency, S_λ , to obtain values of the minority-carrier diffusion length, L , using the expression:^{2,6,7}

$$S_\lambda = \frac{(1 - R_\lambda) \alpha_\lambda L}{1 + \alpha_\lambda L} \quad (4)$$

where R is the reflectivity, α_λ is the absorption coefficient for light of wavelength λ . Spectral response is a very important solar-cell characteristic. The importance of L is that it is described with one parameter, the long-wavelength response of a cell. Even though S_λ may vary rapidly from point-to-point in large-grain polycrystalline silicon, an effective value of L can still be used to describe the spectral response, as described below.

Equation (4) can be rewritten as:

$$\frac{1}{Q_\lambda} = \frac{1 - R_\lambda}{S_\lambda} = 1 + \frac{\alpha_\lambda^{-1}}{L} \quad (5)$$

Figure 26. Electrolyte Technique of LBIC

Figure 27. Current-Voltage Relationship in an Electrolyte Cell on p-type Silicon. The different curves represent different light intensities.

Figure 28. LBIC Scans of an SOC Sample Using the Electrolyte Technique. The drop in current at the edges is due to vignetting of the beam by the platinum electrode which is out of focus.

where Q_λ is the charge collection efficiency. The conventional method of deducing values of L from measurements of S_λ is to plot Q_λ versus $1/\alpha_\lambda$ so that the intercept on the axis where $1/S = 0$ gives the value of L . This procedure is used in the SPV method.^{6,7} The value of L is then obtained from a least-squares fit of the data to a straight line. One problem with this procedure is that it gives larger weight to the largest values of S^{-1} and α^{-1} . These occur at the longest wavelengths, where the signal is smallest and the uncertainty in the values of α^{-1} are largest. Nonlinear least-squares procedures can be used to fit the measured values of S_λ using Equation (4) directly rather than Equation (5).⁷ Another difficulty is that the value of $1 - R_\lambda$ must be known. This may vary if AR coatings or inadvertant thin oxides are present on the sample.

We have used a simple procedure that avoids these difficulties. At each wavelength, λ_j , a value of L_j is obtained from the measured value of S_j , by solving Equation (4):

$$L_j = \frac{\alpha_j^{-1}}{\frac{1-R}{S_j} - 1} \quad (6)$$

These values of L_j are used to give an average value of L as well as a standard deviation which indicates the degree of the fit. Since all the numbers being averaged are about the same magnitude, equal weight is given to all points.

Since the reflectivity may vary due to slight oxides or uncoated cells, or variations in AR coatings, the value of R is chosen to minimize the relative error, $\Delta L/L$.

Writing

$$L = \frac{1}{n} \sum L_j \quad (7)$$

and

$$\Delta L = \frac{1}{n} \sum L_j^2 - L^2 \quad (8)$$

the condition for $\Delta L/L$ to be a minimum with respect to $(1 - R)$ is

$$\sum L_j^2 \sum L_j^2 \frac{\alpha_j}{S_j} - \sum L_j \sum L_j^3 \frac{\alpha_j}{S_j} = 0$$

which follows by direct differentiation. This relation is used in a root-finding procedure to find the best value of R to fit the data.

Another feature of the above procedure is that further systematic errors can be detected from the pattern of deviations of L_j from the mean by printing out the values of $L_j - L$. We find that the absorption α_λ data of Runyan¹ gives the best fit to our data. It was pointed out by Runyan that calibration of the spectrometer and use of narrow spectral line widths is important for accurate measurements of α . It follows that these points are also important in the accurate determination of L_n . The LBIC technique using a xenon lamp provides a self-calibrating feature that is quite helpful. The xenon lamp has a number of peaks in the near-infrared that are conveniently spaced for diffusion length measurements in silicon. A spectrum made with the single-pass prism monochromator is shown in Figure 29. The six peaks labeled above the curve were usually used in our experiments. The wavelengths are those given in a standard handbook for

Figure 29. Xenon Short-Arc Lamp Spectrum Measured with a Single-Pass Monochromator

xenon. The values of α^{-1} obtained by Runyan for these wavelengths are shown in Table 6. Examination of the polynomial fit usually used to describe Runyan's data¹ shows that it does not fit the data adequately near long wavelengths. Accordingly, the value given in Table 6 for the value of α^{-1} at 0.98 μm was obtained by interpolating the actual data. The value shown gives a better fit to our data than the value from the polynomial expression.

Table 6. Wavelengths and Absorption Coefficients Used in L_n Determination

λ (μm)	α^{-1} (cm^{-1})
0.764	8.256
0.823	13.9
0.882	25.2
0.916	37.3
0.946	55.4
0.980	98.2

From equation (4), the response in the long-wavelength limit becomes

$$S_{\lambda} = (1 - R) \alpha_{\lambda} L \quad (10)$$

This suggests that scans at the longest wavelengths provide a mapping of an effective value of $L(x)$. The scale is determined by the determination of L at one point using the above procedure. Of course, it is not obvious that Equations (4), (5), and (6) are valid when the diffusion length is a function of position. The concept of effective diffusion length as a function of position has been discussed by Daud, Koliwad, and Allen,³ who used it as an empirical parameter, useful for polycrystalline solar cells. They measured the variation of L in the vicinity of a grain boundary by an EBIC technique on an angle-lapped sample.

The internal quantum efficiency, $Q(\lambda, x)$, in the vicinity of a grain boundary can be expressed by writing Equation (5) with explicit λ and x dependences:

$$\frac{1}{Q(\lambda, x)} = 1 + \frac{\alpha^{-1}(\lambda)}{L_e(\lambda, x)} \quad (11)$$

If the value of $L_e(\lambda, x)$ obtained from measurements of $Q(\lambda, x)$ is essentially independent of λ , then this equation becomes (approximately):

$$L_e(x) = \frac{\alpha^{-1}(\lambda)}{\frac{1}{Q(\lambda, x)} - 1} \quad (12)$$

which defines an effective diffusion length in the vicinity of a grain boundary.

We have tested the validity of Equation (12) in a number of samples by deducing an effective value of L_e at the grain boundary minima. Generally, we get a good fit, with the value of L_e at a minimum one-third to one-fifth of the value within the grain. The actual value will depend on the scanning spot size relative to the value of L within a grain. Usually the spot size is less than $L/3$ in SOC material. Frequently, we find that a majority of the grain boundaries in a given sample have similar minima, as illustrated in Figure 25.

In order to examine detailed effects, an expanded scan is necessary. Such a scan on an AR-coated 4-cm² solar cell that had an efficiency of 9.9 percent, is shown in Figure 30. The dashed lines show the baseline levels assumed for the bulk diffusion length. The diffusion length measurement procedure gave a value of $L = 40 \pm 2 \mu\text{m}$ and a value of

Figure 30. Expanded LBIC Line Scan of SOC Solar Cell Showing Detailed Structure at Grain Boundaries as a Function of Wavelength

Figure 31. Experimentally Determined Values of $L_e(x)$ Near a Grain Boundary at $x = 0$. The original data are shown in Figure 34. LBIC measurements at each wavelength are used to calculate values of $L_e(x)$ at each point. The coincidence of the curves shows that $L_e(x)$ is independent of wavelength to a good approximation. The dashed line shows the extrapolation used to obtain a value of S .

$1 - R = 0.95$, which was slightly higher than the peak value of Q_λ which was 0.94. The values of $L_e(x)/L$ deduced from Equation (12) are shown in Figure 31. The error bars included the total spread for the values of L deduced from four wavelengths, with αL ranging from 0.4 to 4.7 for both the grain boundary no. 2 in the scan and the right half of grain boundary no. 1. It is clear that the value of L_e is approximately independent of wavelength, and that the function $L_e(x)$ does indeed characterize the photoresponse in the vicinity of a grain boundary.

Results of Measurement

The purpose of the LBIC measurements was to separate the effects of grain boundaries from the effects of impurities. The rationale was as follows:

- 1) LBIC would be used to determine the diffusion length, L , within grains, which should determine the level of impurities in the bulk of the material.
- 2) By studying isolated grain boundaries, the loss in J_{sc} at each wavelength due to a grain boundary could be determined. The total loss in J_{sc} would be the loss integrated over all wavelengths.
- 3) The number of grain boundaries could be counted by simply looking at the scattered light.
- 4) The total J_{sc} should then be given by the value of J_{sc} that single-crystal material with the same value of L has, less the loss per grain boundary times the number of grain boundaries.

The above model of SOC cell performance may still be applicable on the average, but there appear to be numerous exceptions that complicate the picture:

- 1) Different large grains within the same sample may have different diffusion lengths. Even adjacent grains may have values of L differing by 25 percent.
- 2) SOC material appears to consist of large-grain regions and small-grain regions. The small-grain regions may have a significantly smaller diffusion length than the large-grain regions, especially in processed cells. An extreme example is shown by the LBIC scan in Figure 32.

Measurements on several samples from the same runs, before and after processing, are summarized in Table 7. It is clear that the values of L increased significantly due to processing. The increase within large grains is especially noteworthy. The average

Figure 32. LBIC Scan of a 4-cm² Cell on Substrate 185-1.
The base line is shown by the signal level at
the metallization fringes.

value of L_n as determined from an integrated scan at $0.98 \mu\text{m}$ is also shown. The average was calculated during scanning by the use of an integrator circuit. One expects good correlation between the average and J_{sc} , and this is indeed the case, except for sample 185-1-102, which had the largest variations in L_n .

Table 7. Comparison of Diffusion Lengths Before and After Cell Fabrication

Cell No.	Before Processing	Processed (p-n junction)		
	Within Grain (μm)	Within Grain (μm)	Integrated Scan (μm)	J_{sc} (mA/cm^2)
185-1-102	27.1	26.0	20.7	18.2
185-5-202	26.6	58.6	30.3	17.9
185-17-102	14.5	38.9	24.6	17.6
185-20-102	12.2	28.2	22.6	17.2

Effective Diffusion Length and Effective Surface Recombination Velocity at a Grain Boundary (D. Zook)

Quarterly Report No. 12, published 31, July 1979,⁸ described a theory of the short-circuit current due to a single ray of light in the vicinity of a grain boundary perpendicular to the p-n junction. This theory has been further extended and has been tested by detailed comparison with experiment. Theory and experiment appear to be in very good agreement except for some systematic differences that remain to be resolved.

The theory was based on infinite surface recombination velocity at a grain boundary ($s = \infty$), and the results can be given in terms of certain integrals of Bessel functions calculated by van Roosbroeck.⁹ The internal quantum efficiency, $Q_\lambda(x)$, in the infrared depends strongly on the wavelength, λ , and on distance, x , from a grain boundary. An effective diffusion length, $L_e(x)$, can be defined by Equation (9) above, where $Q_\lambda(x)$ can be determined either experimentally or theoretically. Figure 31 is a plot of $L_e(x)$ determined experimentally from LBIC measurements on several grain boundaries in sample 179-4. Figure 33 is a plot of $Q_\lambda(x)$ determined theoretically for $s = \infty$ from van Roosbroeck's graphs. These curves are replotted in Figure 34, by using Equation (9) to give $L_e(x)$. It is clear that the "effective diffusion length" concept works quite well in both cases. The dashed line in Figure 34, is the experimental curve from Figure 31.

Figure 33. Theoretical LBIC Response in the Vicinity of a Grain Boundary with Infinite Surface Recombination Velocity

Figure 34. Theoretical Calculation of $L_e(x)$ Near a Grain Boundary at $x = 0$. The model assumes $S = \infty$, and the curves are replots of van Roosbroeck's calculations.

Figure 35 shows that there is a definite discrepancy between theory and experiment that is not accounted for by the finite size of the scanning light beam. The fact that the experimental dips do not approach zero indicates that the surface recombination velocity is not infinite. The fact that the experimental curve is "fatter" than the theoretical curve indicates a more basic discrepancy that is not so easily explained. The relationship between LBIC line shape and surface recombination at a grain boundary is discussed next.

Figure 35. Boundary Conditions at (a) a Semiconductor Surface and (b) a Grain Boundary. Excess minority carriers are generated at some point $x > 0$, $z > 0$, causing a flux $J_1(z)$ of minority carriers to be incident on the boundary. The recombination current J_s is equal to the surface recombination velocity S times the excess minority carrier density at the surface $(\Delta n)_s$.

The rate of loss of minority carriers at a grain boundary, in the simplest model of recombination, should be proportional to the density of minority carriers. The process can therefore be characterized by a surface recombination velocity, s . The geometry of a grain boundary is, however, different from that of an actual surface. In that case,¹⁰ carriers reaching the surface are either reflected, with a surface reflection coefficient, R_0 , or recombine with a recombination probability, $1 - R_0$ (see Figure 35). Where a nonequilibrium distribution of minority carriers is established (e. g., by a light beam), it results in a net current toward the boundary surface:

$$J_s = -D_n \left| \frac{\partial(\Delta n)}{\partial x} \right|_s \quad (13)$$

where Δn is the excess minority carrier density, D_n is the diffusion coefficient, and the

subscript s indicates the surface. The current is proportional to $(\Delta n)_s$:

$$J_s = s(\Delta n)_s$$

where s, the surface recombination velocity, is proportional to $1 - R_o$, the recombination probability. As shown in Figure 35(a), the incident flux of excess carriers, J_1 , is partially reflected, giving a net recombination current of $J_s = (1 - R_o) J_1$.

At a grain boundary, on the other hand, part of the flux of excess carriers is transmitted, as shown in Figure 35(b). The net recombination current at the grain boundary is given by $J_s = (1 - R_o - T_o) J_1$, where T_o is the transmittance of the boundary.

For either the surface or grain boundary geometry, the $z = 0$ plane of Figure 35 is the p-n junction which collects minority carriers. The case of the free semiconductor surface, Figure 35(a), is discussed by van Roosbroeck.⁹ Application of the boundary conditions at $x = 0$ takes into account the fact that the reflected flux also contributes to the collected current. The grain boundary case, Figure 35(b), has two significant differences: (1) part of the excess minority carriers are transmitted, and (2) the collecting junction extends from $x = -\infty$ to $x = +\infty$ rather than the right half plane only.

One way to solve the grain boundary problem would be to solve the transport problem in each half-plane separately, matching boundary conditions at $x = 0$, with the transmitted flux acting as a source in the left half-plane. However, the problem can be reduced to that of the free semiconductor surface, Figure 35(a), by reflecting the left half-plane onto the right half-plane, and adding the two solutions for $\Delta n(x, y)$. The transmitted flux adds to the reflected flux, giving an effective reflection coefficient of $R_o' = R_o + T_o$. Equally important, the gradients $d(\Delta n)/dz$ at the junction simply add to give the total current collected on both sides of the grain boundary, but calculated by integrating only on one side.

The theory of EBIC, as developed by Berz and Kuiken,¹¹ and by Watanabe, Actor, and Gatos¹² is based on the theory of van Roosbroeck.⁹ The basic equation which was derived for the semiconductor surface case, also applies to the grain boundary case, by the argument given above. For a point source with coordinates (x_s, z_s) , the current collection efficiency is:^{11, 12}

$$Q(x_s, z_s) = \frac{2Z_s}{\pi} \left\{ \int_0^{x_s} \frac{K_1 \left[\frac{\sqrt{x^2 + z_s^2}}{\sqrt{x^2 + z^2}} \right]}{\sqrt{x^2 + z^2}} dx + e^{Sx_s} \int_{x_s}^{\infty} \frac{K_1 \left[\frac{\sqrt{x^2 + z_s^2}}{\sqrt{x^2 + z^2}} \right]}{\sqrt{x^2 + z^2}} dx \right\} \quad (15)$$

where the capital letters denote the reduced-variable $X = x/L$, and $Z = z/L$.

The LBIC response for a ray of light is obtained by integrating Equation (15) over the source function $\alpha e^{-\alpha z}$, where α is the optical absorption coefficient. This gives

$$Q(X_s) = \frac{2A}{\pi} \left\{ \int_0^{X_s} dX \int_0^\infty \frac{e^{-AZ} K_1 \left[\sqrt{X^2 + Z^2} \right]}{\sqrt{X^2 + Z^2}} Z dZ \right. \\ \left. + e^{SX_s} \int_{X_s}^\infty e^{-SX} dX \int_0^\infty \frac{e^{-AZ} K_1 \left[\sqrt{X^2 + Z^2} \right]}{\sqrt{X^2 + Z^2}} Z dZ \right\} \quad (16)$$

where $A = \alpha L$. The second term vanishes if $S = \infty$, and thus the first term gives the LBIC response in that case. This case was discussed in the Quarterly Report No. 12. The values of $Q(x)/Q(\infty)$ given by Equation (16) are shown in Figure 33 as they were derived from the curves plotted by van Roosbroeck, and were replotted as Figure 34 above, using the "effective diffusion length" concept to approximately reduce all the curves to the same curve, $L_e(x)/L$.

Assuming the effective diffusion length concept applies for finite values of S , then the values of $Q(x)/Q(\infty)$ can be obtained from the relationship:

$$Q(x) = \frac{\alpha L(x)}{1 + \alpha L(x)} \quad (17)$$

where $L(x)$ is obtained from Equation (16) by taking the limit $A = 0$.

The limit $A = 0$ can be calculated conveniently by dividing Equation (16) by $Q(\infty) = A/(1 + A)$. This gives:

$$\frac{L(X_s)}{L} = \frac{Q(X_s)}{Q(\infty)} \Big|_{A=0} \quad (18) \\ = \frac{2}{\pi} \left\{ \int_0^{X_s} dX \int_0^\infty \frac{K_1 \left[\sqrt{X^2 + Z^2} \right]}{\sqrt{X^2 + Z^2}} Z dZ \right. \\ \left. + \int_{X_s}^\infty e^{-S(X - X_s)} dX \int_0^\infty \frac{K_1 \left[\sqrt{X^2 + Z^2} \right]}{\sqrt{X^2 + Z^2}} Z dZ \right\}$$

The integrals over Z give $K_0(X)$ (see Table 8). $L(x)$ therefore is given by:

$$\frac{L(X)}{L} = 1 - \frac{2}{\pi} \int_X^\infty \left\{ 1 - e^{-S(X' - X)} \right\} K_0(X') dX' \quad (19)$$

Numerical integration of this equation is straightforward using a programmable hand calculator, tabulated values of K_0 , for $0.1 < x < 1.6$, and the asymptotic expressions for K_0 beyond these limits.

A plot of Equation (19) for different values of S is shown in Figure 36. The curve for $S = \infty$ is shown plotted more accurately than in Figure 33, which was simply obtained from van Roosbroeck's curves. It is interesting to note that if the curves for finite values of S are shifted to the right, they will essentially overlap with the $S = \infty$ curve.

Figure 36. Calculated Values of Effective Diffusion Length, $L(x)$, as a Function of Distance From the Grain Boundary, x . L is the true diffusion length, and S is the surface recombination parameter.

Figure 36 also illustrates a method of deducing S from the data. The slope of the curve at $x = 0$ is such that it extrapolates back to a negative intercept of $1/S$. This feature of the curves follows from the form of the boundary value problem, as shown by von Roos¹³ for the case of EBIC response near a surface. Because of the arguments presented

Table 8. Useful Properties of Bessel Functions

$$\frac{dK_0}{dx} = -K_1(x) \quad (a)$$

$$\int_0^{\infty} K_0(x) dx = \frac{\pi}{2} \quad (b)$$

$$\int_0^{\infty} x K_0(x) dx = 1 \quad (c)$$

$$\int_0^{\infty} \frac{K_1 \left[\sqrt{x^2 + y^2} \right]}{\sqrt{x^2 + y^2}} dx = \frac{\pi}{2} \frac{e^{-y}}{y} \quad (d)$$

$$\int_0^{\infty} \frac{K_1 \left[\sqrt{x^2 + y^2} \right]}{\sqrt{x^2 + y^2}} x dx = K_0(y) \quad (e)$$

$$\int_0^{\infty} e^{-at} K_0(t) dt = F_1(a) = \begin{cases} \frac{\cos^{-1} a}{\sqrt{1-a^2}}, & a < 1 \\ \frac{\cosh^{-1} a}{\sqrt{a^2-1}}, & a > 1 \end{cases} \quad (f)$$

$$\int_0^{\infty} e^{-at} K_0(t) t dt = F_2(a) = -\frac{dF_1}{da} = \frac{aF_1(a) - 1}{a^2 - 1} \quad (g)$$

Integration by parts: $\int_0^{\infty} dx \int_x^{\infty} G(x') dx' = \int_0^{\infty} x G(x) dx$ For $G = K_0, K_1$, etc., (h)

and $\int_0^{\infty} dx \int_x^{\infty} e^{-S(x' - x)} G(x') dx' = \frac{1}{S} \int_0^{\infty} (1 - e^{-Sx}) G(x) dx$ (i)

earlier in this section in connection with Figure 35, the same technique applies to the LBIC response at a grain boundary. In practice, as shown in Figure 31, the technique is limited by the finite size of the light beam. Nevertheless, in most of our experimental LBIC curves, there is a linear portion which seems suitable for extrapolation. In the case of Figure 31, the value of S is about 5, leading to a value of $S \approx 10^4$ cm/sec at the grain boundaries of this sample.

The use of the extrapolation technique is useful for extracting a surface recombination velocity from LBIC scans, and indicates that S is not infinite at the grain boundaries. The finite value of S , however, makes the disagreement in line shapes shown in Figure 33 even worse. The LBIC scans indicate that the diffusion length as determined using absorption coefficient data is not correct. We speculate that this may be due to faulty assumptions regarding the quantum yield in the vicinity of the energy band-edge.¹⁴ Further work is planned to investigate this possibility.

THERMAL ANALYSIS OF SHEET SILICON GROWTH PROCESSES (S. B. Schuldt)

Introduction

The growth rate of sheet silicon appears to be limited by heat extraction efficiency. Our economic analyses indicate that a pull speed of around 0.2 to 0.3 cm/sec is required to meet cost goals, and to date our best solar cells have been grown at one-fourth this speed. We have dedicated a large amount of effort to increasing our understanding of the thermal mechanism of our growth process with the aim of attaining the necessary high throughput.

The present SOC growth appears to proceed from a liquid-solid interface which is roughly perpendicular to the pull direction (see Figure 37). We have been using the word "symmetric" to refer to this type of growth. Annual Report No. 3, published 31 October 1978, gave a thermal analysis for unsupported (i.e., without the ceramic substrate) symmetric sheet silicon growth. It was found that pull speed, v , and sheet thickness, t , were related by

$$v^2 t = C,$$

where C is a function of the radiation environment; $C \approx 3 \mu\text{m (cm/sec)}^2$ for a 300°K ambient and $C \approx 0.6 \mu\text{m (cm/sec)}^2$ for a 1385°K ambient.

The analysis was extended this year to the more complicated SOC structure, and the first part of the present section is a report of that activity. It was found that log-log plots of t versus v were curved according to

$$v^x t = C$$

where x is a variable exponent greater than 2. Throughput is generally less than for the unsupported case, and this is attributed mostly to the increased thermal load imposed upon the system by the sensible heat carried from the melt by the substrate.

We have also been investigating so-called wedge-shaped or asymmetric growth as an alternative to the more conventional, symmetric growth. Asymmetric growth offers high throughput potential and possibly other advantages such as sweeping impurities out of the active solar-cell region. However, very little is known about this growth mode, particularly the thermal and mechanical design factors which have to be incorporated into the growth apparatus to produce and maintain a stable wedge-shaped growth region. We have undertaken an analysis of these factors in the second part of this section. Only unsupported asymmetric growth has been considered here. The extension to substrate-supported growth is left for a future investigation.

Part I. Supported Symmetric Growth

Introduction

Sheet silicon may be grown vertically from the melt either unsupported¹⁵⁻²⁰ or attached to a substrate material.²¹⁻²⁴ In either case, the attainable growth rate is limited by heat extraction efficiency. The steady-state analysis of unsupported silicon growth is greatly simplified by the symmetry of the structure, leading to uncomplicated solution to the heat equations.²³ Important by-products of the analysis are expressions for pull speed versus sheet thickness and for the shape of the crystallization or freezing front. This simplicity does not exist in the case of silicon grown on ceramic, and numerical methods were chosen to solve the heat equations.

The essential features of dip coating SOC are shown in Figure 37. Ceramic wafers are pulled vertically from the silicon melt at constant speed, v . The freezing front appears at a height y_F above the melt. The value of y_F at zero pulling speed may be calculated from hydrostatic considerations.²⁰ Moreover, this appears to remain unchanged in actual steady-state growth for pulling speeds up to well into the millimeter-per-second range.²⁴ Above y_F , the temperatures in the structure begin to fall toward

Figure 37. Cross-Section View of SOC Growth. The meniscus shape is based on hydrostatic equilibrium. Radiative background temperatures T_0 and T_1 are seen above and below the liquid - solid interface, respectively.

some effective radiation temperature, T_o , of the environment. A possibly different radiation temperature, T_1 , is seen by the portion of the structure below the freezing front. In the present study, only radiative heat removal was considered and the temperatures T_1 and T_o were assumed uniform over $0 \leq y < y_F$ and $y_F \leq y < \infty$, respectively. The simple two-part background is used to give a crude approximation to the effect of a heat shield located at y_F . More general heat loss functions are easily incorporated and may be investigated later. As was true in the unsupported case, the rate of heat extraction by radiation must balance the rate of removal of sensible heat from the melt (by convection) plus the rate of release of latent heat at the freezing front. In the present case, most of the sensible heat is carried in the ceramic.

Heat Equations

Two zones are identified because of the different thermal properties of molten and solid silicon. In the zone $y_F \leq y < \infty$, the steady-state heat equations in the ceramic portion follow from two-dimensional heat balance, including convective terms:²⁵

$$\frac{\partial}{\partial x} \left(k_c \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_c \frac{\partial T}{\partial y} \right) - \rho_c C_c v \frac{\partial T}{\partial y} = 0 \quad 0 \leq x \leq t_c \quad (20)$$

$$k_c \frac{\partial}{\partial x} T(0, y) = \epsilon_c \sigma \left\{ [T(0, y)]^4 - T_o^4 \right\} \quad (21)$$

$$T(x, \infty) = T_o \quad (22)$$

The two-dimensional model is appropriate because the width of the structure (z-dimension) is assumed large compared with the thickness, $t_c + t_o$. Physical parameters are identified in Table 9. For the silicon portion, a one-dimensional temperature profile, $U_o(y)$, is used, equivalent to assuming the isotherms are horizontal. This assumption can be checked by estimating the inclination of the isotherms in the solid silicon portion.

The steady-state equations in the solid silicon ($y \geq y_F$) are

$$t_o \left\{ \frac{d}{dy} \left(k_o \frac{dU_o}{dy} \right) - \rho_o C_o v \frac{dU_o}{dy} \right\} = f_o(y) \quad (23)$$

$$f_o(y) = \epsilon_o \sigma \left\{ [U_o(y)]^4 - T_o^4 \right\} - k_c \frac{\partial}{\partial x} T(t_c, y) \quad (24)$$

Table 9. Nomenclature and Numerical Data for Part I

Symbol	Description	Value/Units
C_c	Specific heat of ceramic	1.04 (J/g °K)
$C_o \approx C_1$	Specific heat of silicon	0.954 (J/g °K)
$J_o(y)$	Silicon heat flux density ($y > y_F$)	(W/cm ²)
$J_1(y)$	Silicon heat flux density ($y < y_F$)	(W/cm ²)
k_c	Heat conductivity of ceramic	0.041 (W/cm °K)
k_o	Heat conductivity of solid silicon	343/ U_o (W/cm °K)
k_1	Heat conductivity of liquid silicon	0.6 (W/cm °K)
L	Latent heat of fusion of silicon	1802 (J/g)
$T(x, y)$	Ceramic temperature	(°K)
T_o	Downstream ($y > y_F$) ambient temperature	(°K)
T_1	Upstream ($y < y_F$) ambient temperature	(°K)
T_M	Melt temperature	(°K)
T_F	Silicon freezing temperature	1685 (°K)
t_c	Ceramic thickness	(cm)
t_o	Solid-silicon layer thickness	(cm)
$t_1(y)$	Liquid-silicon layer thickness	(cm)
$U_o(y)$	Silicon temperature ($y \geq y_F$)	(°K)
$U_1(y)$	Silicon temperature ($y \leq y_F$)	(°K)
v	Pull speed	(cm/sec)
y_F	Total meniscus height above melt	0.5 or 0.69 (cm)
δ	Numerical grid spacing	0.02 (cm)
ρ_c	Ceramic density	3.3 (g/cm ³)
$\rho_o \approx \rho_1$	Silicon density	2.33 (g/cm ³)

$$U_o(y) = T(t_c, y) \quad (25)$$

$$U_o(y_F) = T_F \quad (26)$$

The extraction term $f_o(y)$ includes both radiation at the external surface and conduction across the internal surface into the ceramic.

In the zone $0 \leq y < y_F$, the equations for the ceramic portion are similar to Equations (20), (21), and (22), except for the radiation temperature, T_1 , in place of T_o (Figure 37) and a boundary condition at $y = 0$ instead of $y = \infty$:

$$\frac{\partial}{\partial x} \left(k_c \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_c \frac{\partial T}{\partial y} \right) - \rho_c C_c v \frac{\partial T}{\partial y} = 0 \quad (27)$$

$$k_c \frac{\partial}{\partial x} T(0, y) = \epsilon_c \sigma \left[T(0, y)^4 - T_1^4 \right] \quad (28)$$

$$T(x, 0) = T_M \quad (29)$$

In the liquid-silicon portion, the variable thickness t_1 must be taken into account. The following is derived based on the assumption of horizontal isotherms [see next subsection for full derivation of Equation (30)]:

$$\frac{d}{dy} \left(t_1 k_1 \frac{dU_1}{dy} \right) - \rho_o v t_o C_1 \frac{dU_1}{dy} = f_1(y) \quad (30)$$

$$f_1(y) = \left\{ 1 + \left[\frac{dt_1}{dy} \right]^2 \right\}^{1/2} \epsilon_1 \sigma \left[U_1(y)^4 - T_1^4 \right] - k_c \frac{\partial}{\partial x} T(t_c, y) \quad (31)$$

$$U_1(y) = T(t_c, y) \quad (32)$$

$$U_1(y_F) = T_F \quad (33)$$

A final condition expresses the fact that the freezing front is the source of a heat flux density (vertical component) equal to $\rho_o v L$:

$$-k_1 \frac{d}{dy} U_1(y_F) + \rho_o v L = -k_o \frac{d}{dy} U_o(y_F) \quad (34)$$

Derivation of Equation (30)

Refer to Figure 38. We assume horizontal isotherms so that temperature can be denoted $U_1(y)$. Vertical mass flow, independent of y , is equal to $\rho_o v t_o$. If $t_1(y)$ denotes local thickness, vertical heat flux, $H(y)$, per unit width is

$$H(y) = \rho_o v t_o C_1 U_1 - t_1 k_1 dU_1/dy \quad (35)$$

Denoting by $f_1(y)$ the heat flux density lost by radiation at the curved surface and by conduction to the ceramic, we then have

$$dH/dy + f_1 = 0$$

or

$$\frac{d}{dy} \left(t_1 k_1 \frac{dU_1}{dy} \right) - \rho_o v t_o C_1 \frac{dU_1}{dy} = f_1(y) \quad (36)$$

For $t_1(y)$, we use the result from Harrill, et al:²⁰

$$\begin{aligned} (t_1 - t_o)/K &= \cosh^{-1}(2K/y) - \cosh^{-1}(2K/y_F) \\ &+ \left[4 - (y_F/K)^2 \right]^{1/2} - \left[4 - (y/K)^2 \right]^{1/2} \end{aligned} \quad (37)$$

where $K/y_F = [2(1 - \sin \theta)]^{1/2} = 0.79$ if the contact angle, θ , is 11 degrees.

Finite Difference Model

A finite two-dimensional array of nodes was chosen (Figure 39) as the framework to approximate the solution of the above equations by finite differences. The ceramic thickness, t_c , is represented by seven nodes, which are equally spaced except for the edge pairs, where one-half the standard spacing is used. Hence, the standard spacing, δ , is equal to $t_c/5$. The standard spacing is also used vertically, except for the end pairs. An integer, m_F , labels the approximate location, y_F , of the freezing front, separating the liquid and solid silicon phases. If $m = 0$ denotes the bottom row of nodes the correspondence between m and y is

$$y = (m - 1/2) \delta \quad (38)$$

and m_F is the largest integer contained in $(y_F/\delta + 1)$.

Figure 38. Diagram of Meniscus Region

Figure 39. Finite Difference Array for Calculating SOC Temperature Profile. Right-hand column of nodes corresponds to silicon layer (one-dimensional approximation) and right-hand edge of substrate. The rest of the nodes represent locations within and at the left-hand edge of the substrate.

The right-hand column of nodes is sufficient to represent the entire silicon thickness due to our assumed horizontal isotherms. There are no discontinuities in the two-dimensional temperature profile; hence, the silicon temperatures are equal to the ceramic temperatures at the silicon - ceramic interface.

The details of the solution technique, a modified over-relaxation method (Gauss-Seidel),²⁶ are omitted here. The equations are nonlinear due to the Stefan-Boltzmann relations and the temperature-dependent k_o . For the latter, an approximate inverse temperature dependence, $k_o = 343/U_o$, is inferred from recommended data over the range $800^\circ\text{K} \leq U_o \leq 1685^\circ\text{K}$.²⁷ These nonlinearities are handled by means of coefficient updates at each Gauss-Seidel iteration.

The steady-state temperature profile depends on the thicknesses of ceramic and silicon, the pull speed, the melt temperature, and the background temperatures, T_o and T_1 . Of course, T_F is fixed at 1685°K . Not all of the foregoing can be independently specified, since the problem would be overdetermined and a solution would, in general, be non-existent. As a mathematical convenience, we have chosen the melt temperature to be a dependent variable, and this is therefore an output of the calculation along with the temperature profile. Also, we specify the temperature differences $T_M - T_o$ and $T_M - T_1$ rather than T_o and T_1 directly (e.g., $T_M - T_1 = 1385^\circ\text{K}$ will result in T_o being a little above room temperature because T_M will generally be a few degrees above 1685°K).

Interpretation

At the present time, the complete temperature profiles in ceramic and silicon are of only casual interest. Isotherms obtained by interpolation of output data of two computer runs are shown in Figure 40. The sparse, sharply-bent isotherms below the freezing front, and the sudden increase in isotherm density above the point of latent heat release, are features found in all the runs.

On the other hand, the silicon part of the profile is crucial and gives the nucleus of information for our interpretation of thickness versus growth speed. As in the case of unsupported silicon sheet growth,²³ a major assumption here is that stable growth of silicon on ceramic requires the liquid meniscus to be at or above the freezing temperature; that is, heat flow in the liquid must not be away from the freezing front. A condition for the limiting stable growth rate is that the temperature gradient on the liquid side of the interface approach zero. According to Brice,²⁸ maximum silicon thickness at a given velocity may be obtained by adjusting the melt temperature to a point just above the value where the interface becomes unstable and dendritic growth develops. In a computer calculation this would correspond to zero temperature gradient in the liquid at $y = y_F$

Figure 40. Isotherms for $T = T_M - 5n$, $n = 1, 2, \dots$, by Two-Dimensional Interpolation; $t_c = 0.1$ cm, $y_F = 0.5$ cm, $T_M - T_o = 1385^\circ\text{K}$, $T_M - T_1 = 300^\circ\text{K}$. Left: $t_o = 0.003$ cm, $v = 0.153$ cm. Right: $t_o = 0.03$ cm, $v = 0.0685$ cm.

Figure 41 shows calculated normalized heat flux, $Jt/\rho v L t_o$, as a function of y , where

$$J = J_1 = -k_1 \frac{dU}{dy} \text{ (liquid)} \quad (39)$$

$$J = J_o = -k_o \frac{dU}{dy} \text{ (solid)} \quad (40)$$

for three melt temperatures at the same pull speed. In Figure 41, the middle case (II) gives maximum stable t_o because $J_1(y_F) = 0$. Case I, with a higher melt temperature and lower t_o , is within the stability limit, but Case III (lower melt temperature) is unstable.

Figure 41. Normalized Thermal Flux in Liquid and Solid Parts of the Silicon Layer at Height y Above Melt Surface. $v = 0.098$ cm/sec for all three cases. The degree of stability is determined by the melt temperature. Case I (stable): $T_M - T_F = 22.3$ deg, $t_o = 0.0067$ cm, $J_1(y_F) > 0$. Case II (stable): $T_M - T_F = 15.1$ deg, $t_o = 0.0100$ cm, $J_1(y_F) = 0$. Case III (unstable): $T_M - T_F = 6.5$ deg, $t_o = 0.0143$ cm, $J_1(y_F) < 0$.

Figure 42 gives further computed data assuming the same fixed v . $J_1(y_F)$ is seen to be a monotonic increasing function of T_M , and t_o is a monotonic decreasing function of T_M . According to this figure, silicon thicknesses up to 0.01 cm can be stably grown at $v = 0.098$ cm/sec on 0.1-cm ceramic, assuming that heat is removed by radiation to an environment at room temperature.

Figure 42. Normalized $J_1(y_F)$ and Silicon Thickness as Functions of Melt Temperature. Pull speed fixed at 0.098 cm/sec; $t_c = 0.1$ cm; $T_M - T_o = 1385^\circ\text{K}$; $T_M - T_1 = 50^\circ\text{K}$; $y_F = 0.5$ cm.

Figure 43 shows t_o and $J_1(y_F)/\rho_o v L$ as functions of pull speed when melt temperature is held constant. We note that t_o always decreases as v increases, but $J_1(y_F)/\rho_o v L$ reaches a minimum and then increases with v . In general, the model indicates that growth is more stable at both extremes of pull speed (fixed T_M) and tends to become less stable or unstable at intermediate pull speeds. If a lower T_M were used in these calculations there would be a larger range of pull speeds corresponding to unstable growth, and stable growth would be possible at both higher and lower pull speeds outside of this range.

Figure 43. Normalized $J_1(y_F)$ and Silicon Thickness as Functions of Pull Speed. $T_M - T_F$ fixed at 15.1 deg; $t_c = 0.1$ cm; $T_M - T_0 = 1385^\circ\text{K}$; $T_M - T_1 = 50^\circ\text{K}$; $y_F = 0.5$ cm.

Figures 44a and 44b give conditions of limiting stable growth; in other words, v and T_M are simultaneously varied to keep $J_1(y_F) = 0$. The solid curves of Figure 44a compare the effects of high and low background temperature as well as two different substrate thicknesses. Dashed lines are limiting growth conditions for unsupported silicon from the one-dimensional analysis.²³ That analysis predicts a constant $v^2 t_0$ for each background temperature, giving straight lines with a slope of -2 on the logarithmic plot. On the other hand, the $v^2 t_0$ product for SOC is seen to fall rapidly at higher pull speeds, as thermal convection in the ceramic begins to dominate the heat disposal problem. The corresponding melt temperatures in Figure 44b all have maxima at intermediate pull speeds. This phenomenon, which is not readily explained, is consistent with the observations made in connection with Figure 43. The experimental data shown in Figure 44a were obtained with the "fast dipper" on 0.1-cm-thick ceramic with an undetermined background temperature.

The Role of T_1 and y_F

The calculations discussed so far have been based on the values $y_F = 0.5$ cm and $T_M - T_1 = 50$ degrees. To test the generality of the results, the calculations for the Figure 44a curves were repeated for two different combinations of y_F and T_1 : a) $y_F = 0.69$ cm, $T_1 - T_M = 50$ degrees; b) $y_F = 0.5$ cm, $T_1 - T_M = 300$ degrees. It was found that these

Figure 44. Silicon Thickness and Melt Temperature as Functions of Pull Speed for $J_1(y_F) = 0$ [limiting stable growth]. (a) $T_M - T_O = 1385^\circ\text{K}$, $t_c = 0.1$ cm. (b) $T_M - T_O = 300^\circ\text{K}$, $t_c = 0.1$ cm. (c) $T_M - T_O = 1385^\circ\text{K}$, $t_c = 0.2$ cm. (d) $T_M - T_O = 300^\circ\text{K}$, $t_c = 0.2$ cm. (e) $T_M - T_O = 1385^\circ\text{K}$, $t_c = 0$ [unsupported growth]. (f) $T_M - T_O = 300^\circ\text{K}$, $t_c = 0$. Experimental data (+) were obtained on 0.1-cm unslotted substrate as discussed elsewhere in this report.

new combinations gave the same limiting v versus t_0 relationships as before. This is a surprising result and it indicates that neither of these parameters has a significant effect on the important limiting relationship. This also tends to support our earlier analysis of the unsupported sheet silicon growth, in which J_1 was assumed equal to zero, and further details of the liquid meniscus such as its shape and temperature distribution, were ignored.

Isotherm Shapes Within the Solid Silicon

The isotherms were assumed flat in the silicon part of the structure. The error in this assumption may be estimated by analyzing heat flows up the silicon and laterally toward the radiation and ceramic surfaces. In the solid silicon portion, the greatest departure from flatness occurs near the freezing isotherm itself, so the discussion is restricted to that region. No attempt is made to examine the liquid portion. We proceed as follows.

Let $\vec{j}_1$ and $\vec{j}_2$ be flux density vectors at the corners as shown in Figure 45. In a column of cross-section $dx dz$, the latent heat released per unit time is $\rho_0 v L dx dz$. This is obviously the same quantity as $|\vec{j}_1| ds dz$; hence,

$$|\vec{j}_1| = \rho_0 v L dx / ds = \rho_0 v L \cos \alpha_1 \quad (41)$$

Similarly,

$$|\vec{j}_2| = \rho_0 v L \cos \alpha_2 \quad (42)$$

The lateral components are then

$$j_{1x} = \rho_0 v L \sin \alpha_1 \cos \alpha_1 \quad (43)$$

$$j_{2x} = \rho_0 v L \sin \alpha_2 \cos \alpha_2 \quad (44)$$

By continuity of lateral heat flow, j_{1x} is also the heat conducted into the ceramic:

$$j_{1x} = k_c |\partial T / \partial x| \quad (45)$$

and j_{2x} is the radiated heat

$$j_{2x} = \epsilon_0 \sigma (T_F^4 - T_0^4) \quad (46)$$

Figure 45. Analysis of Freezing Front Shape by Means of Heat Flux Components

Combining (43) with (45), and (44) with (46), gives

$$\alpha_1 = 1/2 \sin^{-1} \left\{ 2k_c |\partial T / \partial x| / \rho_o v L \right\} \quad (47)$$

$$\alpha_2 = 1/2 \sin^{-1} \left\{ 2\epsilon_o \sigma (T_F^4 - T_o^4) / \rho_o v L \right\} \quad (48)$$

The angle α_2 may be evaluated directly, but for α_1 it is necessary to calculate $|\partial T / \partial x|$. A three-point interpolation formula may be used incorporating the calculated temperatures at $y = y_F$ and the last three columns in the finite difference lattice, recalling the spacing as shown:

$$\begin{array}{ccccc} \leftarrow & \delta & \rightarrow & \delta/2 & \rightarrow \\ \dot{T}_= & & \dot{T}_- & & \dot{T}_F \end{array}$$

The interpolation formula yields

$$\frac{\partial T}{\partial X} = \frac{1}{\delta} \left(\frac{8}{3} T_F - 3T_- + \frac{1}{3} T_= \right)$$

at the right-hand edge.

Angles α_1 and α_2 are plotted against thickness, t_o , in Figure 46 from data for the cold background case represented by the right-hand solid curve in Figure 44a. The maximum angles occur at the largest t_o , which is 0.1 cm. We restrict our attention to this con-

Figure 46. Inclinations of Freezing Isotherm versus Silicon Thickness. Growth conditions as in (a) of Figure 44. α_1 = inclination at silicon interface; α_2 = inclination at as-grown surface.

dition, which is the severest test of our flatness assumption. In Figure 47, that particular crystallization front is represented as a circular arc. From this geometry, the highest Δy spanned by the crystallization front is calculated to be 0.008 cm. Since the finite difference increment, δ , is 0.02 cm, we conclude that the worst-case Δy is only about half the numerical lattice spacing, and this justifies the flatness assumption.

Figure 47. Approximate Worst-Case Crystallization Front Geometry (Exaggerated Scale)

It would be incorrect to conclude that most of the heat from the silicon is conducted into the substrate, although this is locally true near the interface, where $\alpha_1 > \alpha_2$. In fact, angle α_1 decreases and eventually becomes negative with increasing height above the interface. In the net, heat flows from the ceramic into the silicon and not the other way around. This is certainly to be expected in view of the large contribution made by the substrate to the total heat that must be radiated away.

Summary

A steady-state vertical growth model for SOC yields a system of nonlinear, coupled differential equations for the temperature profiles in ceramic and silicon portions of the structure. Cooling of the structure is assumed to be by radiation to a specified environment, and the cooling rate must balance the rates of latent heat of fusion and convected heat from the melt. Liquid meniscus height is fixed by hydrostatic considerations and does not vary over the normal range of growth speed. Because of the complicated geometry and essential nonlinearity of the system, numerical solution of the equations is the method of choice.

Due to the overall heat balance requirement, only certain combinations of ceramic thickness (t_c), silicon coating thickness (t_o), pull speed (v), and melt temperature (T_M) will yield steady-state temperature profiles. In actual growth, the coating thickness is not arbitrarily specified but is a dependent function of t_c , v , and T_M ($> T_F$).

A theoretical stability criterion²⁸ places a further restriction on the allowable combinations of growth parameters. Growth is not stable if heat flows backwards from the crystallization fronts; in other words, stability requires that $d/dy U_1(y_F) \leq 0$. For a given pull speed, t_o increases monotonically as T_M is lowered toward T_F , but $d/dy U_1(y_F)$ decreases at the same time. Maximum coating thickness for stable growth occurs therefore when $d/dy U_1(y_F) = 0$. This limiting thickness and the corresponding melt temperature both depend on pull speed, ceramic thickness, and radiation environment.

The limiting t_o versus v relationship has an economic significance in terms of process throughput and was investigated (Figure 44a) for various combinations of t_c and T_o . This was compared with unsupported silicon growth ($t_c = 0$). As expected, throughput is penalized by the presence of the substrate, especially at high pull speeds, due to the extra (sensible) heat input to the system.

Finally, the one-dimensional approximation in the solid-silicon portion was critically examined by estimating the maximum departure, Δy , from flatness for the freezing isotherm. This turned out to be of the order of 0.01 cm, which would appear to justify the approximation. Also, the freezing isotherm was found to be bowed upward, making a larger inclination to the horizontal at the ceramic surface than at the as-grown surface. Although most of the latent heat is carried vertically, this would indicate that the net lateral heat transfer in the neighborhood of the freezing front is into the ceramic as opposed to out from the free surface. This is true only locally, however. In fact, over the structure as a whole, net heat transfer across the silicon-ceramic interface is from ceramic to silicon, and not the other way around.

Part II. Unsupported Wedge-Shaped (Asymmetric) Growth

Introduction

The growth of unsupported sheet silicon or silicon ribbon from the melt can happen, in principle, in either of two modes, as illustrated in Figure 48. In the conventional mode (a), the liquid-solid interface (LSI) is oriented approximately perpendicular to the pull direction, as was the case in the supported growth discussed in Part I. The latent heat of fusion released at the LSI is carried in the pull direction and must be disposed of by radiation and convection to the relatively cool environment of the solid ribbon. The word "symmetric" fits this mode because of the plane of symmetry through the half-thickness points. The other mode (b) lacks a plane of symmetry, as diagrammed here, and may be called "asymmetric." Because the LSI is inclined at a small angle, θ , to the pull direction, most of the latent heat of fusion is eliminated immediately by crossing transversely to the free solid surface. Only a small fraction of the latent heat remains to be disposed of downstream (upwards as represented in Figure 48 from the solidification wedge). It is debatable whether asymmetric growth has ever been successfully demonstrated, but it is a critically important technology to pursue theoretically and experimentally. It is inherently much faster than symmetric growth and may have other advantages such as entrapment of impurities.

Figure 48. Silicon Ribbon Growth in (a) Symmetric and (b) Asymmetric Modes. The letters v and t are pull speed and ribbon thickness, respectively.

A heat transfer model was developed for the wedge-shaped region²⁹ in asymmetric growth but it does not address the problem of how to cool the ribbon as it travels away from this region. This report indicates that downstream cooling is too rapid for pure wedge-shaped asymmetric growth if a 300°K ambient is assumed for the entire solid ribbon. The cooling can be retarded to the proper rate by including postheaters in the apparatus. The present analysis applies directly to unsupported ribbon growth. Extension to supported asymmetric sheet growth, as in silicon-on-ceramic, will be done at a later time.

In both symmetric and asymmetric growth, it is useful to consider lines of demarcation between the solidification zones and the fully developed solid, downstream regions. These are indicated as dashed lines in Figure 48. The heat flux approaching the line from below, consisting of convected heat, heat flux from the liquid, and any latent heat of fusion not already disposed of, must balance the heat flux away from the line into the downstream region. This simple conservation principle leads to a v versus t tradeoff in the case of unsupported symmetric growth, as reviewed briefly below. In the asymmetric growth model, the conservation of heat flux does not imply any direct tradeoff limitation, but it does dictate the use of postheaters.

Review of Symmetric Growth Model

The conservation principle for symmetric growth can be expressed

$$t(\rho c v T_F + J_o + \rho L v) = t(k q + \rho c v T_F) \quad (49)$$

where ρ and c are the density and heat capacity of solid silicon at $T \sim T_F$, T_F is the melting temperature, J_o the x-component of heat flux density in the liquid, L is the latent heat of fusion, k is the heat conductivity of solid silicon (independent of temperature in this analysis), and $q = -dT/dx$, the downstream component of the temperature gradient at the dotted line in Figure 48a. Values used in this report are given in Table 10. The first term in Equation (49) represents convected heat flux, the second term is the heat flux from the liquid silicon, and the third term is heat flux due to latent heat of fusion. The tkq term is heat flux by conduction into the downstream solid region. Note that convected heat cancels in Equation (49). If J_o is assumed equal to zero (maximum throughput), the equation becomes

$$\rho L v / k = q \Big|_{T=T_F} \quad (49a)$$

Table 10. Values for Silicon Parameters for Part II

Parameter	Value
ρ	2.33 g/cm ³
c	0.954 J/g deg
k	0.216 W cm/deg
L	1802 J/g
T_F	1685°K
J_o	0.0 W/cm ²

The value of q is derived independent of the solidification zone parameters by integrating the heat equation for the downstream silicon portion, subject to appropriate initial condition. Since symmetric growth is very nearly one-dimensional in character, the following heat equation is convenient to use;³⁰

$$t(kq \frac{dq}{dT} + \rho cv q) = F(T, T_A) \quad (50)$$

where F is the cooling function depending on the ribbon temperature, T , and effective ambient temperature, T_A . This equation is equivalent to the standard one-dimensional heat equation in which the coordinate x is the independent variable. The transformation was made by substituting $-q$ for dT/dx . If heat disposal is by radiation from both surfaces to an effective 300°K blackbody ambient, Equation (50) becomes

$$t(kq \frac{dq}{dT} + \rho cv q) = 2\epsilon\sigma(T^4 - 300^4) \quad (51)$$

The initial condition is that the gradient, q , tends to zero as T approaches ambient, i. e., $q(300) = 0$. The solid silicon emissivity is taken to be $\epsilon = 0.46$, and Equation (51) is integrated numerically³¹ from $T = T_A$ to $T = T_F$, since $q(T_F)$ is the value required in Equation (49a).

The q obtained from the integration depends upon t , and to a lesser extent upon v due to the convective term in Equation (51). Figure 49 is a plot of q versus t for various pull speeds, along with $\rho Lv/k$ (dashed lines). The intersections of the two sets, marked with heavy dots, reveal the v versus t tradeoff and illustrate the flux conservation principle.

Figure 49. Heat Fluxes from Solidification Region (Dashed) and into Downstream Region (Solid). Balance is at the intersection points (heavy data), establishing the v versus t tradeoff for symmetric growth.

Ribbon Thickness in Asymmetric Growth

A thermal model of asymmetric growth is independent of orientation, and the pull direction has been taken vertical (Figure 48) for comparison with symmetric growth. We will use a horizontal orientation in the later analysis. Mechanical factors could dictate other orientations, such as the one shown in Figure 50. In this configuration, point A, which presumably defines the downstream limit of the LSI, is fixed by meniscus stability consideration.³² The wedge angle, θ , is given by

$$\theta \approx \epsilon \sigma (T_F^4 - T_O^4) / \rho v L \text{ radian} \quad (52)$$

if heat flux into the LSI from the melt is neglected.²⁹ If the top-side ambient T_O is 300°K this becomes

$$\theta \approx 0.005/v$$

and for pull speeds of the order of 0.1 cm/sec or higher, the wedge angle is less than 3 degrees. Although θ is established by thermal considerations involving the pull speed, the thickness, t , is not, since

$$t \approx \theta \cdot AB \quad (53)$$

and the length AB is an adjustable parameter based on the design of the apparatus. The position of B might be fixed, for example, by heating the melt surface to the left of B and allowing it to cool on the right. Equations (52) and (53) show that an indirect tradeoff exists between v and t ; given a fixed wedge length AB , t is inversely proportional to v . For the subsequent calculations, this dimension is arbitrarily assumed to be 0.8 cm.

Figure 50. Nonvertical Implementation of Asymmetric Growth

Temperature Profile in the Solidification Region

Subject to a number of assumptions which will be examined, the two-dimensional heat equation yields a nearly linear temperature distribution in the solid portion of the region $x = 0$ to $x = \ell$ (see Figure 51):

$$T(x, y) \approx T_F - \Delta \cdot (x/\ell - y/t) \quad (54)$$

with

$$\Delta \approx \epsilon \sigma (T_F^4 - T_0^4) \cdot t/k \quad (55)$$

and

$$t/\ell \approx \theta \approx \epsilon \sigma (T_F^4 - T_0^4) / \rho v L \quad (56)$$

Figure 51. Linear Temperature Distribution in a Wedge-Shaped Solidification Region

The validity of the assumptions rests on their self-consistency, which we will attempt to establish:

- 1) We assume the LSI is indeed a straight line and an isotherm at temperature T_F .
- 2) Given (1), the linear temperature distribution obviously satisfies the steady-state heat equation:

$$k(\partial^2 T / \partial x^2 + \partial^2 T / \partial y^2) - \rho c v \partial T / \partial x = 0 \quad (57)$$

provided that the $\rho c v$ term can be neglected. Zoutendyk²⁹ gives the following condition for neglecting the $\rho c v$ term:

$$vt \ll k / \rho c = 0.097 \quad (58)$$

We will return to this condition.

- 3) A heat flux emerges from the LSI due to the latent heat of fusion. If there are no temperature gradients in the liquid, this flux is normal to the LSI and of constant density. That is,

$$J = \rho v L \sin \theta \quad (59)$$

because the LSI is a straight line of length $t / \sin \theta$ and the total flux is $\rho v L t$. From Equations (59) and (54) we see that

$$J_x = k\Delta/\ell = \rho v L \sin^2 \theta \quad (60)$$

and

$$J_y = k\Delta/t = \rho v L \sin \theta \cos \theta \quad (61)$$

- 4) The radiated flux density from the surface $y = 0$ is approximately constant, provided that Δ is small, and equal to $\epsilon\sigma(T_F^4 - T_O^4)$. Equating this to the vertical component J_y in (3) gives

$$\Delta \approx \epsilon\sigma(T_F^4 - T_O^4) \cdot t/k$$

which establishes Equation (55) and confirms that Δ is small ($\Delta = 4.9$ deg if $t = 0.1$ cm).

- 5) Combining Equations (55) and (61) also gives

$$\sin \theta \cos \theta \approx \theta \approx \epsilon\sigma(T_F^4 - T_O^4)/\rho v L$$

which establishes Equation (56). Finally, since $\theta \approx t/\ell$, Equation (56) may be rewritten as

$$vt \approx \epsilon\sigma(T_F^4 - T_O^4) \cdot \ell/\rho L$$

or $vt \approx 0.005$ if $\ell \approx 1$ cm. (It has been already noted that ℓ is somewhat arbitrary.) Since $0.005 \ll 0.97$, the condition (49) for neglecting the ρcv term is satisfied.

Matching the Temperature Distribution to the Downstream Region

As observed previously, the component of latent heat carried downstream is much smaller in asymmetric than in symmetric growth. In fact, since $J_x = \rho v L \sin^2 \theta \approx [\epsilon\sigma(T_F^4 - T_O^4)]^2/\rho v L$ from Equations (60) and (56), the conservation principle for the wedge model becomes

$$[\epsilon\sigma(T_F^4 - T_O^4)]^2/\rho v L k = q|_{T \sim T_F} \quad (62)$$

For a cooling environment of 300°K along the whole silicon ribbon, q was found to be in the 10^2 to 10^4 deg/cm range (Figure 49), whereas the left-hand side of Equation (62) is much smaller (e. g., about 5 deg/cm for $v = 0.1$ cm/sec). It is obvious that the cold downstream environment is not compatible with the wedge model. We will see in more detail later (Figure 56) what happens when we try to force the cold downstream environment on the wedge model.

It is not so obvious that the cold environment precludes any kind of asymmetric growth. It is conceivable that some kind of curved LSI is possible with a portion of it nearly parallel to the surface, for higher throughput, and another portion at a large inclination to the surface in order to match the high q .

The approach taken here is an attempt to stabilize the wedge pattern by extending the linear distribution for some distance into the downstream region. This will automatically satisfy continuity of not only $\partial T/\partial x$ but $\partial T/\partial y$ as well. It is assumed that afterheaters can be constructed to provide an arbitrary distribution, $T_A(x)$, of effective ambient temperature on the meniscus side of the ribbon. The other side will remain exposed to the cold ambient. A restriction on this approach is that $T_A(x)$ (i. e., the design of the afterheaters) must depend on v and t . A change in either of these parameters would force a redesign of the afterheaters. The required $T_A(x)$ is estimated using the one-dimensional heat equation, Equation (50), and then "verified" by applying it to a computer program which (numerically) solves the two-dimensional heat equation for the entire silicon ribbon. The method is demonstrated for the particular case $\ell = 0.8$ cm, $v = 0.1$ cm/sec, and $t = 0.04$ cm.

To begin, let $F(T, T_A)$ in Equation (50) be written

$$F[T, T_A(T)] = f(T, 300) + f[T, T_A(T)] \quad (63)$$

where $f(T, U) = \epsilon\sigma(T^4 - U^4)$ and hence $F(T, 300) = 2f(T, 300) = 2\epsilon\sigma(T^4 - 300^4)$. The procedure will be to find a $T_A(T)$ to suit our purposes and then convert to $T_A(x)$ using

$$x = \ell + \int_{T_F}^T -dT/q(T) \quad (64)$$

where q is obtained from Equation (50) with $T_A = T_A(x)$. Let $q_0(T)$ be the integral of Equation (50), with $T_A = 300^\circ\text{K}$. This is plotted in Figure 52 over the range $T \sim 1685^\circ\text{K}$ to $T = 1200^\circ\text{K}$. For the desired distribution, $q(T)$, let the linear temperature range (constant $q = \Delta/\ell$) be extended to $x = 1.2\ell = 0.96$ cm, and let T_1 and T_2 denote the half-thickness temperatures at $x = \ell$ and $x = 1.2\ell$, as in Figure 53. The values of T_1 and T_2 are indicated in Figure 52. Next, let $q(T)$ increase as the temperature decreases from T_2 and join it smoothly to $q_0(T)$ at some T_3 , as in Figure 52. "Smoothly" means that $q = q_0$ and $dq/dT = dq_0/dT$ at $T = T_3$.

Figure 52. Original (q_0) and Afterheater-Modified (q) Temperature Gradients for the Case $v = 0.1 \text{ cm/sec}$, $t = 0.04 \text{ cm}$

Figure 53. Linear Temperature Distribution to be Extended to $x = 1.2 \ell$. Then $T_1 = T_F - \Delta/2$ and $T_2 = T_1 - 0.2\Delta$.

Some observations may be inferred from the approach as outlined so far. It will be noted that q and q_0 satisfy

$$t(k q dq/dT + \rho c v q) = F[T, T_A(T)]$$

and

$$t(k q_0 dq_0/dT + \rho c v q_0) = F(T, 300)$$

Inspection of Figure 52 reveals that $q \leq q_0$ and $q dq/dT \leq q_0 dq_0/dT$. It follows that $F[T, T_A(T)] \leq F(T, 300)$, and, therefore, $T_A(T) \geq 300$. In other words, $T_A(T)$ is realizable with heaters. Second, since both q , q_0 and their derivatives match at $T = T_3$, the value of $T_A(T)$ falls to 300° at $T = T_3$ and remains constant at lower ribbon temperatures. Finally, to the same approximations that were discussed earlier, continuity of both dT/dy and dT/dx is assured at $x = \ell$. That is, the linear temperature distribution is extended past $x = \ell$: (a) Since dT/dx is constant by design throughout the extension, dT/dy is also constant throughout the extension because $d^2T/dx^2 + d^2T/dy^2 = 0$ (neglecting the $\rho c v$ term). (b) Because the ambient seen by the ribbon surface opposite the meniscus is 300°K , it follows that

$$dT/dy \approx 1/k f(T_F, 300)$$

throughout the extension, as it is also in the wedge region. This is the primary rationale for placing the afterheaters on the meniscus side.

A simple function having the required properties is

$$q(T) = \Delta/\ell + a_1(T_2 - T) + a_2(T_2 - T)^2, \text{ where } T_2 \geq T \geq T_3 \quad (65)$$

with a_1 and a_2 chosen so that $q(T_3) = q_0(T_3)$ and $q'(T_3) = q'_0(T_3)$. If $T_3 = 1300^\circ\text{K}$, these are $q(T_3) = 672.17$ and $q'(T_3) = 1027.46$, and the coefficients are found to be $a_1 = 5.0197$ and $a_2 = -0.0085649$. Now $T_A(T)$ is easily determined algebraically from Equation (50) over the range $T_1 \geq T \geq T_2$ using $q = \Delta/\ell$ and $q' = 0$, and over the range $T_2 \geq T \geq T_3$ using q and q' from Equation (65). Then $T_A(x)$ may be found by integrating as in Equation (64) to obtain the relation between x and T . (This temperature distribution appears in Figure 55.)

Two-Dimensional Verification

The two-dimensional steady-state heat equation, Equation (57), was solved numerically on a 7×300 grid representing a rectangular region $t = 0.04$ cm wide and about 2.4 cm long. The first 0.8 cm (~ 100 grid points) corresponds to the wedge portion, the next 0.16 cm (20 grid points) represents the linear extension region, $T_1 \geq T \geq T_2$, and the remainder covers the rest of the afterheater distribution, including a very short final portion (~ 0.04 cm) where $T_A = 300^\circ\text{K}$. Boundary conditions were set up as indicated in Figure 54. Temperatures were specified on segments 1, 2, and 5, whereas derivative conditions were used on segments 3 and 4 corresponding to the nonlinear radiation law. An approximately linear temperature distribution was set up in the wedge region by treating the liquid as an extension of the solid. The temperature on the edge segments 1 and 2 was set to increase linearly from T_F at the LSI corners to $T_F + \Delta$ at $(0, t)$.

Figure 54. Boundary Conditions for Numerical Integration of Equation (57).
 Segment 1: $T = T_F + (y/t)\Delta$. Segment 2: $T = (T_F + \Delta) - (x/\ell)\Delta$.
 Segment 3: $|\partial T/\partial y| = (1/k) f(T, 300)$. Segment 4: $|\partial T/\partial y| = (1/k) f[T, T_A(x)]$. Segment 5: $T = 1275$.

The 2100-point system was solved by means of a successive over-relaxation method. The main features of the calculated temperature distribution are plotted in Figure 55 along with the effective ambient, $T_A(x)$. The partials $\partial T/\partial x$ and $\partial T/\partial y$ are of particular interest and are seen to remain essentially constant through the solidification region, ending at the point marked with an arrow. In other words, the linear profile remains intact throughout this region. The required T_A is approximately constant at just over 2000°K to a distance of 1 cm from the LSI-meniscus juncture and then falls rapidly to 300°K over the next 0.55 cm.

Figure 55. Two-Dimensional Temperature Distribution in Silicon Ribbon Drawn Through the Heated Environment, $T_A(x)$ (dashed curve). T and the partials, $\partial T/\partial x$ and $\partial T/\partial y$, are averaged over the width of the ribbon. A well-established linear temperature distribution is indicated by the near constancy of $\partial T/\partial x$ and $\partial T/\partial y$ up to the end of the wedge (marked with an arrow).

For comparison, Equation (57) was solved with $T_A(x)$ set equal to 300°K , corresponding to the omission of afterheaters. The boundary conditions on segments 1, 2, and 3 were the same as given in the caption for Figure 56 but on segment 4, $|\partial T/\partial y| = (1/k) f(T, 300)$. The results are plotted in Figure 56. Note that the rapid downstream cooling causes drastic variations in both $\partial T/\partial x$ and $\partial T/\partial y$ near the LSI-meniscus juncture. It is clear that the linear temperature distribution is completely destroyed.

Figure 56. Two-Dimensional Temperature Distribution in Silicon Ribbon With No Heated Environment. The linear temperature distribution is totally destroyed, indicating that a wedge-shaped solidification zone is not possible in a cold environment.

PROCESSING EFFORTS

The following processing efforts were performed during this reporting period:

- A standard dip-coating procedure was developed leading to highly reproducible high-yield runs.
- A bakeout procedure was developed which has eliminated ceramic substrate breakage of dye-checked substrates.
- A convective cooling procedure has been incorporated in the dip-coater, leading to increased coating thickness versus pull speed.
- Helium was used as the cooling gas in the experimental coater in place of argon.
- A continuous coating process was developed capable of coating substrates 1 meter long by 5 centimeters wide.
- Dip-coating process parameters were determined, allowing coating of layers from 5 μm to 200 μm thick.
- The LBIC process for measuring L_n was modified to measure L_n in unprocessed material as well as AR and non-AR-coated cells.

PROJECTION OF FUTURE ACTIVITIES

The work necessary to successfully determine the technical and economic feasibility of our SOC technology can be divided into three major areas:

- Cell performance optimization
- Coating speed optimization
- Continuous-coating technology development.

Specifically, we will continue to improve our cell processing techniques with the objective being 11 to 12 percent conversion efficiency SOC cells. These techniques will include optimization of junction depth and gettering experiments on the basic material to improve minority carrier diffusion length.

We will also fabricate "P" on "N" cells to determine the performance relative to our normal phosphorus diffused cells.

Ion implantation will be used to form the p-n junction in an effort to improve performance.

The investigation of the effect of convective cooling on the thickness versus coating speed relationship in the dip-coating activity will be continued.

We will continue to develop our continuous coating technology by coating increasingly larger slotted substrates so as to provide material for solar-cell fabrication.

Work will continue in the areas of thermal and growth modeling to provide support to the experimental growth activities.

Our economic analysis will be updated as new information becomes available.

NEW TECHNOLOGY

Recent results indicate that we can approach our coating speed goal by introducing convective cooling near the liquid-solid interface by the use of cooling shoes. Helium gas introduced through the cooling shoes provides a much greater thickness at a given coating speed than argon because of its higher thermal conductivity.

Our LBIC (light-beam induced current) technique has been modified (by using liquid electrodes) to be able to reproducibly measure L_n on SOC material before processing.

SUMMARY OF ANALYSIS AND CHARACTERIZATION DATA

The analysis and characterization data are presented in detail in the appropriate sections of the report. These analyses are summarized in the following brief statements:

- Dendrite formation during growth runs can usually be eliminated by increasing the melt temperature a few degrees.
- Carbon substrates can be dip-coated but the melt temperature must be 5 to 10 degrees cooler than for mullite substrates.
- Vitreous carbon substrates produced by Tylan Corp. were dipped. A continuous layer of SiC was formed at the silicon-carbon interface.
- When attempting to dip-coat ceramic substrates at high pull speeds with convective cooling, a preheater must be used to minimize substrate breakage.
- Care must be taken in the design of the cooling shoes for convective cooling as a nonuniform gas flow near the liquid-solid interface will result in a nonuniform coating thickness.
- Transverse temperature gradients along the SCIM coater trough must be negligible to obtain a uniform coating thickness.
- The SCIM coater must be inclined to the horizontal in order for stable coating to occur.
- The position of the liquid-solid interface with respect to the melt in angle SCIM coating is identical to that of dip-coating.
- The overall SOC cell efficiency increases 20 percent when the thickness is increased from 100 to 200 μm .
- The optimum base doping concentration for maximum performance of SOC cells is slightly greater than $1 \times 10^{16}/\text{cm}^3$.
- Shunt resistance values are typically $> 10\text{K ohms}$ for SOC cells.

- A calculated L_n based on the dark I-V characteristics of SOC cells is 50 μm .
- Asymmetric growth theoretically offers a greater throughput potential because the liquid-solid interface presents a much larger area for heat transfer.

PROGRAM STATUS UPDATE

Updated versions of the Program Plan, Program Labor Summary, and Program Cost Summary are presented in Figures 57, 58, and 59, respectively.

Figure 57. Updated Program Plan

Figure 58. Updated Program Labor Summary

Figure 59. Updated Program Cost Summary

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