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THICK FILM SILICON GROWTH TECHNIQUES

By

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

First Quarterly Progress Report

Subcontract No. 953365

Covering Period: 18 February 1972 - 31 May 1972

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ABSTRACT

Thick film silicon ribbons have been successfully produced by means of the edge-defined, film-fed growth (EFG) technique. EFG is a process by which single crystals may be grown having a shape controlled by the outside dimensions of a die, the growth taking place from an extremely thin film of liquid fed by capillary action from a crucible below.

The principal problem to be overcome in the application of this process to the growth of thick film silicon ribbon relates to the material, such as the shaping die. For the method to operate, this die material must be wet by the liquid silicon. To preserve semiconductor quality, the liquid silicon must not react significantly with the die material. The most promising die material for this application appears to be SiC and SiC-SiO₂ admixture. In this case good wetting occurs between the molten silicon and the SiC. C is a relatively unharmed contaminant of Si and additions of quartz to SiC are found to decrease the extent of reaction.

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Table of Contents

Section		Page
	ABSTRACT.	iii
I.	INTRODUCTION.	1
II.	TECHNICAL DISCUSSION.	5
	A. EFG Dies	5
	B. Ribbon Growth	11
	C. Equipment.	17
III.	CONCLUSIONS AND RECOMMENDATIONS.	23
IV.	NEW TECHNOLOGY.	25
V.	REFERENCES.	27

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List of Illustrations

Figures	Page
1. Schematic drawing showing crucible and die arrangement for edge-defined, film-fed growth (EFG) of silicon ribbon	2
2. Photomicrograph of SiC-Si interface along the capillary feeding channel of the EFG die (note morphology of SiC crystals at the SiC - Si interface)	7
3. Orifice configurations used in growing Si ribbons. Views are of the top surface and the inside of one side of the orifice. The side view of (f) is intended to show the knife edge bevel which was also used on some type (e) orifices. Typical overall dimensions for type c-f orifices are 0.7 in. × 0.4 in. × 0.065 in.	9
4. Photomicrograph of interface between Si and SiC/10% SiO ₂ near the top of an orifice (140X).	10
5. Single crystal silicon ribbon grown from the melt by EFG (ribbon thickness is 0.5 mm)	12
6. EFG-grown silicon ribbons of the order of 8 to 9 mm in width	13
7. Silicon ribbon showing a relatively smooth surface on one side of the long axis roughness caused by orifice disintegration on the other.	15
8. EFG-grown silicon ribbon showing crystallographic flats developed on one side during growth at approximately 20 in./hr	16
9. Dislocation etch pits in EFG-grown silicon ribbon showing variable distribution across the width of a single ribbon (Dash etch, 35X)	18
10. Quartz furnace assembly incorporating two window ports	19
11. Crystal growth apparatus	20

I. 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:

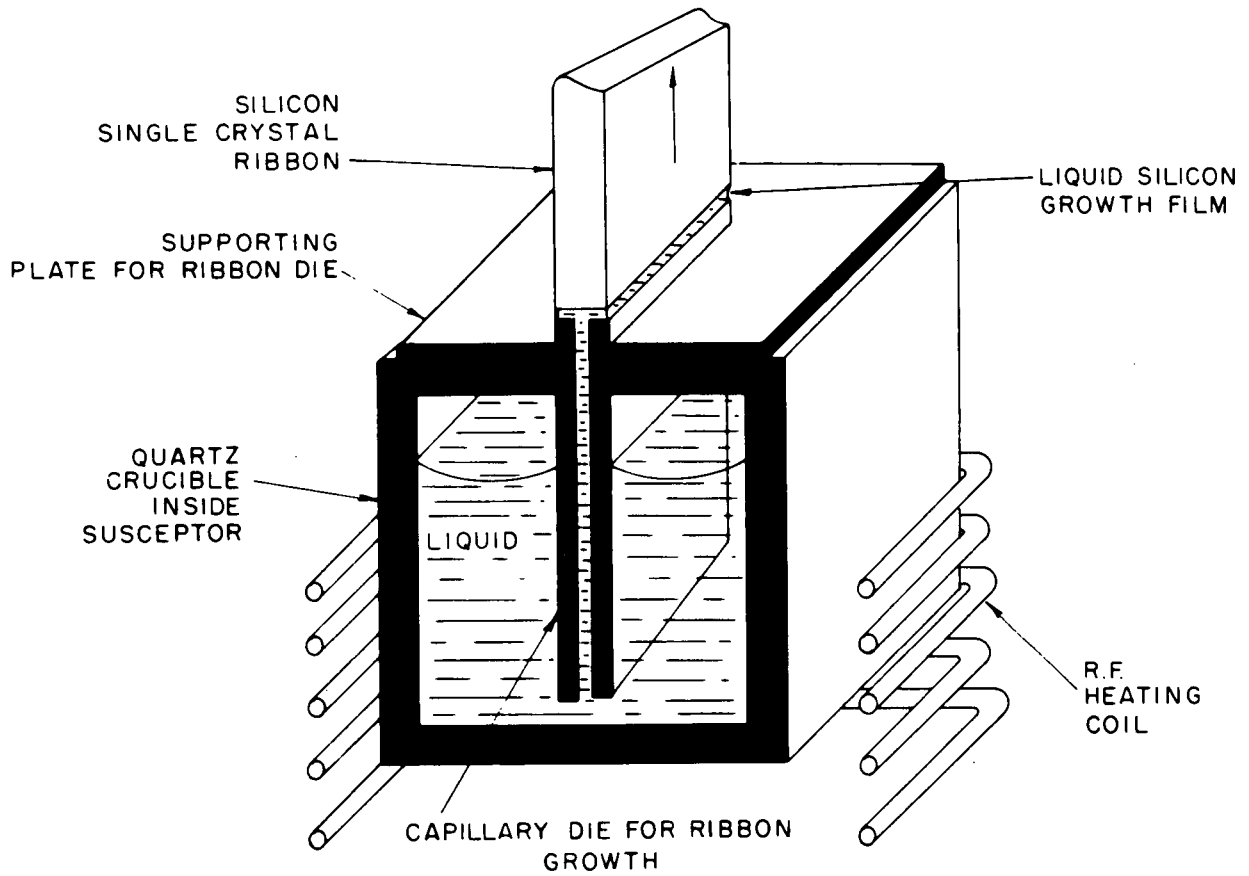


Fig. 1. Schematic drawing showing crucible and die arrangement for edge-defined, film-fed growth (EFG) of silicon ribbon

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.

II. TECHNICAL DISCUSSION

A. EFG Dies

1. Material

It was decided at the outset of the contract to use hot-pressed SiC as a die material. This choice was based on the fact that in the absence of significant amounts of Group V or III impurities, the SiC would only introduce carbon, a relatively harmless impurity. The SiC used in these initial experiments has not been of exceptional purity; however, this was also by choice, since growth parameters could be worked out which do not require high purity. Table I shows a typical analysis of the SiC used. While it is clear that these impurity concentrations can be improved upon, a larger question remains as to the ultimate suitability of any system which allows liquid Si to contact SiC. Fig. 2 demonstrates the ability of Si to dissolve (and precipitate) SiC. This tendency has been found to affect adversely the growth of suitable Si ribbons in three ways: erosion of the orifice which affects the surface of the ribbon; inclusion of SiC crystallites in the solidified ribbon; and inhibition of proper crystal growth by precipitation of SiC at the liquid/solid interface. All of these effects (and potential solutions) will be discussed further in subsequent sections.

2. Infiltration

A number of growth experiments were attempted initially using plain hot-pressed SiC orifices. These were all unsatisfactory since the silicon would not rise in the capillary slots. Since the silicon did seem to be wetting the SiC adequately and even penetrating the fairly porous (~70% dense) structure where they came in contact, it was decided to try to prewet the SiC with Si. An orifice was prewetted by placing small bits of Si on the inner surfaces of the orifice halves and heating them well above the melting point of Si until the Si penetrated the orifice structure.

Table I. Semi-Quantitative Spectrographic Analysis of Silicon Carbide: Haselden Corporation

Si	Principal Constituent
Fe	0.06%
Al	0.05
Zr	0.03
Ti	0.04
V	0.01
Mg	0.007
Ni	0.008
Ca	0.002
Cr	0.002
Cu	0.004
Ba	0.001
Mn	0.001

Such an infiltrated orifice was the first one to allow complete filling of the capillaries and growth of a piece of silicon.

The process of prewetting or infiltrating the porous SiC dies with Si represented an important step in the use of this material and points up a requirement for other materials. Since the Si was obviously wetting the SiC, it appears that the effect of infiltration is primarily to increase the thermal conductivity of the orifice. This was borne out by one experiment in which the same shielding and orifice design was used with, successively, a plain SiC and a Si-infiltrated orifice. The molten silicon rose to the top of the latter, but only a short distance in the former. Thus, infiltration has become an integral part of the preparation of SiC orifices, and it would seem that in trying to use any new orifice material, similar provision must be made to ensure a reasonable conductivity in the orifice as well as a surface which is wet by molten silicon.

3. Configuration

The design of the SiC orifices has gone through a continual (and continuing) evolution. The initial orifices consisted of two plates with matching

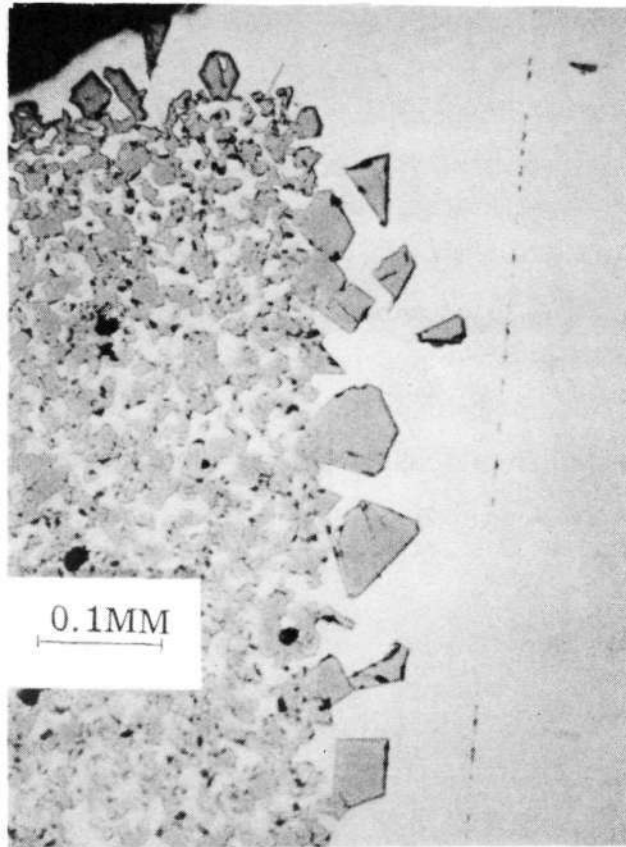


Fig. 2. Photomicrograph of SiC-Si interface along the capillary feeding channel of the EFG die (note morphology of SiC crystals at the SiC-Si interface)

grooves on their inner mating surfaces which provided feed capillaries for the silicon to rise to the top, shaping the surface of the orifice.

This type of orifice is illustrated in Fig. 3a. After achieving some limited growth with this type, the top surface was slotted (b) to promote spreading of the growth interface across the width of the orifice. Orifice type (c) was conceived to provide more ready feeding of liquid silicon to the top of the orifice and, in a similar fashion to (b), to ease the sideward spreading of the growth interface. Type (d) is a modification of (c) for improved strength and stability by addition of the central inner rib. Orifices of this type were able to provide reasonably good ribbon growths when the thermal conditions were properly adjusted; however, the halves of the orifice tended to slip out of alignment. The method of holding the orifice together was then changed. This is reflected in the type (e) orifice. The notches in the edges are engaged by a notched piece of boron nitride, and the alignment is maintained both laterally and vertically. This orifice was also the first in which the edges of the top surface were bevelled to improve the stability of the crystal growth. The type (f) orifice has been used experimentally with very encouraging results. It was unfortunately somewhat unsymmetrical since the curvature had been sculpted by hand, and this asymmetry interfered with achievement of a stable growth condition.

4. New Materials

Because of the dissolution of SiC by Si, as mentioned above, we have begun to assemble a number of compositions of SiC plus SiO₂ hot-pressed powders and SiO₂ plus Si materials to evaluate the effect of reducing the total amount of SiC in contact with the Si and the possibility of eliminating SiC altogether.

One experiment has been conducted with an orifice of 90% SiC - 10% SiO₂. The resistivity of the ribbon grown from this orifice was higher than average, although still not of the required level (0.026 Ω-cm compared to an average of 0.015 Ω-cm for those ribbons measured). On sectioning the orifices (Fig. 4), however, there appeared to be a noticeable decrease in the solution and regrowth of SiC compared to the section shown in Fig. 2. This is favorable evidence for a small quantity of SiO₂ inhibiting the dissolution of the SiC. However, clearly the purity of the SiC still needs to be of a high order to yield Si of 10 Ω-cm or higher. We have obtained some SiC of high purity which we will attempt to have hot-pressed to test the possibility of such a solution.

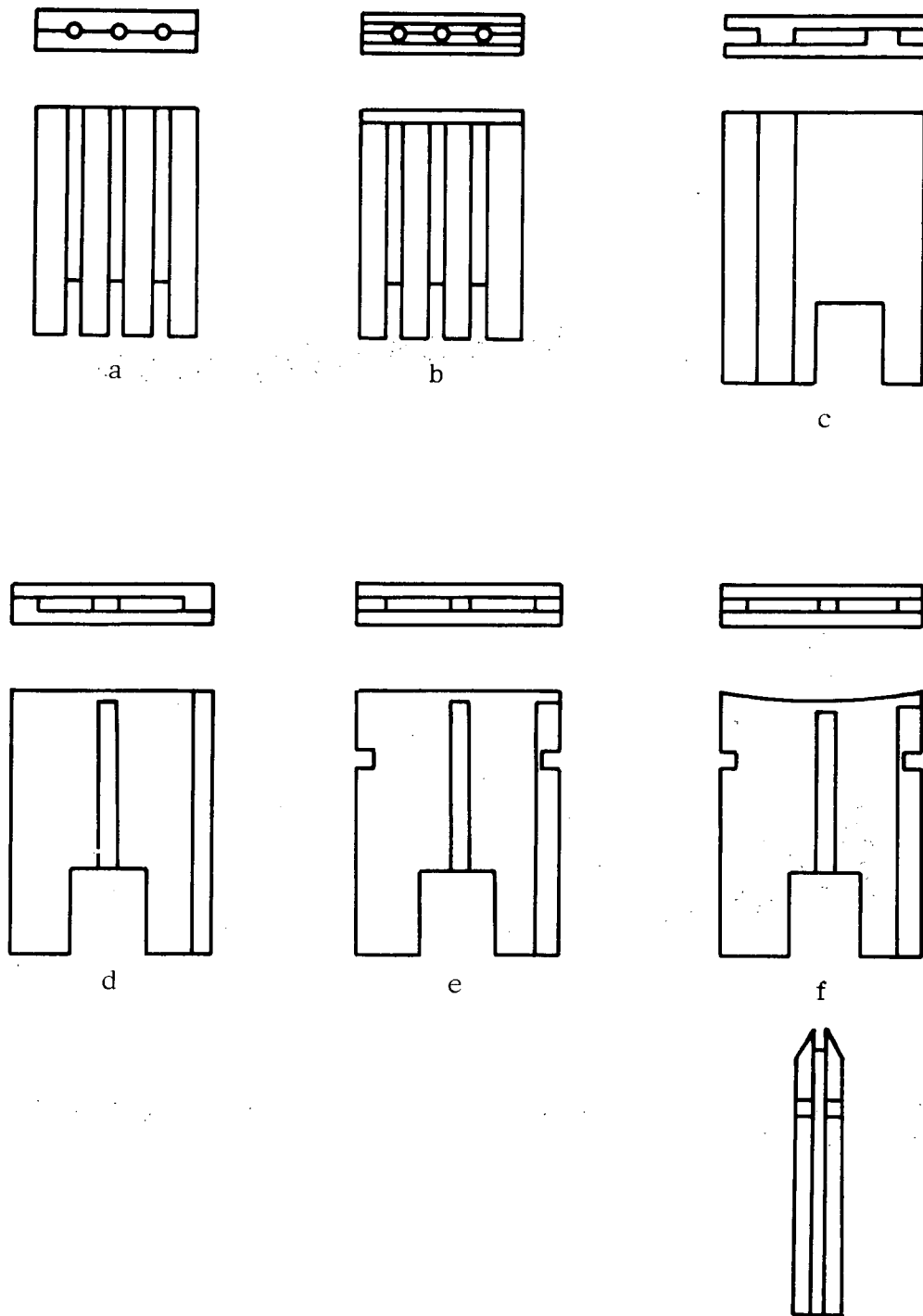


Fig. 3. Orifice configurations used in growing Si ribbons. Views are of the top surface and the inside of one side of the orifice. The side view of (f) is intended to show the knife edge bevel which was also used on some type (e) orifices. Typical overall dimensions for type c-f orifices are 0.7 in. \times 0.4 in. \times 0.065 in

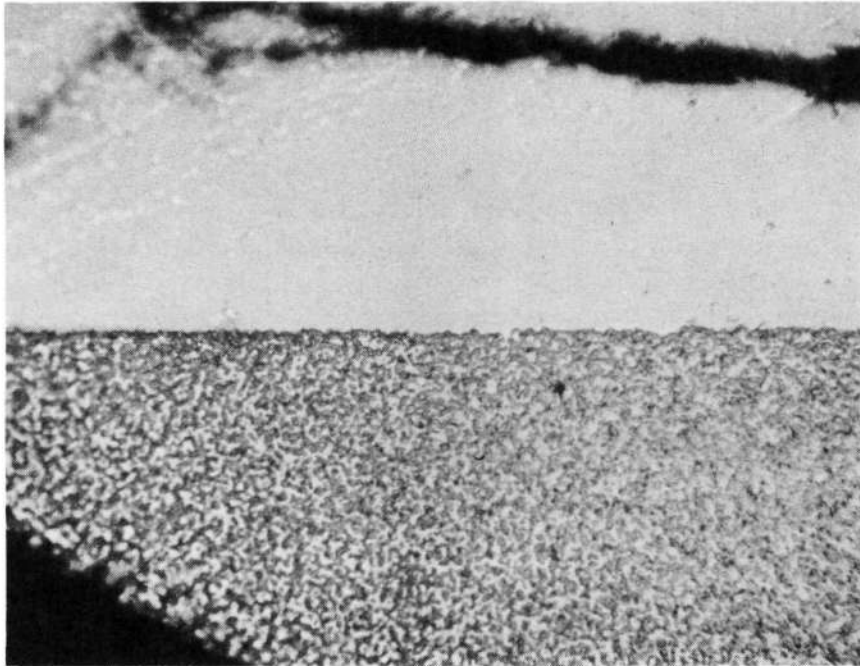


Fig. 4. Photomicrograph of interface between Si and SiC/10% SiO₂ near the top of an orifice (140X)

There are other approaches to the solution of the problem of contamination from the orifice. That mentioned above is one of minimizing the total contact between SiC and Si and reducing the impurity level of the SiC. It is also worthwhile to consider completely isolating a SiC substrate from contact with the melt by coating it with a layer of SiO₂. This approach might even be tried with tungsten or molybdenum. While it seems obvious that an all quartz orifice would be least contaminating, two problems are anticipated from such a solution. First, quartz's low conductivity and unpredictable wetting behavior with Si present a problem in filling the orifice capillaries ("feeding"). Second, at the melting point of Si, quartz, particularly high purity quartz, is somewhat less than rigid, and it is expected that such an orifice will tend to deform gradually. Nonetheless, we intend to try growth from a quartz orifice which, if only partially successful, will give us a baseline for impurity levels introduced into the ribbon in the absence of any other materials. Similarly, we intend to try SiC orifices coated with quartz, for we expect that what is really necessary is a structure with highly refractory physical properties and the inertness of quartz.

B. Ribbon Growth

1. Shapes

A variety of ribbon shapes, some more than a foot long, have been produced in thicknesses from 0.010 to 0.060 in. Initially, these ribbon shapes were relatively narrow, as illustrated in Fig. 5. The thickness of this crystal is 0.5 mm. The growth axis is (112) and the plane of the ribbon surface is (111). This width was subsequently increased considerably (to approximately 1 cm), as shown in Fig. 6. Because of the high thermal conductivity of the liquid silicon (~ 0.65 cal/cm²/sec), the ribbon width is somewhat sensitive to both thermal fluctuations as well as to thermal gradients across the die surface. To produce ribbons of constant uniform width, therefore, we will equip our rf power supply with a constant temperature control system as well as use specially-shaped dies, as illustrated in Fig. 3 (f).

2. Ribbon surface condition

In the case of ribbons produced using thin liquid meniscus growth films, the surface topology of the ribbon accurately conforms to the shape of the die edge. In the case of our pressed and sintered SiC dies, this edge has tended to roughen as growth proceeds, due to fragmentation and SiC dissolution, as illustrated in Fig. 2. This has resulted in concomitant roughness of the ribbon surface, as

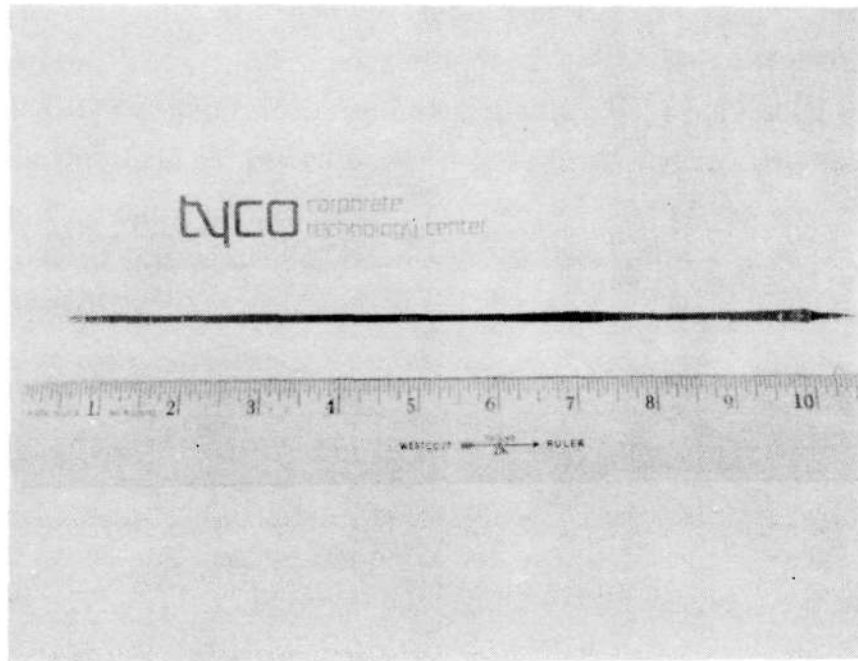


Fig. 5. Single crystal silicon ribbon grown from the melt by EFG (ribbon thickness is 0.5 mm)

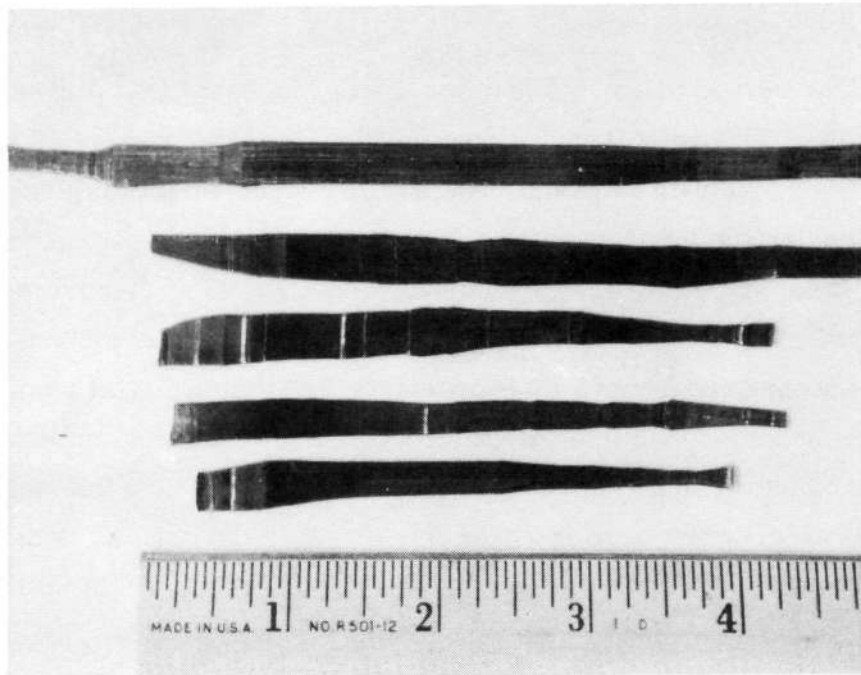


Fig. 6. EFG-grown silicon ribbons of the order of 8 to 9 mm in width

shown in Fig. 7. If, however, a thick meniscus growth film is used, imperfections in the outer die edge are not reproduced on the growing ribbon surface. In fact, it is possible to develop what appear to be atomically flat growth surfaces, as illustrated in Fig. 8. The higher melt temperature needed to produce this condition leads to a more rapid dissolution of the die material. Hence, the useful application of this phenomenon may require the development of more corrosion resistant dies, e.g., the use of SiC - SiO₂ material.

3. Resistivity

The resistivities of a number of ribbons have been measured using a four-point probe. The probe spacing was 0.063 in. and the current 50 mA. The raw resistivity measurements were corrected to account for the influence of the ribbons' thickness on the measurement. At least two, and in most cases five or six, measurements were made along each sample. The high, low, and average values are listed in Table II. When checked with a hot probe, all of the ribbons were p-type.

It would appear from these measurements that a substantial amount of impurities is being introduced into the silicon, since the starting material in most cases was approximately 100 Ω-cm p-type. There are three possible sources for this contamination. The first and most likely source is the orifice, which, as was shown in Table II, is fairly dirty. A second possible source, which would result in p-type material, is the boron nitride used to hold the orifice halves together in the various configurations. Although the liquid Si is not in direct contact with the boron nitride, it is perhaps possible that boron is diffusing through the orifice into the Si. The third potential source of impurities is the quartz crucible containing the Si melt. The crucibles are made from GE 204 quartz, which is of fairly high purity. We plan an experiment to check the contribution of crucible contamination by growing a crystal directly from the melt by the Czochralski technique.

In examining the measurements along the ribbons, no particular correlation was apparent between position (i.e., early or late in the growth) and resistivity. In comparing Sc-11 and 13 to 30, 31, 33-35, it appears that if one accepts the orifice as the major source of impurities, the piece of SiC used for the early orifices was cleaner than that used for the later ones. It is somewhat difficult to tell if the effect of adding 10% SiO₂, as in the case of SC-32, is significantly effective. Its average resistivity is higher than most of the similar ribbons, yet the range of resistivity found in SC-32 is larger than that in any other ribbon. Ribbon SC-35 shows an

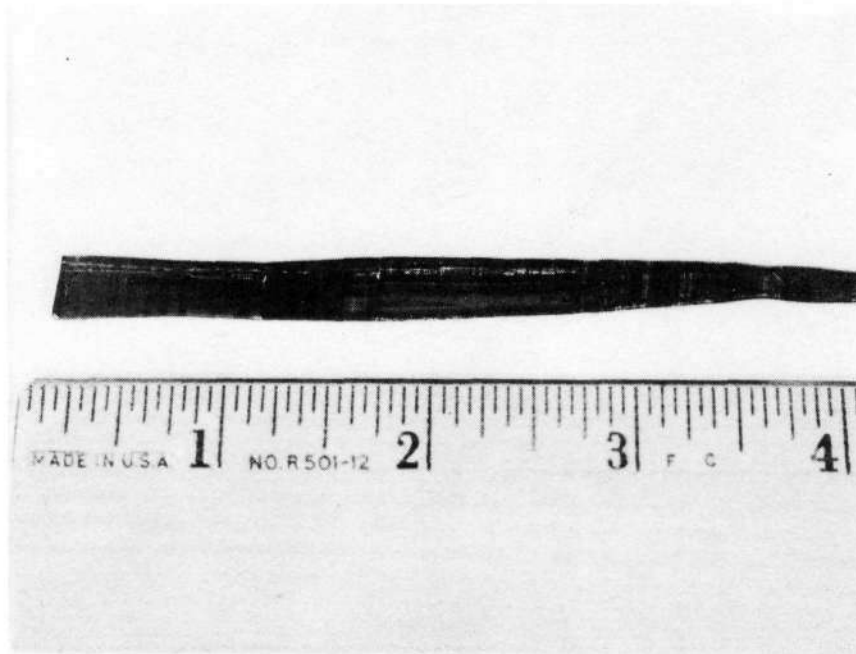


Fig. 7. Silicon ribbon showing a relatively smooth surface on one side of the long axis roughness caused by orifice disintegration on the other

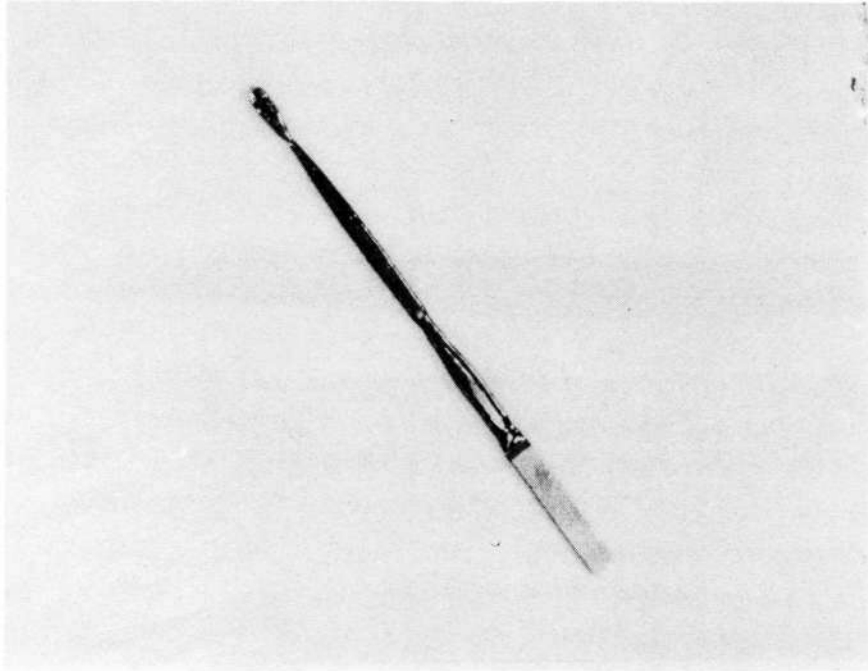


Fig. 8. EFG-grown silicon ribbon showing crystallographic flats developed on one side during growth at approximately 20 in./hr

Table II. Measured Resistivities of Several Silicon Ribbons
Grown from SiC Orifices

<u>Sample</u>	<u>Average Resistivity, Ω-cm</u>	<u>Range of Resistivity Values, Ω-cm</u>
SC-11	0.03	0.025 - 0.033
SC-13	0.09	0.05 - 0.12
SC-30	0.008	0.006 - 0.011
SC-31	0.012	0.008 - 0.016
SC-32*	0.026	0.006 - 0.04
SC-33	0.014	0.014 - 0.015
SC-34	0.015	0.011 - 0.021
SC-35	0.025	0.011 - 0.052

*Orifice was SiC + 10% SiO₂.

interesting effect in that it was grown from the same orifice as SC-34. It would appear that there may be a "leaching" effect; however, it is unlikely to be of any practical use since the same exposure to Si which removes some impurities also causes the disintegration of the SiC.

4. Dislocations

The dislocation density of the silicon ribbons shown in Fig. 6 varies substantially. As shown in Fig. 9, there are regions where the dislocation density is apparently very low with neighboring regions where the density is high. This fluctuation in dislocation density may be due to an uneven local growth rate arising from large thermal fluctuations. If so, the ribbons produced from the system which incorporates temperature control should be substantially more uniform in dislocation content.

C. Equipment

The double window quartz furnace assembly, shown schematically in Fig. 10, has been used for all crystal growth experiments. The overall system, including furnace, stereomicroscope viewer, pulling system, etc., is shown photographed in Fig. 11. An inert atmosphere, argon plus 5% hydrogen, is maintained within the

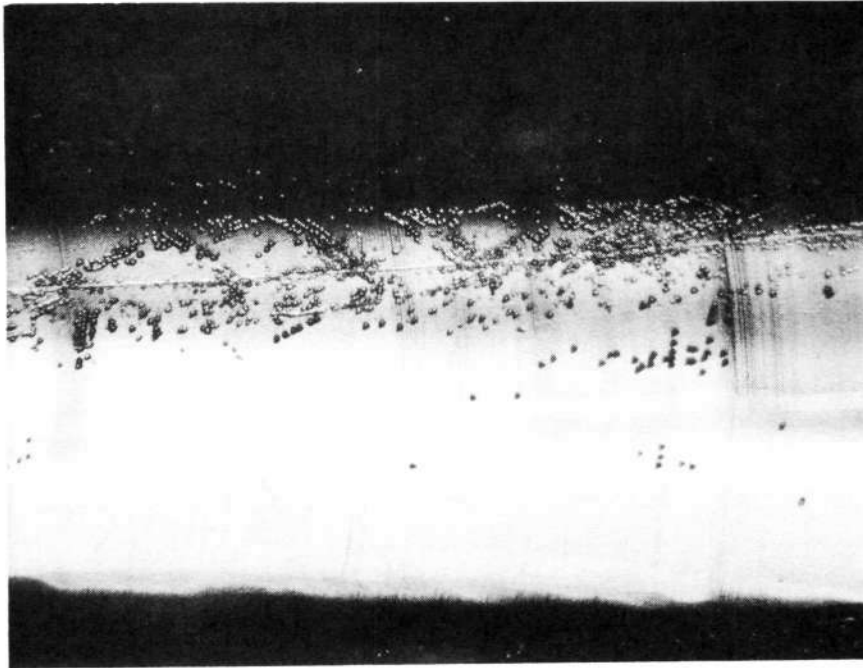


Fig. 9. Dislocation etch pits in EFG-grown silicon ribbon showing variable distribution across the width of a single ribbon (Dash etch, 35X)

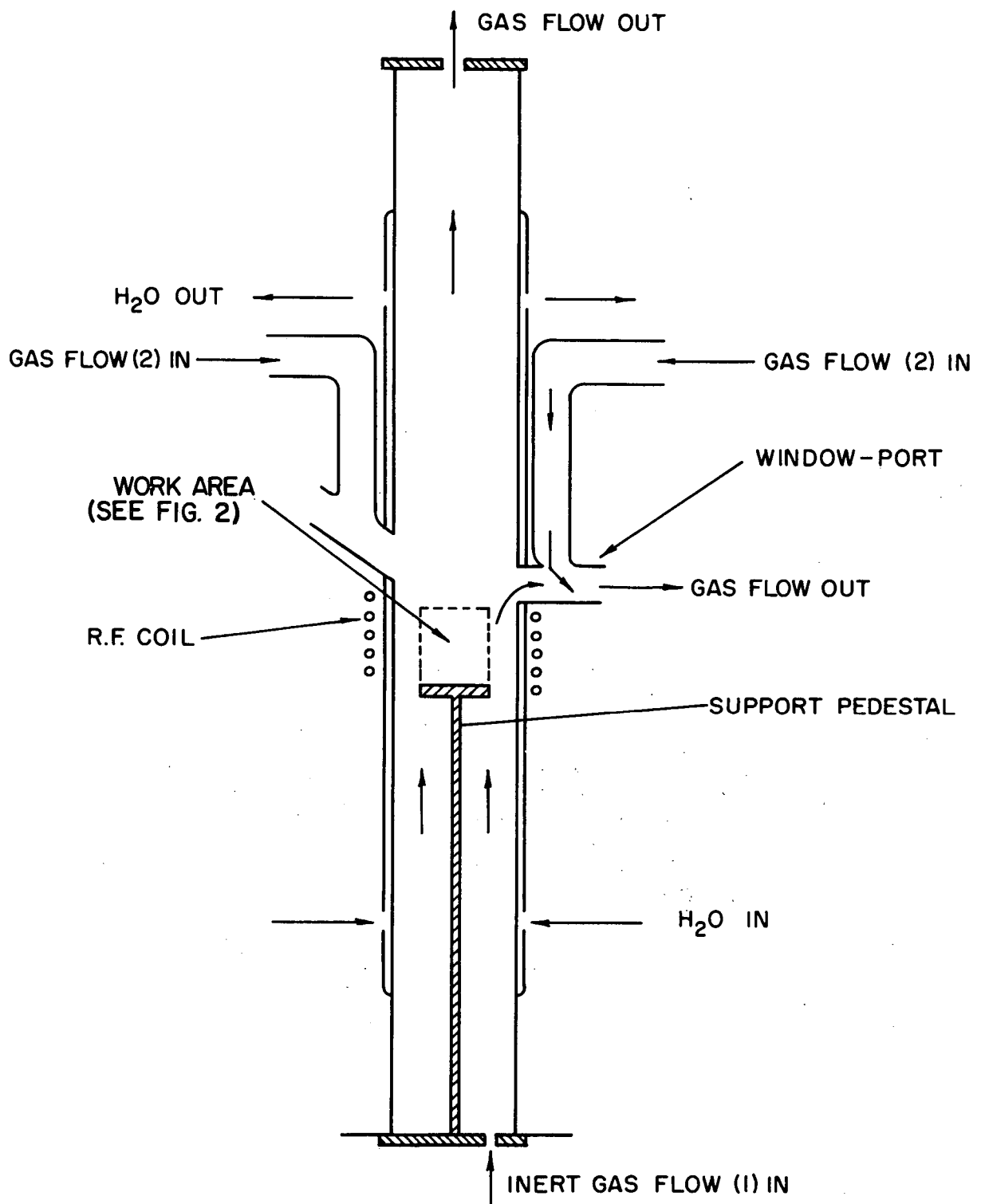


Fig. 10. Quartz furnace assembly incorporating two window ports

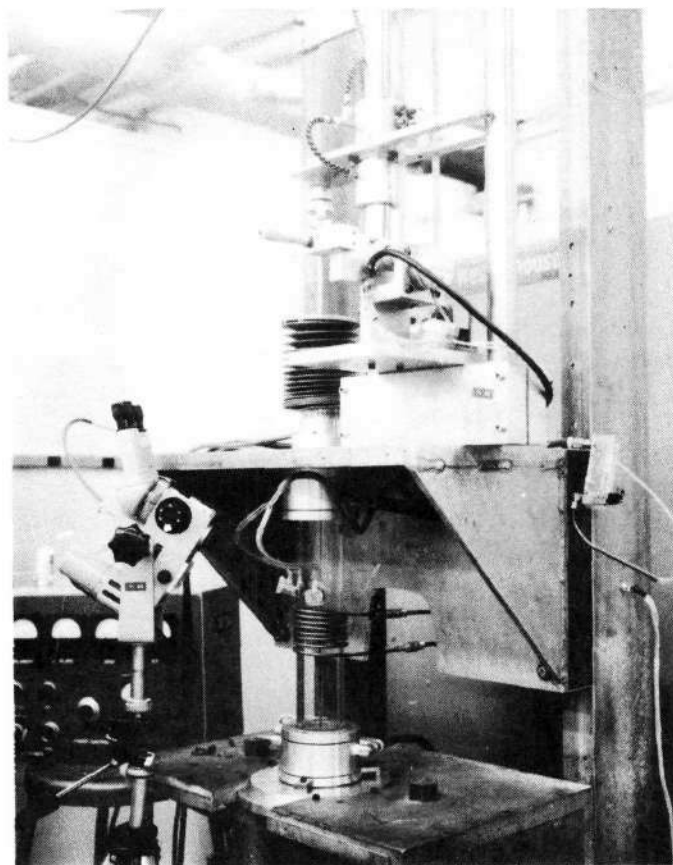


Fig. 11. Crystal growth apparatus

furnace, which consists of two concentric quartz tubes between which cooling water flows. The melt and growth area is viewed directly through either of the ports which allow essentially undistorted observation. The window ports are provided with a cover of optical quality glass. The inert gas flow (2) acts to prevent oxide deposition on the inside of the window and thus maintains clean observation conditions. The two ports are separated by 120° of arc. They allow both temperature measurements and control and optical monitoring of the growth procedures. They are at angles of 90° and 60° to the furnace axis in order to provide additional observation freedom of the area of interest.

A 450 Kc induction unit is used to raise the crucible containing the melt to the necessary growth temperature by susception to a molybdenum susceptor surrounding it. Crucibles are made from quartz. The pulling mechanism may be simply considered as two rigid, parallel vertical shafts, one of which being an air bearing connected to a plate with guide bearings on either side of the opposite shaft. Using compressed air, the system is essentially frictionless. A ball disk integrator and synchronous motor are used to move the shaft holding the seed crystal. The length of growth available is ~ 30 in., and constant growth speeds in the range of 0.001 to 120 in./hr may be selected. In order to maintain the inert furnace atmosphere and to prevent backstreaming of air into the system via the pulling rod exit, an expandable bellows arrangement was used as shown in Fig. 11. However, the bellows has been replaced by a glass tube sealed at each end by an O-ring, with the pull rod passing coaxially through a sliding O-ring compression seal. This arrangement has the virtue of allowing the system to be evacuated as well as being simpler and not subjecting the pulling system and pull rod to lateral and longitudinal loads.

We have made a number of other modifications to the apparatus during this period to improve its flexibility and performance. Formerly, the susceptor was supported on a 0.0125-in. diameter tungsten rod press-fit into a blind hole in the bottom of the susceptor. In time the susceptor tended to become misaligned with the support rod. This has been replaced by a graphite pedestal on which the susceptor sits located by a raised, circumferential lip. This pedestal is fixed to a base which seals the lower end of the chamber and, in turn, is fixed to a two-axis micrometer adjustable table. The table allows precise location of the susceptor/crucible/orifice relative to the seed which may be rotated, but not translated.

Recently, we have added to the rf heating unit a proportional controller in an attempt to improve the temperature stability at the growth interface. The controller is fed by a small induction coil on one output lead of the rf generator. Thus, the output power of the generator is controlled at a nominally constant level. Adjustments in the power level are made by varying the offset bias of the pickup coil signal, introducing an error signal which is then corrected. This system provided a marked increase in stability of the growth temperature, as indicated by the growth of substantially longer constant-section crystals than were possible when the internal regulation of the rf generator was the only control. [After the period of this report, we have incorporated a Ta-sheathed W-Re thermocouple into the system. The thermocouple fits in a hole drilled approximately 0.25 in. into the bottom of the susceptor. We have been able to monitor the temperature response of the system with manual (auto-regulation) control, proportional control of the output power, and proportional control with the thermocouple sensor. Temperature stability with manual control was approximately $\pm 3^{\circ}\text{C}$; with proportional control of the power, the temperature fluctuated approximately $\pm 0.7^{\circ}\text{C}$, while control of the temperature using the thermocouple signal also provided about $\pm 0.7^{\circ}\text{C}$. Response time to deliberately-introduced changes in temperature was 2 to 3 min (to complete the change) with manual control; use of the proportional controller cuts this time to 0.7 to 1.0 min].

A titanium gettering furnace has been added into the gas supply system. This, along with the use of a 5% hydrogen 95% argon atmosphere has eliminated any oxidation of the melt. However, there is still some oxide (SiO) formation when high temperatures are involved, apparently as a result of reaction between the molten Si and the Si-O₂ crucible.

III. CONCLUSIONS AND RECOMMENDATIONS

During this reporting period, growth of single crystal silicon ribbons has been achieved. Continuing improvements in the apparatus have led to improvements in the stability of the growth process. Experiments using hot-pressed SiC as the growth die material indicate that the impurity level in the SiC will profoundly affect the purity of the Si ribbon.

Our efforts in the next quarter will be concentrated in two areas: first, continue to develop and define procedures, process parameters, and orifice configurations to produce suitable single crystal silicon ribbons; and second, develop a non-contaminating orifice material.

In more detail, we will continue to experiment with modifications of the orifice configuration, shown in Figs. 3e and 3f, and also with one-piece orifices, which obviate the need for holding the separate pieces rigidly together. As the orifice design is refined, we must also improve the means of holding the orifice to ensure that it is level and centered. Further modifications to the shielding and afterheater configuration will probably also be necessary to achieve stable, centimeter-wide growth. If it is possible to further minimize temperature fluctuations in the setup, we will attempt to do so either by positioning the thermocouple nearer to the crucible/orifice and/or refinements in the controller.

A number of approaches to the problem of contamination by the orifice will be attempted. Orifices made from hot-pressed mixtures of very pure SiC and SiO₂ will be tried, after our one encouraging result with SiC/10% SiO₂. We will explore the effect of increased amounts of SiO₂ up to SiO₂/20% SiC mixtures. Mixtures of SiO₂ and Si and porous, sintered SiO₂ will be tried as orifice materials. Finally, we will investigate means of producing a quartz-coated SiC or SiC/SiO₂ structure by chemical vapor deposition, sputtering, or simply melting on a thin coating of quartz powder.

If any of these techniques is successful, orifices thus coated will be tested. It is expected that the inner surface of such an orifice, being essentially solid quartz, will require some treatment to facilitate wetting and capillary rise of the liquid Si. This presumably can be achieved by roughening the surface (etching or sandblasting) or by depositing a thin layer of silicon or carbon by evaporation. .

We shall also begin to make more detailed electrical measurements of some of the crystals already grown and those to be grown from the newer orifice materials. Specifically, Hall effect measurements will be used to determine the mobility concentration and type of the majority carriers. In conjunction with resistivity measurements, determination of the mobility should give us a better idea of the kind of impurity doping which is occurring with different orifices. Lifetime measurements will also be attempted. The expected result of these measurements is a clearer indication of the effectiveness of the various measures we propose to counter the introduction of impurities by the orifice in terms of the properties involved in the performance of the ribbons as solar cells.

IV. NEW TECHNOLOGY

Descriptive Title: Improved SiC Dies for the Edge-Defined, Film-Fed
Growth of Thick Film Silicon Ribbon

Names of Innovators: F. H. Cocks
H. E. Bates

Progress Reports: First Quarterly Report

Pages: 8-11

Date: July, 1972

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