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Tyco Laboratories, Inc.
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THICK FILM SILICON GROWTH TECHNIQUES

by

**CASE FILE
COPY**

H. E. Bates
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A. I. Mlavsky
F. Wald

Second Quarterly Progress Report
Subcontract No. 953365
Covering Period: 1 June 1972 - 31 August 1972

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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ABSTRACT

During this period, silicon ribbon growth experiments were conducted using orifices (dies) fabricated from SiC-SiO₂ mixtures, fused quartz, SiC, and fine-grained, high density graphite. The best results were obtained from graphite dies. A number of different approaches was tried in modifying the thermal gradient in the dies and in holding the dies. The best results here were obtained from a 0.25-in. thick Mo disc holding a graphite die directly and fitting the die quite closely. Ribbon growths as wide as 9 mm were obtained, while the longest ribbon was 450 × 3.5 × 0.5 mm. Resistivities of ribbons grown from graphite dies have been measured over the range of 0.03 to 1.6 Ω-cm. Some thoughts and literature findings are presented regarding refractory oxide materials as potential orifices.

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I. SUMMARY

A substantial effort was expended in this quarter on growth experiments with a variety of orifice materials. These included SiC-SiO₂ mixtures in the ratios of 95:5, 90:10, 60:40, and 20:80; fused quartz; SiC made by pyrolytic conversion of graphite; and high purity, high density graphite. Wetting experiments had indicated very favorable behavior of the 20% SiC-80% SiO₂ material. However, this was not borne out in actual performance as an orifice. The major difficulty with the 20% SiC-80% SiO₂ (and to an even greater extent, with 60% SiC-40% SiO₂) material was formation of massive amounts of SiO in the vicinity of the orifice. This was apparently the result of reduction of the SiO₂ by the SiC. Also, the excellent wetting of these materials resulted in poor edge definition when any growth could be obtained and difficulties in working with orifices, since they became entirely covered with molten Si during an experiment. For these reasons, these materials were dropped from further consideration.

Experiments with the lower SiO₂ content materials were essentially a continuation of the effort begun in the preceding quarter to define a set of suitable growth parameters with materials with known shortcomings. A number of experiments were run with various modifications to the way in which the orifice is held and to the means of heat transfer to and from the orifice. These experiments were generally unsuccessful insofar as direct attempts were made to influence the temperature gradient across the orifice. Then, however, the approach was changed attempting to produce a uniform temperature by bringing the molybdenum support structure as close as possible to the orifice and consolidating a number of shields into one. This has yielded a marked improvement in the initiation and stability of growth, particularly with graphite orifices.

One experiment was done using an orifice made from a form of high purity SiC produced by heating graphite in the presence of silane or silicones.* The orifice

*Pyrobond TM of Dow-Corning Corporation.

was not of typical design and the ribbon grown was unexceptional; however, its resistivity was $0.16 \Omega\text{-cm}$ and the rate of dissolution/precipitation of the SiC did appear to be lower than with the hot-pressed materials.

Fused quartz orifices were tried in four experiments. All were unsuccessful. The major problems were inability to produce a uniform, high temperature (i.e., greater than the melting point of Si) over the entire orifice and the unpredictable wetting of quartz by Si. It is possible, however, that recent changes in the thermal configuration of growth setups may permit solid quartz dies to work. Alternative approaches using a duplex structure of pyrolytic graphite and quartz are also being planned.

While graphite dies appear to be effective, it must be remembered that ultimately such dies will "wear out" by reaction and dissolution. The useful life of a graphite die and the parameters affecting it remain to be determined; however, it is clear that a more stable material is desirable. Results obtained by other investigators indicate that beryllium oxide may be a usable orifice material in that there is partial wetting, no apparent reaction with Si, and reasonable doping behavior by Be. We intend to investigate this material closely and also to examine some other oxides, at least on the basis of their relative stability and the stability of their silicides. This group will initially comprise CaO, and Y_2O_3 . Other oxides may be included as they are revealed from literature findings.

II. INTRODUCTION

One primary limitation to the large scale use of silicon solar cells in generating electric power from sunlight has been the lack of an industrially feasible technique in which thin, single crystal silicon ribbons are grown directly and continuously from the melt. Many attempts have been made previously to overcome this limitation. These attempts have included such methods as controlled dendritic growth into supercooled silicon¹⁻⁶ and the use of non-wetting shaping dies.^{7,9} This latter method, in particular, is very closely related to the Stepanov method which, independently of American efforts, has been applied to silicon ribbon growth by Russian workers.^{10,11} The former method, while capable of producing silicon ribbon, does not appear promising from the point of view of producing large amounts of inexpensive silicon ribbons for solar cell applications. This is so primarily because of the difficulty of maintaining stable ribbon growth, since, in the web-dendrite method, it is necessary to maintain growth temperatures constant to $\pm 0.02^\circ\text{C}$, thus making crucible replenishment practically impossible. Ribbon growth based on the use of essentially non-wetting dies in combination with edge-definition offers prospects for economical silicon ribbon fabrication. However, a considerable effort at the basic research level will first be required to establish the microdynamics of shape stability. As we will show, the EFG method overcomes the need for refined temperature control during growth and provides a more inherently stable growth process than previous shaped growth methods. Concomitantly, however, the EFG process puts stringent requirements on the nature of the die material if semiconductor purity levels are to be met.

Edge-defined, film fed growth (EFG) is a process by which single crystals may be grown having a shape controlled by the outside dimensions of a die, the growth actually taking place from an extremely thin film of liquid fed by capillary action from a crucible below.¹²⁻¹⁶ The application of this method to the growth of crystals with a ribbon geometry is illustrated in Fig. 1. The procedure is as follows.

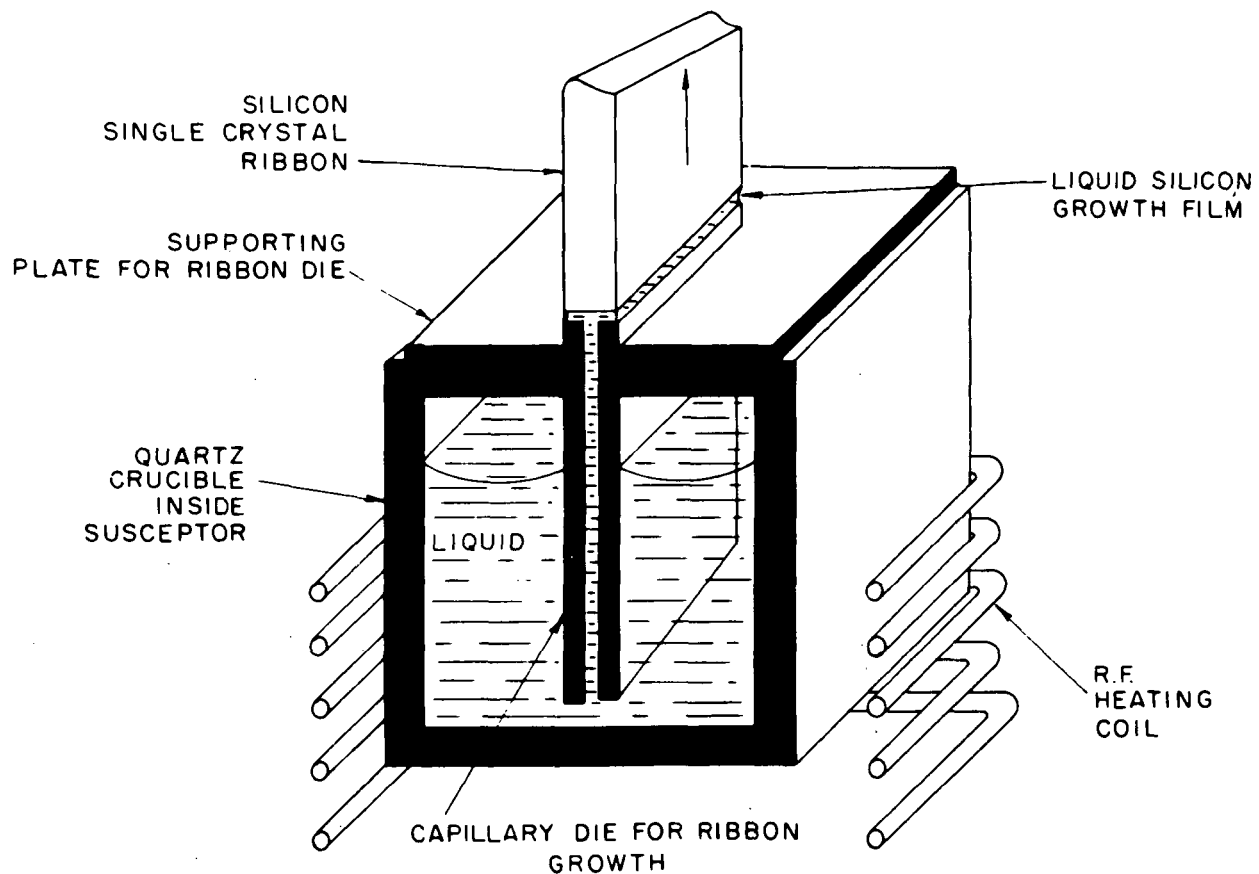


Fig. 1. Schematic drawing showing crucible and die arrangement for edge-defined, film-fed growth (EFG) of silicon ribbon

When the crucible and melt are heated to above the melting point of silicon, the liquid silicon rises to fill the feeding slot by capillary action. A silicon seed crystal is then brought into contact with the liquid silicon in the capillary seed slot. After adjustment of the melt temperature and seed withdrawal rate, the molten silicon spreads across the top surface of the die until the spreading of the liquid silicon is halted by the 90° change in effective contact angle at the outer perimeter. The growth of a silicon crystal ribbon from the thin liquid meniscus shown in Fig. 1 is then established. This method has been applied to the growth of ribbons, filaments, tubes, and other shapes of sapphire, barium magnesium titanate, lithium fluoride, copper-gold alloy crystals, and beta-alumina, as well as to the directional solidification of a variety of eutectic materials:

The basic features of the EFG technique can be summarized as follows:

1. It produces accurately controlled cross sections and, in particular, thin ribbons can be produced directly.
2. It is self-stabilizing over a relatively wide range of power input fluctuations by means of changes in the thickness of molten film.
3. Growth rates can be very fast since they are limited only by latent heat removal from the solid-liquid interface.
4. The growth interface is effectively decoupled from the bulk melt surface, permitting continuous replenishment of the melt during growth.
5. The crystal orientation can be arbitrarily chosen.
6. Because of the fast growth rate and the faster linear motion rate of the liquid supply, segregation effects tend to be completely overcome, and the crystallizing solid has the same average composition as the bulk liquid.
7. The steep thermal gradient between the growth interface and the die prevents the breakdown of planar growth. Thus, crystal perfection is enhanced and cellular substructure suppressed.

In the following sections of this report, we discuss the progress which has been made to date in applying this method to the thick film silicon ribbon growth.

III. TECHNICAL DISCUSSION

A. Die Materials

1. SiO₂

Production of an effective quartz die was approached from three directions. We attempted to produce coatings of SiO₂ on refractory metals and SiC by pyrolysis of silane in the presence of oxygen. The quartz films we were able to get were too thin and/or too porous to resist molten silicon. This coupled with a slow deposition rate led us to drop this technique.

Several attempts were made to fabricate orifices from hot-pressed mixtures of SiO₂/Si in ratios of 5, 10, and 30% Si. These were all unsuccessful due to the low strength of the mixtures. Tests of the wettability of these materials by Si showed a tendency for the Si within the structure to run out when molten and for the material to warp when it was in pieces the thickness of typical orifices.

Finally, four runs were made with solid fused quartz orifices, both one- and two-piece. The inner surfaces of the orifices were variously pre-treated by sand-blasting and coating with a thin wash of colloidal graphite to promote wetting. In addition, thin slabs of silicon were positioned in the feed slots of the orifices to provide some silicon to fill the orifice on melting. The basic difficulty encountered in all four experiments was that the silicon would not feed up the capillary slots until the temperature had been raised to the softening point of the quartz. Even when pressed to this extreme, the wetting and feeding were unpredictable. The problem would appear to be the low thermal conductivity of quartz compounded with the difficult wetting. For this reason, quartz was suspended from active consideration; however we now feel that recent advancements in thermal design made with graphite dies may allow use of fused quartz. Also, we are considering some alternate die structures of quartz and pyrolytic graphite.

2. SiC-SiO₂ mixtures

Wetting experiments with an 80% SiO₂-20% SiC hot-pressed mixture showed an apparently small amount of SiC dissolution/precipitation and excellent wetting. Orifices were fabricated from this material and tried. Two significant difficulties were experienced with this material. First, wetting by the Si was so good that eventually the entire die became covered with molten Si which made it inconveniently difficult to hold the dies in isolation from the molybdenum parts. This also resulted in poor edge definition when any growth could be achieved; essentially, growth occurred from a puddle of silicon. Secondly, during an experiment, massive amounts of SiO were deposited near the orifice. This apparently resulted from reduction of the SiO₂ by SiC. The effect was to seriously distort the thermal conditions at the orifice, generally precluding growth. Dies made from 60% SiC-40% SiO₂ behaved in a similar fashion, with even greater amounts of SiO forming. For this reason, we are no longer considering these materials.

3. SiC - Pyrobond*®

We obtained some sample pieces of a material made by exposing high purity graphite to gaseous silicon at high temperatures. The reaction product, SiC, occurs as a case on the graphite some 0.020 to 0.030 in. deep. The SiC is nominally as pure as the graphite from which it is made. Fixtures treated by this process find wide application for high temperature processing in semiconductor device fabrication. We were able to make a die by slicing two slabs from a piece such that L-shaped sections resulted. The graphite core was burned away at 1000 °C in air, and the pieces were prewetted with Si and assembled. Three pieces of Si were grown from this makeshift die. Their average resistivity was 0.16 Ω-cm, approximately ten times that of the majority of ribbons grown from hot-pressed SiC. It is not clear that this particular piece represented the highest purity attainable by the process, so we intend to have some of our graphite dies treated by the Pyrobond process. This should result in almost complete conversion to SiC because of the generally thin sections in the dies. The performance of these dies will then be evaluated.

® *Pyrobond is a trademark of the Dow-Corning Corporation, Midland, Michigan.

4. Graphite

In light of the generally lackluster results from most SiC and SiO₂ dies, we decided to try graphite. Clearly, reaction to SiC was bound to occur, but a high density graphite would expose less total surface for reaction/solution than had the 70% dense hot-pressed SiC materials, so that conceivably a decrease in physical contamination might be realized. At the same time, since graphites can be produced at very high purity levels (and cleaned relatively easily), it was apparent that much lower impurity levels could be achieved in Si grown from graphite.

Four experiments have been done to date with graphite orifices. All were done with a 0.25-in. thick Mo cover/holding plate of the type shown in Fig. 2. The orifices all fed very readily, and growth could be easily initiated. Reasonable widths were grown in the first two experiments (Fig. 3), while in the third run, because of a misalignment of the orifice, a width of only 3 to 4 mm could be obtained; however, a ribbon 45 cm long by 3.5 mm was grown at a rate of 2.6 cm per minute (Fig. 4).

The major problems encountered are: (1) that the setups, i.e., orifice, are fairly sensitive mechanically – they must be aligned and located with reasonable precision; and (2) precipitation of SiC on the liquid meniscus affects the growth interface and the surface of the ribbon – this seems to be somewhat amenable to control by variation of the thermal conditions, but will always be present as long as the graphite is exposed to liquid Si. We expect that substantial improvement is possible in both of these problem areas and shall concentrate our efforts on making graphite viable as a near-term die material.

B. Thermal Design

A variety of configurations of lids, afterheaters, and direct modifiers were tested during this period.

Three runs were made using a graphite afterheater to supply heat to the seed and growing crystal. It had been observed previously that the addition of a "warm" Mo afterheater had exerted a strong influence on the growth process in the direction of increased stability (this prior to the addition of the temperature controller). The Mo afterheater consisted of a cover with a large oval opening and a vertical Mo tube 0.75 in. in diameter with a rectangular slot cut in the bottom to allow observation of the orifice. The cover ran at ~ 1500° C and the tube operated with a vertical temperature gradient of about 1300° to 900° over 1.5 in. The graphite afterheater had

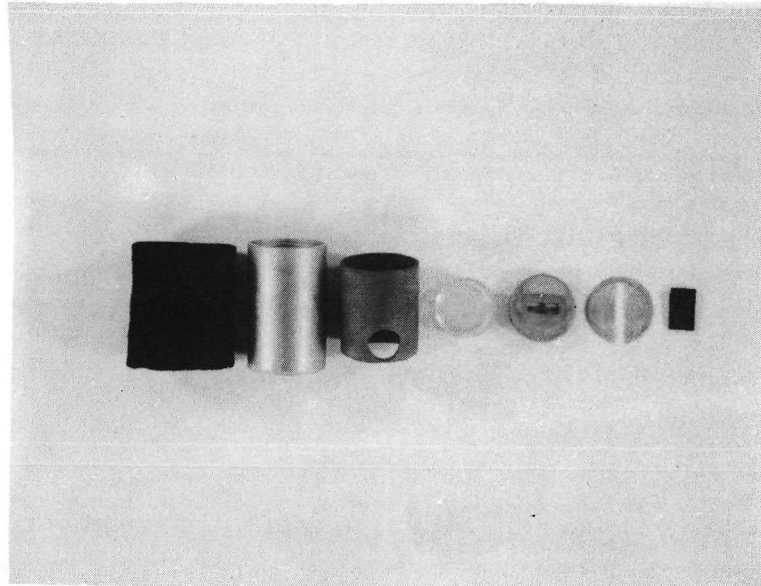


Fig. 2a. Components of ribbon growth setup. From left: graphite felt insulation, molybdenum susceptor, molybdenum afterheater with viewport, quartz crucible, molybdenum lid, molybdenum radiation shield, graphite die.

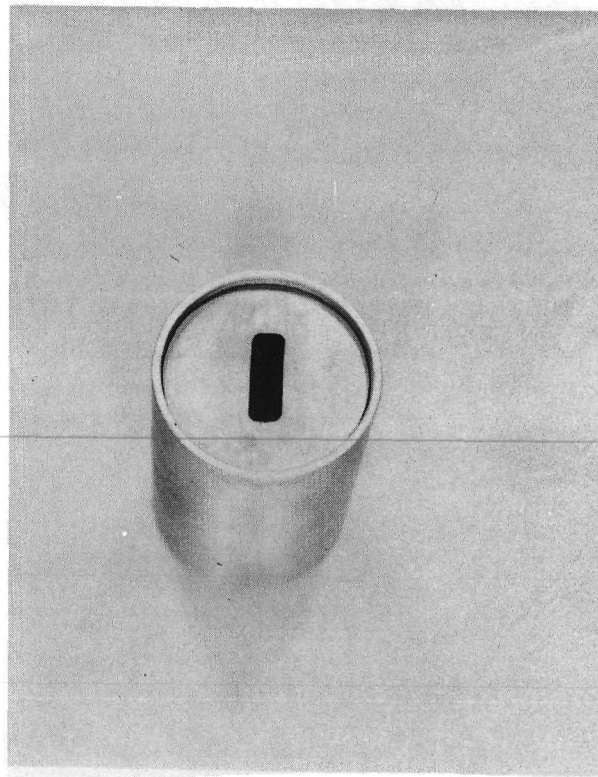


Fig. 2b. Top view of assembled setup showing position of orifice in lid. Afterheater and radiation shield have been omitted for clarity.

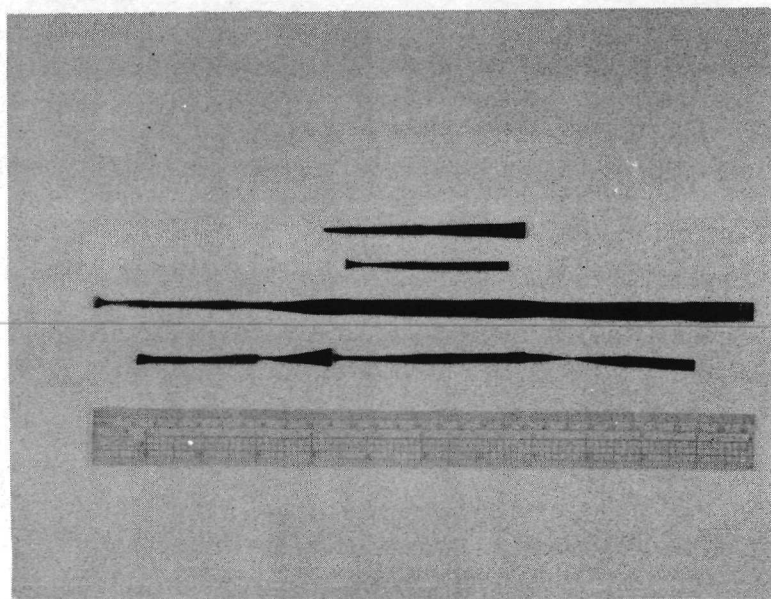
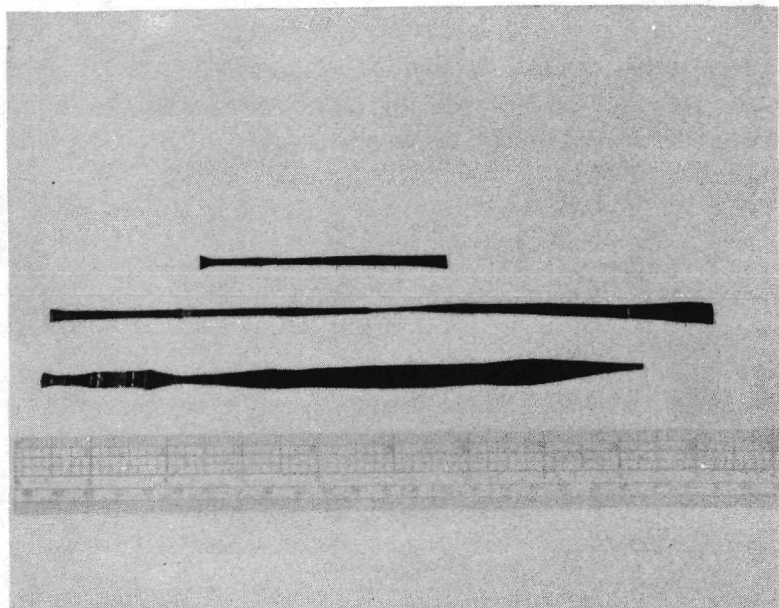


Fig. 3. Ribbons grown from graphite dies, (a) C-55, (b) C-56.

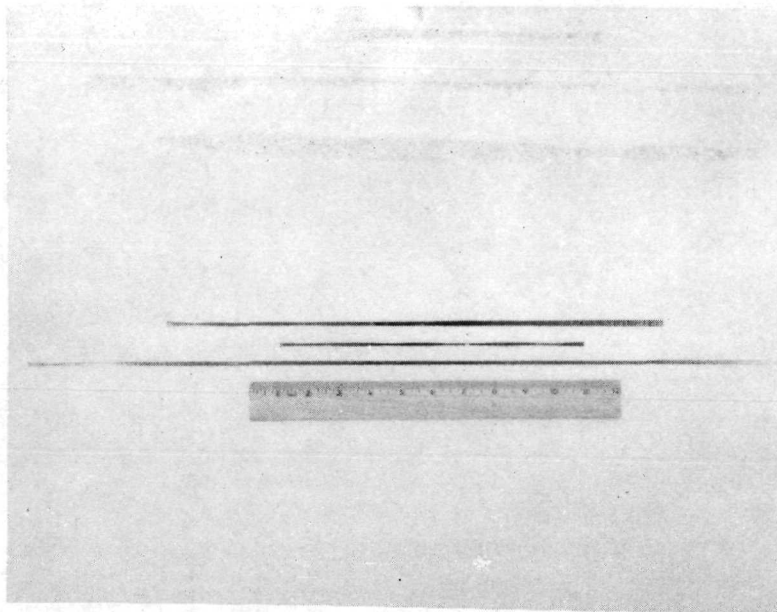


Fig. 4. Ribbon C-57, grown from a graphite die. The piece nearest the ruler grew stably for 18 in. at 1 in./min.

a single 0.5 in. hold in the wall for viewing the orifice. It ran at approximately 1500°C for about 0.8 in. above the orifice, and cooled gradually to about 1000° over the remaining 1.5 in. Given these conditions, it was extremely difficult to obtain stable growth and impossible to achieve spreading of the initial growth across the orifice. These results were taken to mean that provision of a uniformly hot environment in the vicinity of the orifice will inhibit growth by reversing the temperature gradient across the orifice and reducing the effectiveness of the vertical gradient through the seed.

In another experiment, a deliberate modification of the gradient across the orifice was attempted by placing truncated wedges of boron nitride on the top cover plate at the ends of the orifice to block radiation from the susceptor. At the same time, thin molybdenum radiation shields were positioned parallel to the central two-thirds of the orifice, spaced approximately 0.050 in. away. Unfortunately, the radiation shields, in operation, ran at a lower temperature than was expected, so their effectiveness was somewhat dubious. However, the boron nitride blocks appeared to serve their intended function. Only one side of the orifice was fed with molten Si for some unknown reason; however, spreading of the initial growth toward the end of the orifice was readily achieved, a clear indication that the outer end of the orifice was colder than the center.

Another series of three experiments were run with orifices which had an essentially solid top surface with only two small diameter feedholes near the center (similar to the "type a" orifice in Fig. 3 of the First Quarterly Report, save that the sides of the orifices were bevelled to give a flat surface on the top about 0.025 in. wide). These orifices were intended to test the theory that by limiting access of hot molten Si to the center of the orifice, the center could be maintained hot relative to the ends of the orifice. The results of two of the runs were inconclusive because of difficulties in feeding of the molten Si. The third experiment indicated that there was no particularly strong influence from this orifice configuration. Lateral spreading of the solid/liquid interface was not significantly easier than with orifices which are largely open (i.e., subtended by molten Si) at the top.

The overall impact of these experiments led us to revert to a shielding configuration used in early experiments with quite different orifices. This was an hourglass or "dogbone" shaped opening in the holding plates and heat shields which leaves the ends of the orifice rather more distant from the molybdenum pieces

than is the center. Thus, the ends of the orifice receive less heat, transferred by conduction/radiation inward from the susceptor, than the middle. This did not confer any significant improvements in succeeding runs, so a different approach was taken, based on our experiments with fused quartz orifices. There the problem was clearly one of providing a uniform and sufficient amount of heat to the orifice to get it to feed. We had used three 0.062 molybdenum lids stacked up and with rather narrow slots, i.e., close to the orifice. It was then decided to replace this arrangement with a single, thick (0.25 in.) lid. This was just tried with graphite dies, and the results have been encouraging enough that we shall try a configuration in which the clearance between the molybdenum lid and the orifice is only a few thousandths of an inch.

C. Orifice Design

The rate of evolution of the die design has slowed considerably and seems to be settling on a configuration basically like that shown in Fig. 5. This design has a number of obvious virtues in comparison to the two-piece type, not the least of which are strength and constancy of the dimensions and relations of the edges of the orifice. We are planning on eliminating the double rib and support plate and simply engaging a single rib with a matching groove in the lid. This depends on our being able to control spreading of the liquid Si out of the sides of the feed slot. The curvature of the top edge of the orifice is an area which remains to be explored. We have used flat orifices in our experiments with graphite dies, and it is unclear where curvature of the orifice will help. We are having a variety of curvatures put on some orifices for later experiments.

D. Ribbon Growths

1. Resistivity

Table I lists the resistivity measured on a number of ribbons grown from a variety of orifice materials. It should be noted here that all the ribbons examined have been p-type. The low resistivity of Si grown from the hot-pressed SiC is consistent with earlier results. And it is apparent that incorporation of a small amount of SiO₂ does not materially improve the situation. In the case of Q'-51, where a large amount of quartz has been substituted for SiC, a marked improvement results; however, as noted in II.A.2, this material appears to be impractical to use.

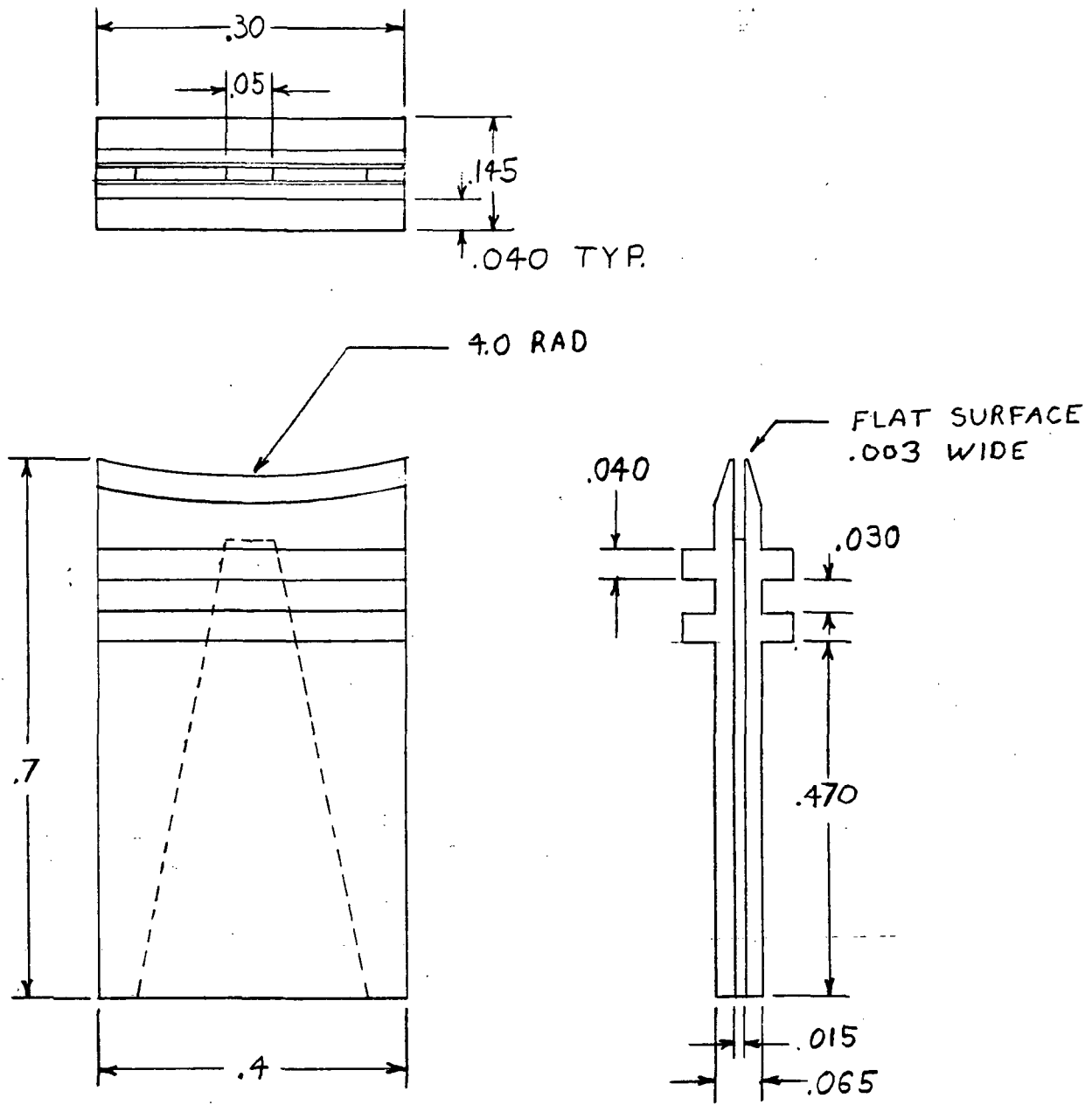


Fig. 5. Orifice design being used currently. An 0.030-in. alumina plate engages the slot between the ribs on the sides of the orifice and itself rests in the recess in a holding plate.

Table I. Measured Resistivities of Silicon Ribbons Grown from a Variety of Die Materials

Ribbon	Die Material	Average Resistivity (Ω -cm)	Range of Resistivity Values (Ω -cm)
SC-30	SiC	0.008	0.006 - 0.011
SC-31	SiC	0.012	0.008 - 0.016
SC-32	SiC + 10% SiO ₂	0.026	0.006 - 0.04
SC-33	SiC	0.014	0.014 - 0.015
SC-34	SiC	0.015	0.011 - 0.021
SC-35	SiC	0.025	0.011 - 0.052
SC-40	SiC + 10% SiO ₂	0.050	—
Q-51	80 SiO ₂ + 20 SiC	1.10	0.9 - 1.3
SC -54	Pyrobond [®] SiC	0.15	—
C-55	Poco Graphite*	0.53	0.45 - 0.68
C-56	↓	0.045	0.030 - 0.060
C-57	↓	0.030	0.025 - 0.035
C-58	↓	1.6	1.1 - 1.8

*Poco Graphite Corp., Decatur, Texas Grade AXF 5QBG1

Ribbon SC"-54 (actually three samples) indicates that Pyrobond SiC offers some improvement over hot-pressed SiC. Probably further improvement can be realized if the initial purity of the basic graphite is closely controlled. We are having a few orifices made in this way to test this material fairly.

The graphite-orifice grown ribbons present a seemingly inconsistent picture, without some explanation. Ribbons C-55 and C-58 were grown from dies supported by sapphire holders, while C-56 and 57 had boron nitride pieces in place of the sapphire. It appears that the higher resistivities of 55 and 58 are the result of partial compensation of a p-type impurity in the graphite, while 56 and 57 simply received additional doping from the boron nitride. The graphite dies were "cleaned" by firing in argon at 1600 to 1700 °C. We intend in the near future to vacuum outgas the dies.*

2. Ribbon surfaces

Physical contamination of the ribbon surfaces by included crystallites of SiC continues to be a problem with any ribbon grown from a graphite or SiC die. Also, vibration in the pulling apparatus contributes its own irregularities. This can be a particularly vexing problem given a pull rod/seed holder approximately 18 in. long with a 12-in. long ribbon growing at the end. Very slight vibrations become amplified considerably. Fig. 6 shows the three C-57 ribbons at almost twice life-size. The bright specks on the top and bottom ribbons are SiC crystallites, stuck to the ribbon surface in many cases where a vibration has perturbed the meniscus slightly and shaken some of the SiC bits loose to float up onto the growth interface. The middle ribbon, grown, in fact, between the other two in time, shows a much cleaner, almost mirror surface. The only difference was a slightly higher growth temperature relative to the other ribbons. This had the unfortunate effect of destabilizing the growth, however, as can be seen from the irregular width. This is merely to illustrate that some degree of control may be possible in dealing with this shortcoming in graphite dies. We feel that both problems can be dealt with to significantly improve the ribbon surfaces.

*Note added in proof: Subsequent ribbons grown from vacuum-baked dies with no holding plates have shown more consistent resistivities of approximately 1 to 3 Ω -cm.

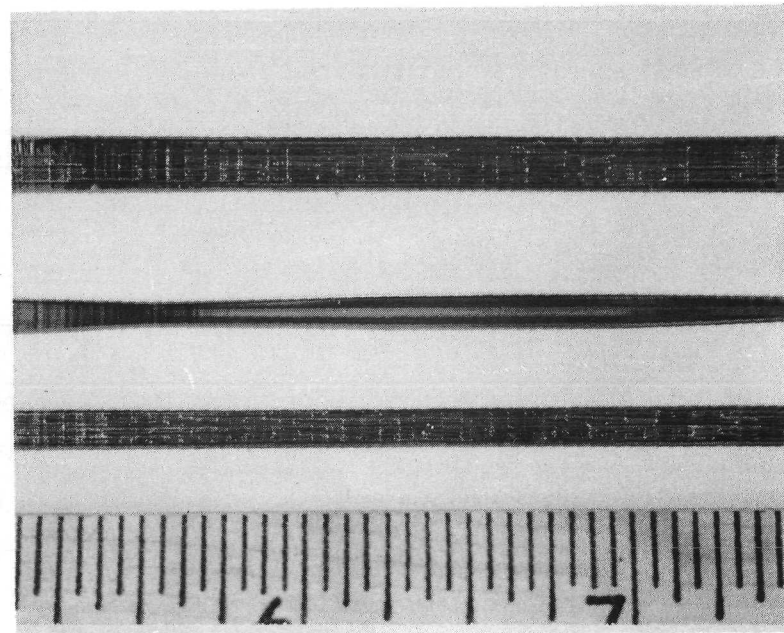


Fig. 6. Surfaces of C-57 ribbons showing lateral striations from vibration and SiC crystallite pickup on top and bottom ribbons. Clean surface of middle ribbon (grown from the same orifice) is attributed to modified growth conditions ($\sim 2X$).

3. Crystallinity and perfection

Evaluation of the ribbons for crystalline perfection has been very sketchy during this period. Having now settled on what seems at least a workable die material, we can begin to evaluate more thoroughly the ribbons grown from it. One of the C-57 ribbons was X-rayed and found to be single crystal, but apparently the orientation of the seed had been lost in starting the growth, since the orientation of the ribbon was not coincident with that of the seed. This is, however, an encouraging result since the ribbon was grown at 1 in./min. Very obvious twins seem also to be a problem, when conditions are such that precipitated SiC is included in or on the ribbons. If, of course, we can reduce the SiC crystallite incidence, then this problem should diminish.

E. New Orifice Materials

The apparent effectiveness of graphite dies is not without some equally obvious drawbacks. It is an inescapable fact that liquid Si will react with graphite, and while it may be possible by careful design to minimize the temperatures throughout the setup and thus the reaction rate, it is still an unstable system. In continuing to experiment with quartz orifices, clearly we are trying to develop a more nearly equilibrium system (although it should be remembered that quartz and liquid Si tend to react to SiO). It seems to still be desirable, however, to try to find a material which does behave more stably than even quartz, if, in fact, such a material exists.

We have some indications that possibly beryllium oxide is non-reactive with Si. For example, Kocher and Muhlbauer,¹⁷ in a study of the behavior of a variety of materials as crucibles for melting high purity silicon, found no reaction, penetration, or corrosion of BeO crucibles by molten Si. Their only real objections to BeO versus quartz were its cost and lack of transparency. They also said that they were not able to grow as high purity (resistivity) crystals as from quartz. There is probably an explanation for this. Littlejohn and Robertson¹⁸ have reported a minimum resistivity of approximately $0.2 \Omega\text{-cm}$ produced by diffusion of Be metal into Si at 1300°C . They claim that this represents the solubility limit for Be at 1300° , and that by reheating to lower temperatures, the resistivity could be increased to several $\Omega\text{-cm}$ by precipitating some of the Be. They also report room temperature mobilities of 300 to $400 \text{ cm}^2/\text{V sec}$ for carrier concentrations of 3 to $6 \times 10^{15} \text{ cm}^{-3}$ (4 to $2.6 \Omega\text{-cm}$). Beryllium is a p-type dopant in Si. Thus, it appears that Si grown from BeO is probably doped with Be, which may account for Kocher's observations.

The interesting point is that there is apparently retrograde solubility of the Be.

Some other indications come from work by Kingery and co-workers who investigated interfacial reactions¹⁹ and contact angles²⁰ in a number of metal-ceramic systems. Their findings for Si are summarized in Table II, adapted from their papers. It would appear from their results, particularly on contact angles, that BeO is the most likely material, but it seems that TiO₂ and ThO₂ are also possibilities. In addition, CaO, on the basis of the stability of the oxide and the relative instability of the silicides, seems to be a possibility. Similar considerations indicate that yttrium oxide should also be investigated.

These investigations will take the form initially of wetting/compatibility experiments and then move on to fabrication of dies and growth experiments with any promising-looking materials.

Table II. Silicon-Oxide Interactions at Elevated Temperatures, after Kingery, et al. 17, 18

System	Temperature	Interfacial Reactions	Phases Found	Contact Angle (θ) at 1450 °C	
				Atmosphere: H ₂	He
Si-Al ₂ O ₃	1400	No reaction	SiO ₂ , Al ₂ O ₃	95	100
	1600	Interfacial film on surface; slight penetration; no corrosion	3Al ₂ O ₃ -2SiO ₂		
Si-BeO	1600	Slight corrosion of oxide; no interfacial phase; slight penetration along grain boundaries		88	76
Si-MgO	1400	Slight surface alteration	MgO	101	95
	1600	Definite interfacial layer of Mg ₂ SiO ₄ ; corrosion of oxide	Mg ₂ SiO ₄		
Si-TiO ₂	1400	Slight surface discoloration		—	107
	1600	Slight reaction with decrease in porosity of oxide near surface; no new phase			
Si-ThO ₂	1400	Slight reaction and adherence	ThO ₂	—	—
	1600	Penetration of metallic phase between grain boundaries and black discoloration of grains; corrosion of surface			
Si-ZrO ₂	1600	Interfacial layer of new phase	ZrSiO ₄ , ZrO ₂	90	96

IV. CONCLUSIONS AND RECOMMENDATIONS

During this period all the components of successful growth of silicon ribbon suitable for solar cells have been achieved: stable growth for over 18 in., centimeter wide growth, and resistivities in excess of 1 Ω -cm. These results have been achieved using graphite dies, which are not ideal but can clearly provide a means to achieve the desired end of single crystal silicon ribbons.

During the next quarter our efforts will be concentrated in three areas: first, continued development of graphite dies and associated technology to produce solar cell quality Si ribbon; second, investigation of the feasibility of quartz dies; and third, investigation of the feasibility of using a more refractory oxide than quartz as an orifice material.

V. NEW TECHNOLOGY

Description Title: Improved Apparatus for the Edge-Defined, Film-Fed Growth of Thick Film Silicon Ribbon from Graphite Dies

Names of Innovators: H. E. Bates and V. White

Progress Reports: Second Quarterly Report

Pages: 6 through 10

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