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LARGE AREA SILICON SHEET BY EFG

Second Quarterly Report, April 1—June 30, 1978

July 15, 1978

Work Performed Under Contract NAS-7-100-954355

Mobil Tyco Solar Energy Corporation
Waltham, Massachusetts

U.S. Department of Energy

MASTER

Solar Energy

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Program Manager: F.V. Wald

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ABSTRACT

The main emphasis in Station No. 1 during this quarter was on the production and evaluation of a series of baseline "clean runs". These were designed to demonstrate that this furnace, when operating without any stainless steel parts in the interior, could produce material of a chemical quality sufficient to prepare solar cells of ~10% efficiency.

However, interpretation of the solar cell results was complicated by the observation in this program and in related internal work at MTSEC, that all EFG ribbon when grown using carbon crucibles has a reduced solar cell performance. It was then hypothesized that oxygen could act as an internal gettering mechanism for transition metal impurities, thus reducing their deleterious effects on the minority carrier lifetime in EFG silicon. Hence, experiments were undertaken to add oxygen to the melts contained in carbon crucibles. These experiments revealed that even small traces of oxygen, when introduced in the gas phase above the melt and near the meniscus, can significantly destabilize growth and may also generate excess silicon-carbide at the meniscus and thus cause an excessive number of "freezes". If this observation can be definitely confirmed, it is obviously very important since so far it is believed that all SiC occurring on the ribbons is an inevitable consequence of growing the silicon from carbon dies. These developments have, therefore, somewhat retarded work on the hypothesis concerning the effect of oxygen on the lifetime in EFG silicon contaminated with transition metals. We plan, however, to continue our investigations on all these complex effects during the next quarter.

Machine No. 3A also participated in these experiments and in an important way served to solidify some of the preliminary conclusions, although the situation in this machine with its larger volume and greater number of parts is even more difficult to analyze completely.

In Section IV we discuss in detail the construction of the new Machine 17 which is now basically functioning as designed.

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I. INTRODUCTION

Phase I of this program, perhaps best termed the "demonstration phase", is now complete. It included a detailed economic evaluation of several EFG ribbon growth technology scenarios using the "SAMICS" interim price estimation guidelines. The main conclusions were that the growth of ten ribbons from a double five ribbon furnace of the general type represented by the existing Machine 3A, which is now being operated under this contract, would meet the requirements of producing ribbon at a price below \$20/m², the 1986 JPL goal. The technology requirements are that one operator can operate two of the five ribbon growth stations in which each ribbon grows at a speed of 7.5 cm/min and is also 7.5 cm wide. The machines also would have to achieve a duty cycle of 67% at minimum and yields above 75%. Finally, silicon must be available at \$10 to ~\$25/kg, depending on the yield assumed, or achievement of the stated goal becomes quite difficult. These conclusions are the final results of the economic analysis task under the contract.

At the end of Phase I, the status of technical work, which addresses itself to the various elements that are clearly needed to meet the economic goals, may be summarized as follows:

1. Machine 18 (JPL No. 1)

Goal: Development of a cartridge to allow growth of 7.5 cm wide ribbon at 7.5 cm/min.

Towards the end of 1977, after several design changes had been made in the original cartridge, considerable improvements in the growth conditions were realized.

Nearly 25 m of ribbon were grown in eight of the runs. The width was up to 7.0 cm and speeds up to 6.3 cm/min were realized. The 7.5 cm belt puller has been routinely used in these experiments; in one run, continuous growth of ribbon over a 1 3/4 hour period were achieved.

These experiments permitted important observations with respect to thermal stress in fast and wide ribbon growth. These problems include: (i) high residual stresses in the ribbon which show up in problems of cutting in into solar cell blanks, or (ii) generation of buckles in the ribbon during growth, which makes the ribbon useless for cell fabrication because it is not flat.

It was found that residual stress in the ribbon could be avoided by running the afterheater $> 1100^{\circ}\text{C}$. However, there are still unsolved problems since it is difficult to keep the afterheater temperature this high if one has to use helium to cool the interface region. The helium then has a tendency to carry too much heat away from the afterheater. This will have to be solved by redesign of the cold shoe-heat shield-afterheater combination.

The most pressing problem at this time is the persistent presence of buckles in almost all ribbon. The reasons for this are not clear and the buckles have occasionally disappeared for no obvious reasons during a run. Under low speed growth conditions (< 4 cm/min), the ribbon was essentially always flat for widths up to nearly 7.5 cm. At faster growth rates, buckles were generated in all ribbon ≥ 2.5 cm in width.

2. Machine 16 (JPL No. 3A) - Multiple Furnace

Goal: Simultaneous growth of five 5 cm wide ribbons at 7.5 cm/min.

The requirement that a growth speed of 7.5 cm/min should be achieved was waived during the last quarter of 1977, since it was considered impossible to build a new set of five cartridges for 7.5 cm/min growth, and because of the various problems at high growth speeds discovered in Machine 18. Hence, the major goal for this machine was a demonstration that simultaneous growth of five 5 cm wide ribbons could be achieved using a melt replenishment system to feed silicon into the furnace.

After a complete overhaul of the furnace, which uncovered the necessity for a number of design changes to make the system more reliable, two growth attempts were made with the aim to keep all ribbons growing for 10 - 20 hours with the help of only a single operator on the machine.

All these experiments were also preceded by an evaluation of "bulbous end" dies which were introduced to confer the necessary "edge stability" onto the ribbon to allow long growth runs. The automatic edge control system which had been developed had not undergone sufficient testing at this time to guarantee the exceedingly high reliability of all parts which is required when five ribbons are to be grown.

It has now been demonstrated that in the resistance heated machines, which employ edge heaters for the trimming of the temperature over the width of the die, bulbous end dies are quite effective in stabilizing the edges.

In the first full scale five ribbon experiment, it was discovered however that no more than three ribbons could be grown due to a gross temperature inhomogeneity along the length of the furnace proper. For 24 hours the three ribbons grew with the melt being continuously replenished; this was the first solid demonstration of multiple growth for any length of time. After this, the insulation at one end of the furnace was improved and the heater elements were trimmed to selectively apply more heat in certain critical places.

Then on January 26 through January 27, 1978, a 12 hour continuous five ribbon run was successfully conducted with the following outcome:

Cartridge No. 1 grew ~9 m of 2.5 - 4 cm wide ribbon;
Cartridge No. 2 grew ~12 m of largely 5 cm wide ribbon;
Cartridge No. 3 grew ~2 m of 2.5 - 4 cm wide ribbon;
Cartridge No. 4 grew ~13 m of largely 5 cm wide ribbon;
Cartridge No. 5 grew ~9 m of largely 5 cm wide ribbon.

(The average growth speed for all cartridges was ~3 cm/min.) Several problems have been discovered aside from the significant achievement that most of the many parts required worked quite reliably together for the 12 hour run. Cartridge No. 1 which is located next to the melt replenisher could never be brought up to full width; the thermal interaction between it and the melt replenisher made that impossible. In Cartridge No. 3, a short circuit developed in the electrical system shortly after the run started, and we decided not to attempt to withdraw and repair it during this critical run.

Otherwise, the most general problem discovered was that we know too little about the phenomena which influence spreading of ribbons to full width. The spreading phase takes too long at present and requires the full attention of the operator. It is, however, a transient phase; as soon as the ribbon is spread to the "bulbous ends" of the die, it is anchored there. The phenomenon which then interferes with growth is the "freeze", a condition in which the liquid film collapses and the ribbon attaches to the die. If a "freeze" occurs, the ribbon must be "unfrozen" by increasing the die temperature and reseeded the ribbon and spreading it again. It is obvious then that frequent "freezes" in multiple growth are quite intolerable.

3. Characterization and Basic Materials Studies

Three significant pieces of information were derived here:

a. Chemical analysis efforts on many ribbons have now fairly conclusively shown that the main culprit which influences the quality of ribbons grown from resistance heated machines is the stainless steel used in the construction of various hot parts. A program to redesign these parts using other materials will now be undertaken.

b. It has been demonstrated experimentally and theoretically that fluid flow effects in the ribbon strongly affect the impurity distribution. By using a center capillary only, to transport liquid silicon to the top of the die, the impurity distribution in a "dirty" 5 cm wide ribbon was manipulated such that the center 2.5 cm width could be used to prepare solar cells of up to 10.6% efficiency. These effects will now be vigorously explored to see whether their use is indeed practicable, i.e., can we concentrate all impurities into the very edge of the ribbon so that removal of the dirty part does not consume too much silicon.

c. Ribbons grown at higher speeds (≥ 4 cm/min) have shown a deterioration of the grain structure through the ribbon thickness. It was feared that this might negatively impact solar cell efficiency. It has now been rather conclusively demonstrated that this is not the case. Hence, all the basic elements which are necessary to achieve multiple five ribbon growth and fast growth have now been demonstrated to function.

In the next phase, then, these crystal growth stations must be evolved toward prototype status, i.e., they must be further developed to achieve higher reliability in their functioning so that the machine duty cycles projected in the economic analysis can be attained, and also their contaminating influence on the silicon melt must be controlled so that the cell yields and efficiencies used in the economic projections become a reality.

II. WORK ON CRYSTAL GROWTH STATION NO. 1 by J.P. Kalejs

A. Overview

An initial series of twenty-four clean runs has been completed with the 7.5 cm cartridge. Its purpose has been to establish baseline quality levels for this cartridge with two different designs of cold shoe and to test a number of end heater and die designs. These runs have produced nearly 70 m of ribbon, 34 m of it full width. The ease of growth and success in achieving satisfactory growth conditions in nearly every run have demonstrated that routine full-width growth in the speed range from 3 to 5 cm/min is now possible in the 7.5 cm cartridge.

An end heater design, which provides heating over a span of about 1.2 cm along the die sides, has shown to be the most effective in allowing full-width growth (≥ 7 cm wide, with the ribbon edge within 0.3 cm of the end of the die) for most of the die designs tested. The degree of edge stability has been observed to be a function of the details of the die design/end heater combination.

A number of die designs with different die top capillary feed arrangements have been used to investigate the effects of fluid flow-induced impurity redistribution on material quality. Initial results indicate material quality and solar cell performance are improved through the use of a central capillary feed arrangement as compared to that found for ribbon grown with a multicapillary die, in which the capillaries are evenly spaced across the width of the ribbon.

The mini cold shoe has been incorporated into the series of clean runs to determine if there are measurable effects on solar cell performance on account of the introduction of different materials in its construction or the changed gas flow pattern near the growth interface. Results from the initial runs have shown no detrimental effects on cell quality which could be attributed to these factors.

Attempts have been made to introduce oxygen into the ribbon both through changing the furnace and cartridge atmosphere and via the presence of quartz in contact with the melt. More than 0.02 of one percent of oxygen in gas introduced through the cold shoe was found to have an immediate destabilizing influence on growth conditions and made routine growth impossible. In the future, the electrical properties of material grown from melts containing high purity quartz as well as grown from a quartz crucible will be examined and compared to the baseline established in earlier runs using a graphite crucible.

B. Crystal Growth

1. Experimental

Successful full-width growth conditions have continued to be realized in the 7.5 cm cartridge, while work has proceeded on the evaluation of cold shoe and end heater performance and on the study of the effects of changes in die design on growth conditions and material quality. A summary of the experiments done in this reporting period is given in Table I. Earlier experiments demonstrated that 1.2 cm coverage end heaters were the most effective in establishing conditions conducive to full-width growth,⁽¹⁾ and they have been used in all the runs reported here.

The important findings of the experiments testing end heater and die top design influence on full-width seeding and growth and ribbon edge stability are summarized in Table II. The effort has been directed at examining conditions required for full-width growth in the 7.5 cm cartridge. In the context of its present design, full-width growth has been defined as growth with the ribbon edges located within 0.3 cm of each end of the die (whose overall width dimension is 7.62 cm). In order to achieve it, extra heating over the outside 2 cm extent of the die top was necessary to overcome deficiencies of the face heater in the heating of the die ends. This has been provided through utilization of the 1.2 cm coverage end heaters described in a previous report.⁽¹⁾

In satisfying the immediate need to achieve reliable full-width growth, these initial studies have only started to explore fundamental problems associated with edge stability in full-width growth. Possible directions to take in a continuation of this study, which are suggested by the experiments done to date, are discussed below. It is important to emphasize at this point that full-width growth conditions have been essentially realized in all runs to date utilizing 1.2 cm coverage end

Table I. JPL No. 1 Run and Ribbon Data. All-Molybdenum Cold Shoe with 0.32 cm Opening, Located 0.07 cm above the Die Top and 1.2 cm Coverage End Heaters used in all Runs, Except as Noted.

Run No.	Growth Speed (cm/min)	Ribbon Width (cm)	Total Length (m)	(Full-Width) (m)	Comments
18-68	3.6 - 5.7	6.4 - 7.5	3.6	(3.4)	Fourth run of clean sequence. First test of end-slotted multicapillary die.
18-69	3.2 - 4.0	3 - 7.5	3.7	(1.2)	Fifth run of clean sequence. First test of double radius die with end slots.
18-70a	-	-	-	-	No growth. Main zone power failure.
18-70b	3.6 - 4.0	3 - 7.5	3.0	(1.2)	Sixth run of clean sequence. First test of central 5-capillary die with end slots.
18-71	3.9 - 5.0	5.3 - 7.5	3.2	(2.5)	Seventh run of clean sequence, repeat of 18-70.
18-72	2.3 - 4.5	2 - 7.5	3.0	(1.9)	Eighth run of clean sequence. Repeat of 18-67 with nonuniform cross section end heaters. Slow growth (< 2.5 cm/min) performance of cartridge tested.
18-73	2.5 - 4.6	2 - 6.3	3.5	(0)	Ninth run of clean sequence. Repeat of 18-71 at varying speeds and narrow widths.
18-74	-	-	-	-	No growth possible, silicon flood to main zone heater.
18-75	3.8 - 5.7	5.0 - 7.4	4.3	(2.7)	First run for mini cold shoe in clean series; eleventh run in series.
18-76	2.8 - 4.3	3.3 - 7.5	4.6	(3.0)	Twelfth run of clean series, second with mini cold shoe.
18-77	3.8 - 5.7	6.5 - 7.4	3.2	(3.0)	Thirteenth run of clean series; third with mini cold shoe.
18-78	3.8	7.1 - 7.4	0.9	(0.9)	Fourteenth run of clean series; return to all-molybdenum cold shoe. First test of single capillary die.
18-79	3 - 3.8	3 - 7.5	4.3	(1.5)	Fifteenth run of clean series; first test of wide-slotted central 5-capillary die.
18-80a	-	-	-	-	No growth attempted; error in cartridge assembly resulted in end heater short.
18-80b	3 - 4.6	2 - 7.2	1.6	(0.6)	Sixteenth run of clean series. First test of crucible cover. Limited growth with Ar-O ₂ mixture introduced to interface region via cold shoe.
18-81	3.7 - 4.6	2.5 - 7.4	2.1	(1.3)	Seventeenth run of clean series; high purity quartz introduced into melt. Heavy SiC particle density.
18-82	3.7 - 3.9	7.0 - 7.4	2.6	(2.6)	Eighteenth run of clean series; high purity quartz introduced into melt. Heavy SiC particle density.
18-83a	-	-	-	-	No growth attempted due to die misalignment.
18-83b	3.8 - 4.0	4.8 - 7.5	2.5	(2.1)	First test of 0.15 cm spacing, all-molybdenum cold shoe; nineteenth run of clean series.
18-84	3.6 - 4.7	4.3 - 7.3	3.5	(0.3)	Twentieth run of clean series; first test of central slot die. Mini cold shoe.
18-85	3.3 - 5.0	1.5 - 7.2	3.8	(0.5)	Twenty-first run of clean series; high purity crushed quartz introduced into melt. Poor growth conditions; ribbon surface degraded Mini cold shoe.
18-86	3.4 - 4.7	3.0 - 7.4	3.6	(2.3)	Twenty-second run of clean series. Poor growth conditions part of time.
18-87	3.4 - 4.7	5 - 7.5	6.4	(1.1)	Twenty-third run of clean series.
18-88	2.2 - 3.8	2.5 - 7.3	5.7	(1.8)	Twenty-fourth and last run of clean series; quartz crucible, crucible emptied. Good growth conditions with increasingly heavy SiO deposits on cold shoe as run proceeded.

Table II. Summary of Die Top Growth Conditions for Various Die and End Heater Designs. All End Heaters have 1.2 cm Coverage. The Mini Cold Shoe was used in Runs 18-75 to 18-77, 18-84 and 18-85, All Molybdenum Cold Shoes in all the Others.

Run No.	End Heater	Die Type*	Capability for Full-Width		Edge Stability	Comments
			Seeding	Spreading		
18-66	Uniform cross section	MC - no end slots	No	Yes	Poor	Full-width seeding fails because meniscus (ribbon thickness) variation across width is too extreme. Spreading excellent. Growth at extreme die ends difficult - die ends too cold.
18-67	Uniform cross section	MC - no end slots	Yes	No	Poor	Spreading not possible. Growth at extreme die ends difficult - die ends too cold.
18-68	Uniform cross section	MC - end slots	Yes	-	Excellent	End slots add to ribbon edge stability. Thickness variation over central portion of ribbon decreased.
18-69	Uniform cross section	MC - 2.5 m radius with end slots	Yes	Yes	Poor	Ribbon edge control difficult. Wider range of stable growth conditions. Ribbon thickness variations reduced from those of run 18-68.
18-70	Nonuniform cross section (thick sides)†	CC - end slots	Yes	Yes	Good	Effect of hot regions near die ends reduced. Ribbon thinner above capillary exits.
18-71	Nonuniform cross section (thick sides)†	CC - end slots	Yes	Yes	Excellent	More stable growth than in run 18-70.
18-72	Nonuniform cross section (thick sides)†	MC - no end slots	No	Yes	Poor	Growth and seeding wider than 7 cm difficult due to cold die ends.
18-75	Uniform cross section	MC - end slots	Yes	Yes	Excellent	Mini cold shoe; growth conditions comparable to run 18-68 with all-molybdenum cold shoe.
18-76	Nonuniform cross section (thick sides)†	CC - end slots	Yes	Yes	Excellent	Mini cold shoe; excellent full-width seeding and spreading conditions.
18-77	Nonuniform cross section (thick sides)†	MC - end slots	Yes	-	Poor	Ribbon edge control difficult; growth near die end slots unstable.
18-78	Uniform cross section	SC - end slots	Yes	-	Good	Initial growth conditions excellent; later deterioration attributed to capillary blockage.
18-79	Nonuniform cross section (thick sides)†	Modified CC - end slots	Yes	Yes	Good	Some difficulties in full-width seeding; degree of edge stability reduced from that in run 18-71. 0.05 cm wide die top slot with 0.075 cm diameter capillaries.
18-80b	Nonuniform cross section (thick sides)†	Modified CC - end slots	Yes	No	Poor	Growth conditions poor from start; appeared to be melt feeding problems. 0.025 cm wide die top slot with 0.075 cm diameter capillaries.
18-81	Uniform cross section	MC - end slots	Yes	-	Good	Growth conditions good for first ribbon, then deteriorated quickly thereafter.
18-83	Uniform cross section	MC - end slots	Yes	-	Good	0.16 cm spacing all-molybdenum cold shoe. Good growth conditions.
18-84	Uniform cross section	CS	No	No	Poor	Mini cold shoe. Growth at full-width not possible due to cold die ends. Good edge stability at 6.9 to 7.0 cm width.
18-86	Uniform cross section	CS	Yes	Yes	Poor	Repeat of 18-83 with 0.32 cm spacing all-molybdenum cold shoe. Poor growth conditions.
18-87	Uniform cross section	CS	Yes	Yes	Good	Good growth conditions and reasonable end stability.
18-88	Uniform cross section	CS	Yes	Yes	Good	Growth at extreme die ends unstable; ends too cold.

*MC - multicapillary die; CC - central 5-capillary die with 0.025 cm wide die top slot and 0.16 cm diameter capillaries; SC - single capillary die; CS - central saw cut die.

†Heater dimensions (see Fig. 1 of Ref. 1) of $b = 0.2$ cm, $c = 0.3$ cm.

heaters. Moreover, differences in seeding and growth capabilities and edge stability among the different die and end heater configurations tested, as reported in Table II, contrast the relative ease of achieving stable growth with the ribbon edges located within 0.3 cm of the die ends. These differences are examined in more detail below.

The three main areas of investigation in the series of clean runs will now be discussed.

a. Cold Shoe Performance

Three different cold shoes, each in its own cartridge, have been tested. An all-molybdenum cold shoe, with a 0.32 cm heat removal element spacing, was employed in the majority of runs. The mini cold shoe was utilized in runs 18-75 to 18-77 and again in runs 18-84 and 18-85. A second all-molybdenum cold shoe, with a 0.15 cm heat removal element spacing, was introduced for one run only, run 18-83.

Growth conditions achieved with the three different cold shoes were, in most respects, indistinguishable from one another. In addition, changing the cold shoe-die top separation (in the range from about 0.070 cm to 0.15 cm) or the heat removal element spacing did not have measurable effect on ease of growth. An important aspect of the runs with the mini cold shoe was to aid in establishing a baseline level for material quality for it relative to the all-molybdenum ones. Material grown using these cold shoes will be compared in several areas to determine if differences exist between the designs which may be reflected in as-grown material or solar cell quality.

b. Ribbon Edge Stability

The thermal mechanism for ribbon edge stability described in an earlier report⁽¹⁾ was found to be operative, to a greater or lesser degree, for all of the die and end heater design variations tested, as summarized in Table II. The configuration which most consistently produced the greatest degree of edge stability was the uniform cross section end heaters in combination with a flat-topped die with end slots (e.g., as in runs 18-68 and 18-76). In particular, the presence of liquid silicon melt in the end slots appears to interrupt the steep temperature decline as the die edges are approached in such a way as to

create a thermal "well" in which the ribbon edge is more stable.* In the absence of these end slots, as in runs 18-66, 18-67 and 18-72, the degree of stability of the ribbon edge at comparable widths was markedly reduced. In run 18-72, additional loss of stability may have resulted from a decrease in the level of heating of the central portion of the die by the use of nonuniform cross section and heaters. These were designed to increase the level of heating at the die ends relative to that along the die sides and so reduce the overall level of heating in the region of the end and face heater overlap. However, they consequently had to be operated at a higher power level and this appeared to decrease the effectiveness of the thermal edge stability mechanism.

The variation of ribbon thickness across the width for full-width growth which typifies steady-state growth under conditions for which the thermal edge stability mechanism was observed to be optimized is shown in Fig. 1. The main features of the ribbon thickness profile, such as the rapid increase in thickness at the extreme ribbon edges and the minima at locations about 1 cm from each ribbon edge, were reproduced in most other runs. While the variations between maximum and minimum ribbon thicknesses were the most extreme for the case of the uniform cross section end heaters, the ribbon edge was also the most stable. In the case of the nonuniform cross section end heaters, which were designed to reduce this thickness variation, the degree of edge stability appeared to be reduced for growth with the ribbon edge at or very near to the end slot (i.e., at a width ~7.5 cm). Nevertheless, growth at narrower widths with a degree of edge stability equal to that observed in the best of cases with the uniform cross section end heaters was often possible.

Die design was also observed to affect the degree of edge stability realized for a given end heater configuration. This is to be expected in that changes in die design which alter the distribution and flow pattern of liquid silicon in the die will also have some effect on the die top thermal field. In particular, the degree of edge stability for growth with the ribbon edge close to the die end slot was noticeable reduced for a radius die (run 18-69), and for the central saw cut dies (runs 18-84 to 18-88).

*The end slot does not appear to markedly affect the spreading rate of the ribbon as it encounters the slot edges. The ribbon edge also does not show preference for growth in any given location in the neighborhood of the slot. The influence of the end slot on edge stability is thus mainly thermal for this die design.

The price of gaining edge stability in full-width ribbon growth with the die and end heater configurations presently in use has been a marked increase in the variation of the ribbon thickness across the width, particularly near the edges, as evidenced in Fig. 1. In order to investigate the possibility of growing a more uniform thickness ribbon while taking advantage of the experience gained with the 7.5 cm cartridge growth configurations in use, a radius was cut in a regular flat-topped multicapillary die which was then tried out in run 18-69. The radius of 2.5 m used depressed the center of the die top by about 0.03 cm relative to the ends in addition to widening the die top flats to a maximum of about 0.025 cm. The resulting thickness profile across the ribbon width for this double radius die is shown in Fig. 2 for a ribbon grown using otherwise identical cartridge components to those used in run 18-68. The extreme variation of the thickness present in the ribbon grown in 18-68 and other runs has clearly been reduced. However, as noted above, ribbon edge stability was found to be poorer. In addition, full-width seeding was not successful, mainly because a larger range of growth conditions due to an increased range of available meniscus heights made finding full-width seeding conditions more difficult. Clearly, additional experimental work is desirable and warranted in order to explore the full range of potential for this type of die in the 7.5 cm growth system.

c. Fluid Flow Dies

The emphasis in tests of die design variations has been on searching for melt flow configurations which could use to advantage theoretically predicted impurity redistribution to improve material quality. In earlier experiments on Station JPL No. 3A,⁽²⁾ it was found that material grown from above the capillary exit in a single capillary die improved considerably in quality from that grown from the same melt with a multicapillary die. This was in accordance with redistribution theory, which predicts that certain impurities may be swept away from the region of the capillary exit toward the ribbon edges in the former fluid flow configuration.⁽³⁾

The single capillary die has been observed to have two disadvantages from the standpoint of promoting reliable growth. First, in higher speed growth (≥ 4 cm/min), the region of ribbon grown from directly above the capillary becomes thinned as a result of heating by melt exiting from the capillary. In addition, silicon carbide growth in the capillary exit

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Fig. 2. Thickness profile for ribbon grown with 2.5 m double radius die in run 18-69. Profile is for ribbon growing at full width under steady-state conditions.

region was often found to partially or entirely block melt flow and so contribute to growth difficulties. In run 18-78, for example, this appeared to be responsible for growth termination after only about 1 m of growth despite excellent initial conditions. A number of central capillary melt feed configurations for which these conditions may be alleviated have been chosen for testing (see also Table II) and evaluations are being continued in conjunction with material quality studies.

In summary, die top thermal conditions under which the ribbon edge is very stable and which permit full-width growth in the 7.5 cm cartridge have been identified and achieved. The basic requirement is a steep temperature decrease at the die end. Since this naturally promotes spreading of the ribbon edge, the end heater can then be used to counteract this tendency so as to thermally "lock" the edge into an equilibrium position. The degree of edge stability seems to be enhanced greatly by local perturbations on the steep die-end temperature gradient. These have been achieved in one case in the form of "hot" spots arising from overlap of the end and face heater spheres of influence, and in another by the presence of a die top end slot containing silicon melt.

Preliminary experiments indicate that the thermally controlled ribbon edge stability achieved in the flat-topped multicapillary die with end slots is affected by such die design changes as introducing a radius in the die top or by modifying the capillary feed geometry. Further work in examining full-width growth conditions with these and other die modifications will continue next quarter.

2. Material Quality Considerations

The experiments carried out in this reporting period have continued to be run under clean conditions. The silicon flood of run 18-74 required replacement of the crucible holder and main zone heater, which were not reusable. The mini cold shoe runs 18-75 to 18-77 utilized a separate cartridge to better monitor quality levels of ribbon grown with this system and to permit a recheck of material quality produced in later runs with the all-molybdenum cold shoe cartridge system. The melt for all the reported runs was boron-doped to 1 Ω -cm.

All the runs in the clean series, starting with run 18-65, have utilized graphite crucibles. One of the chief advantages of graphite over the usual material, quartz, is that it does not lead to generation

of SiO which quickly degrades system performance by depositing on many components. However, recent results from JPL No. 3A have shown that use of a quartz crucible results in material having a higher level of solar cell performance than that grown with a graphite crucible.⁽⁴⁾ This improvement could possibly arise from the presence of oxygen in the melt.

The first attempt to introduce oxygen into the environment of the growing ribbon was made in run 18-80b. Pure oxygen in an argon-1% oxygen gas mixture was further diluted with argon and then mixed with the helium usually used in the cold shoe in order to enhance heat transfer from the growing ribbon surface. In the all-molybdenum cold shoe used in this run, the gas exited about 0.12 cm above the growth interface and for reasonable flow rates easily reached the die top. The highest oxygen concentration at which growth could be sustained was at about 0.02 of one percent oxygen in the gas flowing through the cold shoe. At this level it exerted an almost intolerable destabilizing effect on the growth interface, leading to sudden ribbon tapering and uncontrollable meniscus height fluctuations generally terminating in a freeze. This behavior was attributed to rapid SiO formation in the neighborhood of the interface which could both affect the liquid silicon surface tension and also change heat transfer rates between the ribbon and meniscus and their environment. Only about 20 cm of 2.5 to 3 cm wide ribbon were grown under these conditions.

High purity quartz was introduced into the melt in runs 18-81, 18-82 and 18-85 with successively increasing surface area in contact with the silicon melt. Growth conditions in the first two of these runs were not noticeably changed. A graphite crucible cover, first tested in run 18-80b, helped to protect the cartridge from SiO generated in the melt. The level of SiO was quite low (as judged by the amount deposited on the crucible cover and cold shoe surface). However, the level of SiC particles on the ribbon surface was markedly higher in both these runs than in earlier runs.

In run 18-85, the quartz placed in the melt was crushed to a considerably finer powder than in the previous two runs. The levels of SiO deposits increased, and growth conditions were generally poor. Much of the ribbon grown had a pitted and rough surface, with an appearance quite uncharacteristic of any grown previously in JPL No. 1.

The final run of the clean series, run 18-88, utilized a quartz crucible. Considerable amounts of SiO were deposited on many of the cartridge components. The cold shoes were particularly severely affected,

with deposits increasing as the run progressed to the point where appreciable amounts of deposit were loosened and fell on the shields in the vicinity of the die top. The SiO also appeared to degrade the speed performance of the cartridge, perhaps by reducing the rate of heat transfer to the cold shoe. In spite of these difficulties, growth conditions remained reasonable and the crucible was emptied of melt.

Some general observations made during the course of the runs from 18-80 to 18-88 have led to speculation as to the role of furnace and cartridge atmosphere in contributing to growth instability. A perceptible deterioration in growth conditions was noticeable throughout the period in which deliberate attempts to introduce oxygen into the ribbon were being carried out. In several runs, particularly 18-84 and 18-86, prolonged periods of very unstable growth, with many freezes and erratic spreading behavior, were experienced. On many occasions, these growth instabilities bore similarities to the instabilities observed in run 18-80b, where they were associated with the presence of the deliberately introduced oxygen. On the other hand, such erratic and unstable growth behavior was singularly absent throughout the preceding 15 runs of the clean series. Investigations into the manner in which oxygen, either in pure form or in compound gases, may contribute to promoting growth instability will be continued next quarter.

The oxygen related experiments carried out in runs 18-80 to 18-88 also point to a possible role for oxygen or oxygen-bearing gases in the formation of SiC particles in the meniscus region which then eventually end up on the ribbon surface. In particular, heavy SiC particle densities were observed in the first two runs, 18-81 and 18-82, in which high purity quartz was placed in the melt. Changes in the amount of surface film and the density of SiC particles were also observed in runs 18-85 and 18-88. More experimental work will be needed to establish whether these changes are related to the concentration of oxygen-bearing gases in the furnace atmosphere or to oxygen in the melt.

III. MULTIPLE RIBBON FURNACE by B.H. Mackintosh

In the first Quarterly Report, work during the current year on the multiple ribbon furnace was outlined into three subtasks called (a) Quality Subtask, (b) Productivity Subtask, and (c) 7.5 cm/min Growth Rate Development Subtask. This definition of division of efforts will be retained for the discussion of progress in the second quarter. The experimental activity of this quarter is summarized in Table III.

A. Quality Subtask

One of the significant goals for this growth system in 1978 is to produce, in multiple cartridge operation, ribbon yielding solar cells of at least 9% AM1 efficiency. Toward this end, several subsystems of the furnace are to be redesigned to eliminate materials believed to contaminate the melt, and to better exclude atmosphere-borne contaminants from outside the furnace. The largest item to be redesigned is the hot zone, originally made of stainless steel. A prototype for a new, much cleaner hot zone which was built a year ago and initially operated just prior to the beginning of this reporting period, was used to perform a series of highly routine single cartridge growth runs, numbers 16-110 through 16-118, as listed in Table III. The first seven runs of this series were essentially identical, while the last two had deliberate differences as noted in "comments". Solar cells were made from ribbon from all these runs and various other measurements were carried out on some as listed in Tables IV and V in the Characterization Section. Ribbon growth was generally difficult during these runs, as a spreading condition could not be obtained and freezes were frequent. Between 4 and 7 m of ribbon were produced per run. With the exception of one run in this series, the average length of growth between freezes was less than 25 cm. We associate the high density of silicon carbide particles on the surface of these ribbons with these poor growing conditions, although the mechanism of

Table III. Multiple Ribbon Furnace Run Data.

Run No.	Cartridge Type	Crucible Type	Hot Zone Used	Purpose	Comments
16-110 through 16-116	Conventional	Graphite 2-Station Poco	Short	Quality evaluation of new hot zone.	Most growth not full width. Much SiC. Frequent freezes.
16-117	Conventional	Graphite 2-Station Poco	Short	Same as 110 - 116, but not boron doped.	
16-118	Conventional	Silica	Short	Same as 110 - 116 except for crucible type.	Performed similarly to 110 - 116.
16-119	Conventional	Graphite 2-Station Poco	Short	Test wraparound end heaters and end heater ramp.	Ribbon could not be spread. Charge not completely melted.
16-120	Conventional	Graphite 2-Station Stackpole	Short	Test wraparound end heaters and end heater ramp.	Crucible broke. Major flood. No growth.
16-121A	Conventional	Graphite 2-Station Poco	Short	Test wraparound end heaters and end heater ramp.	Ribbon could not be spread. Successful full-width growth from full-width seed.
16-121B	High Speed	Graphite 2-Station Poco	Short	Test high speed cartridge heat removal elements 0.19 cm high.	Growth to 4.4 cm/min and 2.8 width.
16-121C	Conventional	Graphite 2-Station Poco	Short	Test 50 cm radius die.	Growth unstable. Apparent Si feed problem.
16-122	Conventional	Silica	Short	Test 50 cm radius die.	Fairly stable growth, to 4.5 cm wide.
16-123	High Speed	Silica	Short	Test high speed cartridge. Heat removal elements 0.16 cm high.	Growth to 4.8 cm/min and 2.5 cm wide. SiO deposits impaired growth.
None	None	Graphite 2-Station Stackpole	Long	Test two crucibles of type that failed in run 16-120. Crucibles placed in silica boat.	Two crucibles withstood heat-up cycle and molten silicon.
16-124	High Speed	Graphite 2-Station Stackpole	Long	Test high speed cartridge in long hot zone (better thermal symmetry).	Poor growth - deposits on die inhibited wetting. Crucible failed but had been placed in silica boat.
16-125	High Speed	Graphite Suspended (used in earlier run)	Long	Test high speed cartridge with suspended crucible (has given good stable growth in past).	No growth. Deposits on die inhibited wetting.
16-126	High Speed	Graphite Suspended	Long	Test high speed cartridge with suspended crucible.	One side of die hot. Growth to 2.5 cm wide, speeds to > 5 cm/min.
16-127	High Speed	Graphite Suspended	Long	Test high speed cartridge with plate capillary die.	No growth - deposits on die; die did not fill.
16-128	High Speed	Graphite Suspended	Long	Test high speed cartridge with plate capillary die.	Growth to 5.1 cm/min and 2.8 cm wide. SiO deposits impaired viewing.
16-129	High Speed	Graphite Suspended	Long	Same as 16-128, but different heat-up procedure to reduce SiO deposits.	Growth to 5.3 cm/min and 2.2 cm wide. Void in die created thermal imbalance.
16-130	High Speed	Graphite Suspended	Long	Test high speed cartridge with conventional (face slotted) die.	Growth to 5.1 cm/min and 2.8 cm wide. SiC particles hindered stability.
16-131	High Speed	Graphite Suspended	Long	Test high speed cartridge with cold shoes lowered from previous runs.	Little growth. Charge not completely melted (operator error). Run shut down.
16-132	Conventional	Graphite Suspended	Long	Return to baseline cartridge.	Growth good at start of run. SiC built up to very heavy on die. Growth became erratic.
16-133	Conventional	Graphite 2-Station	Short	Hot zone modified to place cartridge in center for thermal balance.	SiC built up quickly. Ribbon could not be grown over 2.5 cm wide.
16-134	Conventional	Graphite 2-Station	Short, central cartridge	Re-installed trap doors to reduce air contamination. Test gear drive puller.	Conditions improved from previous run. More stable; will spread, but difficult near ends. Fuller works well.
16-135	Conventional	Graphite 2-Station	Short, central cartridge	Test results of leaving furnace under vacuum four days between runs. Different cartridge of same type substituted.	Conditions improved from previous run. More stable; will spread, but difficult near ends.
16-136	Conventional	Graphite 2-Station	Short, central cartridge	Repeat of 16-135, but compare performance of two cartridges (same type) used in sequence.	Full width grown with both cartridges - conditions very similar. More SiC after changing cartridges.

degradation is not understood. The presence or absence of this silicon carbide probably depends on the interactions between silicon, carbon, and oxygen in the melt and/or SiO, O, and CO in the atmosphere over the melt. Water vapor, hydrogen, and methane (from reaction of water with hot carbon) may also play a role.

As discussed in the Characterization Section, most of the solar cells made from material grown in these quality evaluation runs exhibit shunted junctions attributable to silicon carbide particles. Small sections free of these inclusions, cut from cells from these runs display conversion efficiencies of 5 to 6 percent without antireflection coating. Cell short circuit current, which is relatively insensitive to shunting effects, may be an approximate indication of impurity level in the material. The averages of I_{sc} for groups of cells made from these runs are shown in Fig. 3. However, impurity concentration alone does not determine cell performance. Crystal structure, homogeneity of distribution of impurities, and the complexing of impurities with each other can also play important roles. Figure 3 suggests a deterioration in I_{sc} with successive runs, perhaps due to increasing contamination of a newly purified furnace (first used in run 110). More striking is the evidence already mentioned that use of a silica crucible may contribute to higher I_{sc} , although such a general conclusion cannot be based on this single run.

Five samples of ribbon from runs 110, 113, and 118 were analyzed using a special emission spectroscopy method which includes a chemical pre-concentration procedure. The data, listed in Table IV (in the Characterization Section) show the impurity levels in Furnace No. 3A to be similar to those in Furnace No. 1 for the conditions prevailing during the runs in which this material was produced. The high concentration of aluminum which has often in the past been indicated by IR absorption measurements on ribbon from No. 3A has been reduced to a level where its detrimental effects are probably less than those of iron and titanium.

The results of switching from the old stainless steel hot zone to the "cleaner" short hot zone are disappointing when the solar cell characteristics of material from runs 108 and 113 are compared (see Ref. 1). Number 108 was a single cartridge "quality baseline" run in the old hot zone. Run 113 was the exceptional run in the series of 110 to 118 in which silicon carbide particle density was relatively low. In both runs 108 and 113, the operator noted an unusually high, stable meniscus and grew for long periods (> 30 minutes) without a freeze. The resulting attainment of steady-state conditions of impurity distribution probably

Fig. 3. Average I_{sc} , cells from runs 16-108 through 118.

accounts for the uniformity in characteristics of samples from these runs, although cell performance parameters are low. Samples from run 113 have been sent for emission spectroscopy to provide further insight into the similarity of device characteristics of these two batches.

The results of this series of runs which constitute the most significant work done in this quarter on the Quality Subtask can be summarized as follows. Ribbon grown from this furnace displays widely variable surface densities of silicon carbide particles. When present in high densities, they severely degrade solar cell performance. Either the conditions that give rise to high particle density or the particles themselves deleteriously affect growth stability as well. The cause of the variability of this phenomenon is not known. It has been shown that significant numbers of ribbon segments selected to be free of silicon carbide yield solar cell efficiencies in the range of 5 to 6+ percent without antireflection coating (7 to 8½ percent with AR), performance which approaches the 9 percent figure which is the goal for this phase of the contract. We postulate that the efficiencies of these selected cells reflect the level of impurities, notably iron and titanium, which have been found in this material, and that cell performance will be improved in direct relationship to reduction of the quantities of these impurities.

Runs subsequent to the series 110 to 118 discussed above shed further light on the problem of high SiC particle density. In this growth activity, various changes in cartridge components and growth techniques related to higher growth rate and improved stability were evaluated. Clean handling procedures were not used (except in runs 133, 134, and 135). In those runs in which the high speed cartridge was under investigation, growth was difficult for several reasons, and we could not conclude that the high silicon carbide density was responsible. However, at the end of this period, we experienced unusual difficulty growing ribbon from the reliable and well-defined standard cartridge. In addition to the thick crust of silicon carbide particles on the die top, symptoms were: (a) Ribbon spreading could generally be attained only with a very low meniscus, but sometimes not at all. (b) A growing ribbon that was thermally well balanced would sometimes abruptly cease to grow from a spot on the die, i.e., rapid asymmetric tapering would occur or a hole would grow in the ribbon. Such an anomaly would occur at random places on the die. These symptoms were similar to those seen in Furnace No. 1 during the experiment which consisted of adding small

amounts of oxygen to the interface region (run 18-80). No likely source of air contamination of System 3A was found, but these difficulties with growth coincided with the arrival of hot, humid weather and were tentatively blamed on water absorbed in the graphite furnace insulation between runs. Prior to the last two growth runs of this period, the practice was adopted of keeping the furnace under positive pressure of dry argon between runs and minimizing its time of exposure to atmosphere when recharging. The cartridge used for most growth work in June was repaired following the discovery of corrosion around the seals of the cooling water passages. One or both of these measures was effective, as the growth performance in the subsequent runs was dramatically improved insofar as the meniscus was high, and full ribbon width was attained. Silicon carbide particles were still present at the die tip, but no longer as a continuous crust. They also remained as a feature of the ribbon surface, at lower densities. Solar cell fabrication from this material will show whether or not this lower level of carbide particle density still seriously shunts the devices. We are currently discussing the possibility that formation of these particles may be sensitive to small changes in composition of the furnace atmosphere. The experimental work begun on Furnace No. 1 (addition of silica to the melt in runs 81, 82, and 85) will be continued in the coming quarter with experiments in which we will study the effects on silicon carbide particle formation of various gases added to the furnace atmosphere. Experiments of this type, although they are primarily to be carried out in Furnace No. 1, will also be conducted in Furnace No. 3A if there appears to be a practical method of increasing solar cell efficiency by reduction of silicon carbide.

The improved solar cell parameters of material grown in Furnace No. 1 with a central-capillary die relative to that grown from multicapillary dies is encouraging (see Fig. 9, Characterization Section). This type of die will be evaluated in Furnace No. 3A in the next quarter.

Design of the new, cleaner furnace internals (hot zone and trap doors) will begin in mid-July. Several important details of the projected hot zone design were incorporated into Furnace 17 when it was designed in February. These design features were verified by the recent successful test of this furnace. The all-graphite quarter-turn trap doors have likewise been successfully tested and can now be incorporated in the design of Furnace No. 3A.

The investigation of the effect on material quality of continuous melt replenishment, planned for this reporting period, has not yet been carried out.

B. Productivity Subtask

The goals of this subtask are to increase the duty rate of this system by improving stability of growth, by developing techniques to minimize the time required to initiate full-width growth, by designing machine features which facilitate control of five ribbons by a single operator, and by improving reliability of system components. The most significant progress in this quarter was the identification of the effects on growth stability of water and oxygen in the furnace. Although several refinements in cartridge thermal and control components were investigated in this quarter, their effectiveness could not clearly be assessed due to erratic growth related to these atmospheric contaminants. In the two runs completed since these contaminants have been reduced, growth has been so stable as to give confidence that five cartridges at the present state of development could be operated at a significant overall duty rate. The modification made to the cartridge in this quarter which is most definitely useful is the ramped end heater control. This device facilitates both initial seeding and restarting after freezes by decreasing power to the end heaters simultaneously with "ramping down" the face heater temperature set point. Full-width ribbon growing on a bulbous-ended die can now repeatably be restarted after a freeze with almost no loss of width. In two runs in this quarter in which spreading behavior could not be attained, use of full-width seeds and the end heater ramp control allowed full-width ribbon to be grown.

While it is not in general the case that narrow seeds cannot be spread to full width in the 5 cm growth system, the time saved by initially starting growth near full width may justify the extra care required to select and prepare full-width seeds. Full-width seeds may be either long segments of ribbon, or smaller silicon wafers held in a seed holder. Very little of the ribbon grown to date has possessed the necessary qualities of uniformity of thickness, freedom from stress, and, especially, flatness. On the other hand, it has been found quite difficult to make and handle seed holders for wafers which are thin enough to pass through the belt pullers without perturbing growth. At present, the best seeds seem to be pieces of ribbon produced specifically for that purpose, i.e., grown thicker and slower (for better flatness) than ribbon for solar cells. Some improvements are being made to the afterheater, as discussed below, which may benefit the flatness of all ribbon.

A second modification which clearly improves the stability of growth was made during this reporting period. As mentioned in the first Quarterly

Report, the pullers were found to have excessive variations in speed due to the toothed-belt drive mechanism used. A gear drive system designed and built during this quarter reduced periodic speed variations by a factor of two and, more importantly, provides greater mechanical stiffness to overcome variations in resistance to pulling due to ribbon scribing, rubbing of ribbon against guiding surfaces, incipient freezes, etc. Subjective impressions of this puller, used in the three most recent runs, were highly favorable. Furnaces No. 1 and No. 17, which use similar pullers, will also benefit from this design improvement.

The afterheaters in the Furnace No. 3A cartridges possess a fault related to growth stability for which a solution has been designed. The power input to these afterheaters is limited by the current which can be supplied by the power transformers and interconnect wiring. The requirements for tight packaging of the equipment for five cartridges discourages the use of larger transformers and wires. The attainable temperature is marginal for stress relief, and drifts due to changes in helium concentration in the cartridge. Before closed-loop control can successfully be used, more heating power must be made available. Accordingly, a heating element has been designed with a resistance about twice as great as the previous standard design. A secondary effect of this new heater may be to change the nature of buckles. Thermocouple traces of the linear cooling structure ("afterheater") show a hot spot in the temperature profile at the position of the heating element; this is a deviation from the ideal profile for ribbon cooling as it is currently understood.^(5,6) The redesigned heating element which has 2.5 times the surface area will generate heat over a larger vertical distance and will operate at a lower temperature as well, decreasing the severity of this hot spot.

C. 7.5 cm/min Growth Rate Development Subtask

The "high speed" growth cartridge designed during Phase I was used in ten of the growth runs of this quarter. The overall purpose of this activity was to develop the performance of this cartridge to the point of attaining full-width growth at 6 cm/min or greater. This goal was not reached in the time allotted to this activity. Two faults in the cartridge hindered growth at any rate. Given additional time, these faults could be solved by minor changes in design and it is highly likely that ribbon could then be grown at the 6 cm/min rate. Extrapolating from the experience that 5 cm ribbon grown at over 3.2 cm/min is buckled, we can predict that further development work on this cartridge would then be

directed to the elimination of a severe buckling problem.

The experimental work of this quarter was also severely hindered by factors not related to the cartridge. Graphite crucibles of the batch which were to be used were defective, causing a major furnace flood and attendant loss of time. Silica crucibles and graphite suspended-type crucibles which were on hand were substituted while new crucibles of the standard graphite-type were procured. Use of these different crucible types added a variable which confused some aspects of growth performance. Operating this cartridge off-center in the two-position short hot zone seemed to result in lateral temperature gradients which seriously affected growth stability. When the long hot zone was brought back into use to eliminate this difficulty, growth behavior was erratic and melts were extremely dirty, due to the water contamination problem later identified.

In six of these ten growth attempts, at least 1 m of ribbon was grown. Maximum width attainable in these runs was 2.2 to 2.8 cm; maximum speeds were in the range 4.5 to 5.7 cm/min. The design of the cold shoes of this cartridge make it difficult to set or maintain precise spacing from the ribbon surfaces. This is one of the faults to be corrected by minor design modification. The other problem correctible by design is the condensation of silicon monoxide on the cold shoes when a silica crucible is used. These deposits, which build up rapidly, block viewing of the interface and interfere with heat transfer to the cold shoes. A design solution would be to tighten up the spaces through which gases can enter and exit from the cartridge, and install inlets for a purging flow of argon so that positive outflow is maintained through these openings. (Such a solution is also being considered for the 7.5 cm cartridge).

These experimental results are not well enough defined to warrant further conclusions about this cartridge. The additional work required to solve the problems encountered to date, plus attempting to significantly reduce the buckling expected from high-speed growth, and to then investigate the crystal quality and correlate it with ribbon electronic properties, probably could not be finished in time for the "9% solar cell multiple demonstration runs" scheduled for the end of this year. We will, therefore, continue to use the "standard" cartridge which grows ribbon at 3.3 to 3.8 cm/min.

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IV. MACHINE 17 by E. Sachs

A. Overview

At this writing, Machine 17 is very near to completion. Figure 4 shows the overall machine layout. The furnace itself is a stainless steel, water-cooled design with a slide-out hot zone. The hot zone is shown in closer perspective in Figs. 5 and 6. Figure 5 shows the hot zone assembled in a skeleton manner so as to illustrate the relationships of base plate, heater, crucible, furnace shell and slide-out door. Fig. 6 shows an assembled view of the hot zone. The heating element is a single phase device, fed by two spring loaded graphite current connectors. The crucible supports extend up through it from the base plate. This hot zone features all-graphite construction of "hot" parts. All metallic components are very effectively water-cooled. The heater element support technique is reliable and amenable to rapid parts interchange. The hot zone is a flat-top type, providing the advantages of ease of manufacture, robust design, and excellent interface with the trap doors.

The furnace is designed to accept both a 2 and 3 inch cartridge. The 3 inch cartridge will be the growth cartridge, the 2 inch part will accept a melt replenishment cartridge similar to that described in an earlier report.⁽²⁾ The problem of unreliable, dirty trap doors has been solved by the implementation of a set of cylindrical, argon vane powered trap doors to interface between the hot zone and the external shell.

The overhead structure (Fig. 4) acts as support for the belt puller-cartridge combination as it is lowered into the furnace.

The cartridge power supplies are visible in the first rack panel to the left of the furnace, the power leads from the rack panel to the furnace are compact and water-cooled.

The left-most rack panel houses the instrumentation package for the system. Supported above it is a TV camera, imaging the bank of 8 digital panel meters.

Fig. 4. Overall view of Furnace 17.

Fig. 5. Hot zone assembly without insulation.

Fig. 6. Hot zone assembly with insulation.

Fig. 7. Anamorphic optical system.

The table to the right of the furnace supports the TV monitor, video tap recorder, and growth control panel.

Shown close up in Fig. 7 is the anamorphic optical system. Through the use of a series of 6 prisms this device enlarges an image by a factor of 20 in one direction over the other. It yet remains to attach the second TV camera to this optical system, and set it up on the furnace. However, the heart of the system - the objective lens and prisms - seems to function well indeed.

Machine 17 not only holds promise for future research projects, its very existence represents progress on several fronts. It is, in effect, the next generation of machine design, directly scalable to a multiple ribbon production furnace. Novel aspects (already in operation, or shortly to be) include:

- A highly versatile, reliable, rugged, and serviceable hot zone.
- Reliable, clean, simple trap doors.
- Anamorphic optics to permit high resolution TV viewing of an entire 3 inch wide meniscus.
- Split screen TV presentation of the growth and the data relevant to growth including: main zone, face heater and afterheater temperatures, growth speed, cartridge helium flow, distance grown, cartridge heater power levels, and time.

This video image will also be recorded for future reference and analysis. It is expected that a unified presentation of growth and growth data will greatly reduce operator fatigue.

B. Summary of Runs

17-001: This was the first run of the hot zone, no cartridge was inserted. On the whole, the run went very smoothly. Some minor trouble areas manifested themselves, such as slightly inadequate water-cooling to the heater element feeds which was corrected during the run by a slight plumbing change. The power supply and heater were found to be well matched. The dynamic response of the system was found to be rapid and controllable, yet the power consumption was as expected - approximately 6000 watts.

The single major problem encountered was a severe temperature gradient in the main zone as measured by probing two cavities in a dummy crucible with a thermocouple. Over a separation of 9 cm, a temperature difference of 120°C was recorded! This, then, was the main problem attacked in the next three runs.

17-002: The heater used in run 17-001 was trimmed at the ends to increase local heat generation. Almost no effect was noted as the drastic temperature profile shown in Fig. 8 was measured. The asymmetry is due to greater heat loss out the 3 inch port on the right than the 2 inch port on the left.

17-003: Having noted little result from slight trimming of the main heater, a more drastic step was taken. A main heater with heating on the ends was designed and machined. In addition, several resistance paths were omitted from the center and one from the left end (to balance asymmetries).

The resulting measured profile is shown in Fig. 8. It is completely turned around from that of run 17-002.

17-004: Some resistance paths were cut in the main heater of run 17-003, in the center and ends. The resultant measured profile is also shown in Fig. 8. The maximum deviation, crest to trough through the hot zone is 15°C.

In summary, to date the furnace has demonstrated a gratifying lack of fundamental problems. Its design permits rapid and easy alterations such that with a few short runs a potentially severe thermal balance problem has been corrected.

The work that remains before the first growth run mainly consists of:

- Mounting of the second TV camera and the anamorphic optics.
- Wiring of the main control panel.
- Interconnection of the instrumentation.
- Attachment of belt puller and cartridge to the overhead support.

It is anticipated that this will be accomplished by the end of July.

Fig. 8. Temperature profiles along hot zone for three different main heaters (see text for run number explanations).

V. MATERIAL AND CELL CHARACTERIZATION by C.T. Ho and M.C. Cretella

A. Overview

Detailed quantitative information of metallic impurities contaminated in ribbon materials grown from both JPL Furnaces No. 1 and No. 3A have been obtained from emission spectrographic analyses. The results are compared with the material grown with graphite crucibles from induction heated furnace. From the solar cell output characteristics, we found that material grown from Furnace No. 1 with central capillary dies consistently produces higher performance than that produced using multi-capillary dies. It appears that the die configuration is indeed playing an important role in the improvement of material quality.

1. Chemical Spectrographic Analysis

Silicon ribbon samples grown from both JPL furnaces have been chemically analyzed by an emission spectroscopy technique which includes a chemical pre-concentration step to lower the detection limits (Kent Laboratory, Waltham, Mass.). Strips of 5 cm x 2.5 cm were cut from runs 18-66, 18-68, and 18-70 of Furnace No. 1, and from runs 16-110, 16-113, and 16-118 of Furnace No. 3A. The concentrations of the detectable metallic impurities in ppm by weight are listed in Table IV. With the exception of sample 18-70-26, which has an unusually high Fe level, the average impurity concentration for each contaminant level does not differ much between the two JPL furnace systems. It might also be noted that these impurity concentrations in general are not significantly higher than those found in materials produced from rf heated growth stations at Mobil Tyco, although erratic occurrences like the high Fe levels noted in sample 18-70-26 are totally absent there.

2. Solar Cell Characterization

During the reporting period, ribbon materials from nine growth runs in the multiple furnace (runs 16-110 to 16-118) were evaluated.

Table IV. Results of Emission Spectrography Analysis for Impurities in Stations JPL No. 1 and No. 3A. Concentrations are in ppm by Weight.

Run No.	Sample No.	Ag	Al	Ba	Ca	Cr	Cu	Fe	Mg	Mo	Ni	Ti	Total Imp.
18-66		0.04	0.05	0.005	0.01	nd	<0.005	0.12	0.16	0.07	0.04	0.01	0.51
18-66		0.04	0.15	0.020	0.40	nd	0.015	0.30	<0.01	0.53	0.08	0.15	1.80
18-68	5A	0.028	0.21	1.5	1.2	<0.01	0.023	0.04	1.3	nd	0.25	<0.1	4.61
18-68	2C	0.004	0.25	0.22	<0.05	0.41	0.006	5.40	0.02	nd	0.05	0.04	6.50
18-70	2L	0.10	1.08	1.4	1.8	1.7	0.11	10.0	1.5	nd	<0.10	0.21	18.00
18-70	2N	0.042	<0.05	0.75	0.50	0.01	0.048	0.20	0.4	nd	<0.10	0.04	2.17
Average of 3 Runs		0.04	0.29	0.65	0.68	0.36	.035	2.68	.57	0.10	0.10	0.09	5.60
16-110	004	0.12	0.47	1.0	1.1	0.10	0.029	1.1	1.2		<0.1	0.13	5.35
16-110	012	0.98	0.72	0.50	0.30	0.10	0.044	2.2	0.80		<0.1	0.20	5.94
16-113-1	26	0.058	<0.05	0.48	0.20	0.028	0.021	5.4	0.29	nd	<0.1	0.10	6.73
16-113-1	54	0.10	<0.05	0.03	0.80	0.019	<0.005	0.75	0.50		<0.1	<0.03	2.38
16-118-1	24	0.24	0.87	1.10	0.90	0.09	<0.005	5.60	0.90		<0.1	0.26	10.07
Average of 3 Runs		0.30	0.43	0.62	0.66	0.07	0.021	3.01	0.74		<0.1	0.14	6.09

Table V summarizes the results. As can be seen in the table, problems with the existence of high SiC particle density persisted throughout most of the runs. This high density appears to be independent of the type of crucible used during the growth. For example, run 16-118 was grown from a quartz crucible but it had as high a SiC density as those runs grown from graphite crucibles with the exception of run 16-113. Some of the possible reasons for this behavior are discussed in Section III.A.

Solar cells were fabricated according to the standard PH_3 diffusion and Al/Cr/Ag metallization procedures. The averaged cell performance under 100 mW/cm^2 tungsten simulated illumination is summarized in Table Vb. The low photovoltaic output characteristics were caused by the shunting of the junction (low V_{oc} and FF) due to the presence of SiC particles. Cells with the highest output were fabricated from the low SiC density growth run 16-113. Several cell samples were selected from runs 16-114, 116 and 118, and the high SiC density portions were removed by scribing them off from the cell. The smaller area, SiC-free cells were then retested. The results are shown in Table Vc. The drastic improvement of the cell efficiencies was mainly due to the recovery of V_{oc} and FF of the cell after the elimination of shunting effects. These photovoltaic characteristics represent the optimum performance of the cells that one would expect if the SiC particle density were minimized.

Upon examination of the optimum performance in Table V, it appears that the ribbon material grown from the quartz crucible (run 16-118) yields better photovoltaic characteristics than that grown from graphite crucibles (runs 16-114 and 116). A light enhancement measurement showed that the diffusion length of quartz crucible grown cells increased from L_n (dark) = 7-14 μm to L_n (1 sun) = 29-33 μm , whereas the graphite crucible grown cells increased from L_n (dark) = 2-3 μm to L_n (1 sun) = 13-15 μm . The effect of the presence of oxygen in ribbon silicon on the photovoltaic properties is not well known at the present time. However, there are suggestions which indicate that the presence of O in Si may have some beneficial effect in complexing or gettering transition metal impurities.⁽⁷⁾ We shall continue to explore this subject in order to improve the cell output efficiency for the resistance furnace grown materials.

3. Wide Ribbon Growth Furnace (JPL No. 1)

The silicon ribbons grown from JPL No. 1 are highly buckled and, as a result, cell fabrication is difficult. In order to attempt to

Table Va. Material Characterization for Ribbon Grown from Furnace No. 3A.

Run No.	Run Conditions	SiC Particle Density*	SPV L (μm) ⁿ	IR Absorption
16-110	Doped graphite crucible 1 3/4" wide	High	-	
-111	"	"	0 - 5.1	
-112	"	"	1 - 6	
-113	"	Low	0.5 - 2	No Al. SiC detected.
-114	"	Medium to High	0 - 2	
-115	"	Low to High	0	
-116	"	Medium to High	n	
-117	Undoped graphite crucible	High	0 - 23	No boron. No Al. Trace of SiC. Low C.
-118	Doped quartz crucible	High	2 - 5	O.C. CO complex. SiC are detected.

*Low = 0.5 parts/cm²
Medium = 1 - 2 parts/cm²
High $\geq$ 3 parts/cm²

Table Vb. Averaged Solar Cell Characteristics for Ribbons Grown from Furnace No. 3A after Standard Processes.
100 mW/cm². 28°C. No AR Coating.

Run No.	No. of Cells	Area (cm ²)	J _{sc} (mA/cm ²)	V _{oc} (Volt)	F.F.	η (%)	L _n (dark) (μm)
16-110	3	21.2	15.15	.403	.43	2.76	5.5 - 7.5
-111	1	"	16.57	.304	.32	1.61	9 - 15
-112	7	"	14.05	.398	.43	2.42	4 - 12
-113	15	"	12.36	.478	.63	3.73	3 - 7
-114	6	"	14.19	.369	.35	1.84	-
-115	2	"	10.13	.275	.31	.88	-
-116	8	"	11.87	.302	.33	1.22	2 - 3
-117	3	"	12.13	.146	.25	.46	-
-118	6	"	16.53	.329	.35	1.93	7 - 14

Table Vc. Photovoltaic Characteristics of Solar Cells after SiC Removal.

Run No.	Cell No.	Area (cm ²)	J _{sc} (mA/cm ²)	V _{oc} (Volt)	F.F.	η (%)
16-114	1A	10.9	14.33	.510	.729	5.33
	3B	9.44	14.83	.522	.678	5.25
	5A	4.90	14.50	.506	.681	5.0
-116	1B	4.18	13.21	.493	.691	4.50
	3B	4.05	12.86	.482	.629	3.90
-118	2A	2.20	14.36	.524	.725	5.46
	2B	2.16	15.0	.528	.754	5.97
	2C	1.87	15.83	.532	.749	6.31
	4A	3.30	16.85	.533	.712	6.39
	7A	5.94	17.17	.532	.680	6.21
	7B	3.30	17.45	.526	.584	5.36

increase the yields, we have cut the material into $7.5 \times 2.5 \text{ cm}^2$ blanks with the larger dimension along the ribbon width direction, and we have adopted special handling procedures. Cells from eight growth runs were fabricated by a modified diffusion process. The Al/Ti/Ag metallization process was left unchanged. The average solar cell output characteristics under 100 mW/cm^2 tungsten simulated illumination for non-AR coated cells are summarized in Table VI. A projected conversion efficiency range from 6.15 to 8.47% is expected if AR coating were to be added.

The various growth runs were characterized by the type of die design (multicapillary die vs. central capillary die) and the cold shoe (standard all-molybdenum cold shoe vs. "mini" cold shoe). By comparing the photovoltaic characteristics of the two cold shoes used in the growth runs for a given die design (e.g., see Table VI, run 67 and run 75 for multicapillary die, run 71 and run 76 for central capillary die), we can conclude that the type of cold shoe does not have a noticeable effect on the quality of the grown material. However, the die design does show discernible influence on the solar cell output performance. Figure 9 shows the photovoltaic characteristics of cells from these two types of die design. The materials grown from central capillary dies consistently produces higher performance than that grown from multicapillary dies.

We selected four representative solar cells fabricated from material prepared using the central capillary die (Nos. 71-1, 71-4, 76-13, and 76-21) and two typical cells fabricated from multicapillary die grown material (Nos. 75-4 and 75-5), and made IR scan measurements either parallel and/or perpendicular to the growth direction. The scan spectra show large local random variations and do not yield any definitive pattern or trend to correlate with the photovoltaic output results. Although at the present time we do not have enough experimental evidence to use the fluid flow model⁽³⁾ to explain the higher output of materials grown from a central capillary die, it appears that the die configuration is indeed playing an important role in the improvement of material quality.

Table VI. Summary of Solar Cell Characteristics for Ribbon Materials Grown from Furnace No. 1. No AR Coating on Cells.

Run No.	Growth Condition	Symbols (Fig. 9)	No. of Cells	J_{sc} (mA/cm ²)	V_{oc} (Volt)	FF	η (%)
18-67	Multicapillary Die Mo-Cold Shoe	O	9	14.37	.504	.632	4.58
-69	Multicapillary Die Mo-Cold Shoe	O	1	13.68	.504	.632	4.35
-70	Central Capillary Die Mo-Cold Shoe	Δ	1	15.36	.520	.644	5.15
-71	Central Capillary Die Mo-Cold Shoe	Δ	7	14.98	.509	.688	5.24
-73	Central Capillary Die Mo-Cold Shoe	Δ	3	15.30	.507	.637	5.01
-75	Multicapillary Die Mini-Cold Shoe	O	8	14.80	.50	.593	4.40
-76	Central Capillary Die Mini-Cold Shoe	Δ	10	16.09	.518	.70	5.84
-77	Multicapillary Die	O	6	14.37	.504	.587	4.24

Fig. 9. Solar cell performance of central capillary vs. multicapillary die material.

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APPENDICES

1. Updated Program Plan

The original program plan, as amended, is still in effect except that crystal growth experiments using the new Machine 17 are not expected to begin before August 1, 1978.

2. Man Hours and Costs

Previous cumulative man hours were 40,598 and cost plus fixed fee was \$1,433,448. Man hours for the second quarter are 7,136 and cost plus fixed fee is \$261,608. Therefore, total cumulative man hours and cost plus fixed fee are 47,734 and \$1,695,056, respectively.

3. Engineering Drawings and Sketches Generated During the Reporting Period

None.

4. Summary of Characterization Data Generated During The Reporting Period

See Section V.

5. Action Items Required by JPL

None.

6. New Technology

Section IV and the general effort on building Machine 17 generated certain items of potentially "new" technology. Some have been separately reported pending possible patent action, and all are now being scrutinized for the same purpose.

7. Other

"Multiple Silicon Ribbon Growth by EFG", by B.H. Mackintosh et al. Presented at the 13th IEEE Photovoltaic Specialists Conference, Washington, D.C., June 4-8, 1978.

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APPENDIX 7

"Multiple Silicon Ribbon Growth by EFG", by B.H. Mackintosh et al. Presented at the 13th IEEE Photovoltaic Specialists Conference, Washington, D.C., June 4-8, 1978. (Preprint)

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MULTIPLE SILICON RIBBON GROWTH BY EFG

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ABSTRACT

The background and progress to date of EFG ribbon growth for solar cell applications are briefly reviewed. The design and operation of a multiple ribbon-per-operator manufacturing system are then described. Results are presented of cost studies of this system at three stages of development. In the latter stage, believed to be attainable by 1986, conversion costs for polycrystalline silicon into wafers are attained which are consistent with manufacture of photovoltaic systems at \$0.50 per peak watt. Principal technological problems in the ribbon growth process are discussed.

INTRODUCTION

The EFG process of growth from the melt, applied to silicon ribbon for solar cells, has been under development for nearly seven years at Mobil Tyco and its predecessor company, Tyco Laboratories. Papers presented at previous Photovoltaic Specialists Conferences have discussed the early stages of development of the process (1), and characteristics of solar cells made from material grown at various stages of process development (2,3). Another report being given at this conference presents recent results on the fabrication of high efficiency solar panels from ribbon cells (4). The present paper discusses progress being made toward implementing ribbon growth as a large-scale manufacturing process and, in particular, the design and development of a multiple ribbon growth system.

Background

Development of a multiple ribbon growth system was started in 1975 when material grown in small induction-heated furnaces had attained such quality as to routinely produce solar cells with efficiencies of 8% (AM1). Economic analyses of photovoltaic panels based on EFG ribbon solar cells had indicated the need to reduce the labor content in the processing cost of polycrystalline silicon to ribbon wafers by growing multiple ribbons per operator (5). It was not until late 1974, however, that the theoretical bases of the process were well enough understood that a choice could be made between two basic multiple growth technologies. Whereas Tyco Laboratories was at that time in routine production of EFG sapphire ribbons grown multiply from a single pull head, it was recognized from theory and experience that silicon ribbon required more stringent

control of temperature and coordination between temperature and pull rate than was afforded by such a system. The multiple silicon ribbon technology was thus to be based on complete individual thermal pulling controls for each ribbon. These multiple growth station units were to share a common furnace to conserve power and floor space, reduce equipment cost, and bring them close together for convenience of the crystal growth operator.

Overall System Design

Figure 1 is a photograph of the system today, relatively little changed from its appearance when first assembled in late 1975. It was originally configured for ten one-inch ribbons. To mount the dies and to accurately position, relative to each die, the trimming heater elements, thermocouples, radiation shields and other components, the cartridge concept of growth system design evolved. Figure 2 shows a cartridge similar to the ones presently in use, with the essential elements pointed out. Each growth station consists of a cartridge, belt puller, cartridge heater power supply, cartridge temperature control system, and operator control panel. These system elements are shown in Fig. 3. A lift mechanism lowers the puller and the attached cartridge into the furnace; an air lock/valve mounted to the cartridge entry port closes it when the cartridge is withdrawn. The furnace is resistance heated and contains a trough crucible from which all growth stations are fed by a common melt replenishment unit constructed in modular form similar to a growth cartridge (Fig. 4). The bulk of development work on the multiple EFG silicon ribbon process is focused on phenomena related to components of the growth system cartridge, and therefore little more will be said about the overall furnace design.

Growth Process Development Goals

The cartridge method of growth component assembly and mounting has greatly facilitated the research and development efforts. From the original unit which grew 1 inch wide ribbon at 0.8 in./min, 2 and 3 inch versions have evolved, and 3 inch wide ribbon is now routinely grown at almost 2 in./min. Mobil Tyco now operates three cartridge-type furnaces, among which several existing cartridge designs can be used interchangeably to accomplish various research goals. To illustrate where the current research program on this technology is headed, the results of an economic analysis of EFG ribbon manufacturing based on the SAMICS standard

adopted by the DOE Low-Cost Silicon Solar Array (LSSA) project are reviewed here briefly (6). Table I shows the cost figures derived from this study; since the input data are based on three years' experience with design and operation of this type of equipment, the analyses are deemed to be quite accurate. The value added costs for conversion of polysilicon to solar cell wafers are calculated for three production units. The first is the present furnace with its five 2 inch wide ribbons. The second is a production unit consisting of two similar furnaces, each growing five 3 inch ribbons, set up to be overseen by one operator. The third is the same production unit as the second, but it is operated in a plant of 100 such units. Costs of equipment and replacement parts are reduced somewhat by the large quantities involved.

Fig. 1. Multiple Ribbon Furnace.

The conversion prices of polysilicon to wafers for these three production units are \$86.26, \$25.09, and \$16.57, respectively, per square meter at 67% duty rate and at 65%, 80%, and 80% yield, respectively. If we may assume that by 1986 the equipment will be capable of operating at 83% duty rate and 90% yield, the value added price drops to \$11.89 per m^2 (10). With suitable polysilicon available at \$10 per kg (unburdened), the total price for solar cell blanks becomes \$15.85 per m^2 . To place the output of this 100-unit manufacturing operation in perspective, its yearly output of 1.1×10^6 square meters represents 25% of the 1986 silicon wafer market estimated by JPL (7).

The technological problems to be overcome to achieve the large scale manufacturing operation are represented in Table II and discussed in the following four sections.

Fig. 2. Ribbon growth system cartridge.

Fig. 3. Multiple ribbon furnace cross section.

Table 11. Development Goals, Multiple IFC Silicon Ribbon Technology.

Parameter	1976 Goals	1978 Goals	Demonstrated to Date Conditions
Ribbon width	3 in.	3 in.	3 in.; single station furnace
Growth rate	3 in./min	3 in./min	1.5 in./min flat ribbon, > 2 in./min buckled ribbon
Thickness	0.006 in.	0.010 in.	.002 in. to .015 in.
Ribbons per operator	10 x 3 in.	5 x 2 in.	5 from 2 in. cartridges; low duty rate
Run length	116 hrs.	24 hrs.	~20 hrs.; two multiple growth demonstration runs
Machine duty rate	0.83	0.70	0.3 to 0.4
Yield	0.90	0.70	Not previously defined
Cell efficiency	12%	≥ 9%	10% occasionally; 5% to 6% routinely

Fig. 4. Silicon feeding system.

Fast, Stress-Free Growth

A principal feature of EFG ribbon growth is the rapid growth rate attainable as a result of the large surface-to-volume ratio of the ribbon which enhances the removal of heat of crystallization from the growth interface. The gradient which would be required to grow a 0.010 in. thick ribbon at 3 in./min is approximately $\sim 6000^\circ\text{C}/\text{in.}$ (5); this can be readily achieved by radiative heat loss to a cold environment. The deleterious effect of such rapid heat loss from the ribbon surface is the generation of nonuniform temperature gradients in the ribbon; these give rise to large thermal stresses during growth and excessive residual stresses in the grown ribbon.

A simple analysis of the cooling process shows the origin of these stresses to be as follows: During cooling, each ribbon element will contract in proportion to its temperature fall. If adjacent elements contract differently, they will restrain each other's contraction, and hence thermal stresses result. By considering contraction of adjacent longitudinal elements of the ribbon, it can be readily seen that the ribbon will be stress free if it is in a uniform temperature gradient (and if the coefficient of thermal expansion is independent of temperature). If the temperature gradient is non-linear, then adjacent elements must fit together by lateral deformation in the plane of the ribbon. Thus, thermal stresses must arise which will be proportional to the curvature or bending that must be imposed to fit the elements together. These stresses will increase with increasing curvature, (i.e., d^2T/dx^2) of the temperature profile and with increasing ribbon width. Thermoelasticity calculations (8) predict that the thermal stress components should be proportional to $(\text{width})^n$ where $n = 2$ to 4. A strong dependence of stress on width is found qualitatively to be present in many growth systems which tend to grow stressed ribbon. The ribbon will consistently shatter when spread beyond a certain width.

At high temperatures, stress relaxation occurs rapidly in silicon by the diffusion controlled climb of dislocations (8). Below about 1200°C , however, stress relaxation becomes slow with respect to the time scale of the cooling process, and stresses resulting from the variation of dT/dx will not be completely relieved. Below about 600°C , no stress relief can occur in silicon. Accordingly, in order to achieve fast, stress-free ribbon growth, one must impose a three-zone cooling profile on the ribbon. In the first zone, from the melting point to $\sim 1200^\circ\text{C}$, a high gradient is required to attain the desired fast growth rate. From 1200°C to 600°C , the ribbon should be cooled in a constant, relatively shallow gradient, while in the third zone below 600°C , the profile is unimportant as long as d^2T/dx^2 does not cause the fracture stress of the ribbon to be exceeded.

A combination of cooling block and actively heated "linear cooling structure" (see Fig. 2) were designed to generate this profile and a computer program was written to calculate temperature profiles for various temperatures, sizes, and spacings of these gradient-shaping elements (9). An additional feature of the cooling block which allows it to remove more heat over its small vertical extent, is helium flowing from jets in the block. The helium enhances conductive heat transfer from the ribbon to the block; the effects of this heat transfer mode are included in the calculations. Figure 5(a) defines the parameters of the program and Fig. 5(b) illustrates two typical profile plots for two sets of values of the parameters. Curve A is a profile of a case where excessive cooling of the ribbon takes place in the initial zone before it is reheated by the linear cooling structure. This "undercooling" to well below 1200°C would produce an unnecessarily large number of dislocations and possibly cause the ribbon to fracture within the growth cartridge. If this fracture did not

Table 1. Price Breakdown for Multiple EFG Ribbon Manufacturing at Three Stages - Costs Treated Per SAMICS.

		Five 2" Ribbons	Ten 3" Ribbons	
		Existing Unit	1 Unit Operation	100 Unit Operation
System Characteristics				
Growth Rate	(In./Min)	2.0	3.0	3.0
Run Length	(Hrs.)	116	116	116
Duty Rate		.67	.67	.67
Yield: Poly to Wafers		.65	.80	.80
Ribbon Thickness	(In.)	.010	.006	.006
Quantity				
Output from One Run	(Sq. M/Run)	38.936	215.643	215.643
Total Quantity	(Sq. M/Yr.)	2024.646	11213.425	11213.425
Equipment				
Furnace Lifetime Subsystems	(\$/Sq. M)	7.261	2.622	1.748
Cartridge Lifetime Subsystems	(\$/Sq. M)	10.891	3.933	1.966
Control Equipment	(\$/Sq. M)	3.630	1.311	0.655
Melt Replenishment Subsystems	(\$/Sq. M)	2.178	0.787	0.393
Total Equipment	(\$/Sq. M)	23.960	8.652	4.763
Floor Space	(\$/Sq. M)	4.791	1.427	1.427
Total Labor	(\$/Sq. M)	30.204	5.453	5.453
Materials				
Furnace Insulation	(\$/Sq. M)	1.284	0.464	0.232
Heating Elements	(\$/Sq. M)	0.642	0.232	0.116
Crucible	(\$/Sq. M)	2.671	0.965	0.482
Melt Replenishment Materials	(\$/Sq. M)	1.336	0.482	0.241
Die	(\$/Sq. M)	2.504	0.603	0.121
Cartridge Materials	(\$/Sq. M)	6.678	2.411	0.603
Furnace Argon	(\$/Sq. M)	0.871	0.315	0.284
Cartridge Argon	(\$/Sq. M)	2.142	0.774	0.698
Cartridge Helium	(\$/Sq. M)	3.058	1.104	0.828
Total Material	(\$/Sq. M)	21.186	7.349	3.604
Utilities				
Furnace Power	(\$/Sq. M)	3.743	1.352	0.811
Cartridge and MR Power	(\$/Sq. M)	2.380	0.859	0.516
Total Utilities	(\$/Sq. M)	6.123	2.211	1.327
Price-Conversion of Poly to Wafers (total or Above)	(\$/Sq. M)	86.26	25.09	16.57
Silicon Usage	(kg/Sq. M)	.909	.444	.444

occur, however, the linear cooling structure would perform the function of an annealing afterheater. Curve B in Fig. 5 shows the temperature profile for a smaller value of cooling block size Y_C ; the maximum temperature in the linear cooling structure is also lower than for the previous case. This latter profile closely approximates the ideal three-zone profile described above. (Only the first and second zones are shown in the figure.)

Fig. 5. (a) Model for computation of thermal profile in ribbon; (b) computed profiles for two sets of parameter values.

Measurements of the profiles in actual growth systems by the technique of vertical tracing with conventional wire thermocouples have shown good agreement with design theory for the constant, shallow gradient zone, but have yielded information of dubious value about the critical region near the growth interface because of lack of heat conducted to the thermocouple from below, and the different conduction/radiation characteristics of thermocouple wires from those of ribbon. A recent advance in technique has allowed the temperature profiles actually undergone by ribbons to be measured.

Reliable thermocouples have been formed on ribbons by junctions with graphite. Temperature profiles are measured by slowly melting these "instrumented" ribbons into the die. Figure 6 presents profile measurements of a growth system which tended to produce buckled ribbon, one made with a conventional thermocouple and one with a carbon/silicon ribbon thermocouple (10). The primary difference between the two cases is the large error in minimum temperature recorded near the cooling block.

Fig. 6. Comparative temperature profile measurements - conventional and Si ribbon thermocouples.

The relatively simple analysis of ribbon stress and the solution presented above had led to significant increases in speed and width. As speeds are pushed above the present state-of-the-art level of 1.5 to 1.8 in./min, however, an additional phenomenon sets in which requires further analysis of thermal stresses and additional refinement of cooling profiles. This latter phenomenon is the generation of stress-induced buckles or large deviations from flatness which makes the ribbon unsuitable for cell fabrication. Buckling occurs during growth to relieve compressive stresses acting over some length of the ribbon; these are the stresses left by incomplete stress relief in the region below 1200°C in a nonuniform gradient. The tendency of ribbon to buckle is enhanced for wider and thinner ribbons and when longer ribbon segments are under compression. Some of the current buckling problems are believed to be caused by the "undercooling" in the vertical temperature profile, such as shown by A in Fig. 5(b).

Width Stability

At the time of each scale-up in ribbon width from 1 cm wide ribbons to the current 3 inches, a great amount of experimental effort has been devoted to obtaining spreading behavior from the given growth system. Spreading and width maintenance are the first characteristics which a growth system must display before the other aspects of its performance may be analyzed. While edge-defined, film-fed growth of silicon ribbons from wetting dies involves a meniscus that has is highly stable along the faces of the ribbon, this is not the case at ribbon edges. There, a complex set of thermal, fluid flow, and interfacial phenomena determine whether spreading will or will not occur. Although

these phenomena are not fully understood, an analysis of meniscus geometry based on surface tension indicates that to be stable, the end meniscus must be lower than the face meniscus of the same ribbon (5). In practice, a freezing temperature isotherm which is relatively low at the ribbon ends is generally observed to be a feature of growth systems which display spreading.

Two factors are important in considering the distribution of meniscus height across die width. One is the relationship between meniscus height and ribbon thickness, including the limiting height at zero thickness. The other is the magnitude of random fluctuations of overall die temperature, and changes in meniscus height resulting from these fluctuations. Here, the lower limit to meniscus height is imposed by the gradient in the meniscus and the magnitude of these fluctuations. If the end meniscus height were .004 in. and gradient in the meniscus were $250^{\circ}\text{C}/\text{in.}$, both typical values, then a decrease in die temperature of 1°C would cause the ribbon to freeze. Conversely, these factors determine the stability required of the temperature control system.

To produce a freezing isotherm which is relatively low at the ends for a range of ribbon widths, two approaches are in use at Mobil Tyco. In vertical axis cylindrical furnaces, the prevailing isotherm across the top of the susceptor or crucible is nearly matched by the radius of curvature of the die, as shown schematically by Fig. 7. This technique does not lend itself well to scaling up in width, as thickness variation becomes excessive and the meniscus detaches in the center. The cartridge type growth systems use flat-topped dies surrounded by three heating elements to alter isotherm shape during spreading (see Fig. 8(a)). The face heater, controlled in closed-loop manner, maintains die center temperature; the end heaters are controlled manually. The variation of isotherm shape by end heaters is shown schematically by Fig. 8(b).

It must be pointed out, however, that in both the system configurations described above, spreading a ribbon that is less than full width is an unstable process, since the ribbon is moving onto a region of the die that is at a lower temperature. Therefore, constant temperature corrections are required. Furthermore, two unstable ribbon edges must be controlled at once. For these reasons a growth system which displays spreading angles (between ribbon edges and growth direction) of more than a few degrees, is extremely difficult to control. In principle, an electro-optical control device with a proper feedback algorithm could perform this task. Techniques for sensing ribbon width and meniscus height are under development at Mobil Tyco (11), but have not yet been applied to automation of growth startup and spreading.

In the ideal production-worthy ribbon growth system, spreading would, of course, never be required. Full-width seeds would be used and no width would be lost in starting transients. Only one startup would be required per run period (e.g., per week). In practice, perfect coordination of die temperatures and pull rate is difficult, and

full-width seeding is rarely accomplished. Work is presently underway to facilitate this coordination with better interface controls for the human operator. A decision to further the work with automated growth startup will be predicated on improvement of these controls, and on improvements in the long-term stability of growth.

Fig. 7. Meniscus shape in vertical axis cylindrical growth setup.

Two recent developments have enhanced the stability of steady-state growth. One of these is a die with enlarged, rounded flats or bulbs on the ends. Not only do the ribbon ends become edge-defined on this die in the same way as the ribbon faces, but the larger radius around the ribbon end promotes a higher meniscus which tolerates larger temperature excursions without the ribbon freezing or tapering away from the die end. The bulbs can be readily scribed and broken from the ribbon before processing into solar cells.

Growth stability has also been improved by continuous replenishment of the melt. In the present apparatus, melt level is sensed by an electrical probe and is controlled closed-loop.

Ribbon Quality

The above discussion has dealt with the growth process parameters related to the quantity of production, i.e., rate, width, stability, and multiplicity of production units. Of equal importance is the quality of the product, expressed in terms of solar cell efficiency. Several unique aspects of the EFG process give rise to crystallographic and electronic properties not seen in conventionally grown silicon. Attempts to increase the productivity of the growth process (especially growth rate) have tended to exacerbate these unusual characteristics. Considerable effort must be applied to the task of reconciling these characteristics with the solar cell efficiencies needed to attain the prescribed price goals. Concerns and work in

three such areas will be mentioned here:

(i) Growth takes place at speeds about two orders of magnitude greater than in conventional melt growth of silicon. The effects of growth speed and of the cooling profile in the initial fast cooling and afterheater regions (e.g., Figs. 5 and 6) of the cartridge on material quality for these systems are not known at present. EFG ribbon grown without a cartridge in induction furnaces at speeds from 0.5 to 1 in./min exhibits a distinct equilibrium growth structure featuring parallel sets of twin boundaries oriented along the growth direction and extending through the thickness cross section of the ribbon (12). AM1 solar cell efficiencies in the range from 10 to 12% are common for this material. On the other hand, the cartridge has been developed to grow ribbon in the speed range of 1 to 3 in./min. A breakdown of the equilibrium defect structure observed at lower speeds is already in evidence at 1.5 in./min in cartridge grown material (11). In addition, the extreme cooling/heating/cooling cycle in the cooling block and linear cooling structure regions adds the possibility that dislocations will be generated in greater numbers and will complex with impurities more readily to the detriment of solar cell performance. Although solar cells with AM1 efficiencies as high as 10 to 11% have been made on occasion from cartridge grown ribbon, more data needs to be gathered in order to determine the effects of speed and cartridge thermal environment on solar cell quality. This task is further complicated by other factors discussed below.

(ii) The EFG die, in intimate contact with the melt, has an important bearing on material quality, due both to the material from which it is made, and the geometry presented to the melt on its journey from the bulk melt to the growth interface. Graphite has been used almost exclusively in silicon growth at Mobil Tyco because of its wetting behavior, its relatively low reactivity with silicon, ease of fabrication, and availability in highly purified form. It is, however, dissolved by silicon, so that it is present both as a substitutional impurity in the ribbon and as silicon carbide particles which precipitate and aggregate at the growth interface. These particles are detrimental to growth stability and, when incorporated into the ribbon, to solar cell performance. Cells made from ribbon segments containing more than a few silicon particles display high leakage current, low open circuit voltage and, generally, low fill factor (13).

The EFG die also isolates the bulk of the melt from the growth interface, and thus growth takes place with an effective segregation coefficient of unity. In other words, all impurities drawn up the die must be incorporated into the growing ribbon. However, the redistribution of impurities across the ribbon width at the growth interface has been predicted theoretically (14). The inhomogeneity in impurity concentration across ribbon width predicted for some die designs could possibly be used to advantage.

(iii) The complexity of a multi-cartridge EFG system poses a problem with material quality due to

the large number of components and the variety of construction materials used. Many of these materials (aluminum, copper, molybdenum, etc.) are known to be detrimental, as impurities in silicon, to solar cell performance (15). However, they cannot be functionally replaced by other materials more acceptable with regard to melt contamination, without incurring severe penalties in cost, fabrication time, component lifetime, and thermal efficiency. We are thus compelled to try to understand the mechanisms of transport of these impurities to the melt, and design means of preventing them, case by case. Many construction materials are not commonly available in highly purified form and therefore several components may be possible sources of a given impurity.

Fig. 8. (a) Die face and end heaters; (b) variation of isotherm shapes.

DEMONSTRATION OF MULTIPLE GROWTH

In January of this year, we operated the multiple ribbon furnace for the first time with five 2 inch growth cartridges. One of the principal difficulties in arriving at this milestone was the design of a satisfactory trough crucible for the full 28 inch length of this furnace. Fused silica was rejected as a crucible material, primarily because SiO disproportionates and reacts with the die bottoms as they are lowered into the furnace, thus inhibiting wetting by the silicon. The same grades of high-strength, low porosity graphite from which dies are made are suitable for crucible fabrication,

but these grades are generally molded in maximum lengths of 18 inches. Crucibles were finally made in 9 inch sections of this graphite material, interconnected with graphite tubes. Future options to the crucible material problem include vitreous carbon and silicon carbide coatings on graphite of lower quality or on ceramics. We have demonstrated on numerous occasions that graphite crucibles can be sufficiently drained of silicon to survive cool-down to room temperature, so even an expensive crucible may be cost-effective.

Simultaneous growth of five ribbons from a continuously replenished melt by one operator was demonstrated for several 15 minute periods during a run lasting about 20 hours (10). Three of the growth cartridges were working well by current standards; these three were simultaneously growing full-width ribbon about 25% of the time. Bulbous-ended dies were instrumental in stabilizing those ribbons which could be spread to full width. Had the operator been able to devote full attention to any of these, they could have been kept growing for much longer periods; due to the division of the operator's attention, however, the duty rates from these stations were only in the range of 30% to 40%.

In subsequent multiple runs, these figures will be substantially higher solely because various shortcomings in operation of the equipment will be corrected and standard operating procedures will be adopted. These measures alone are not expected to permit the goals of 70% duty and 70% yield targeted for the end of this year to be attained. The duty rate will be further augmented by detail refinements of the temperature control and ribbon puller subsystems; these refinements will lengthen the average time between freezes. Duty rate will be increased if full-width seeding, as discussed above, can be implemented. Also, some simple automation devices are being designed to perform tasks such as seed insertion and warning of ribbons which have ceased to grow due to freezes. To improve the solar cell performance, major parts of the furnace are being redesigned using materials and methods less likely to cause contamination.

SUMMARY

In summary, the following statements describe the status of the EFG process with regard to large-scale manufacture of solar cells for terrestrial power generation:

a) The technique has been developed to the point of pilot production of 1 inch wide ribbon which consistently yields 11% efficient (AM1) solar cells.

b) Concepts have been developed for multiple ribbon growth which presently appear to have excellent potential as the basis of large-scale manufacturing of solar panels at a price of \$500 per peak kilowatt.

c) Progress needs to be made in the following areas, in approximate order of priority:

- The relationships among crystal structure, impurity concentration, growth rate, and solar cell performance must be better understood;

the reasonably good cell efficiencies seen in ribbon grown at 1 in./min must be demonstrated at 3 in./min.

- The current problem of buckles in fast, wide ribbon growth must be solved.

- Construction materials must be chosen and apparatus designed which will not, despite the size and complexity of the overall system, add impurities to the silicon ribbon.

- The yield and duty cycle of the multiple growth system must be raised by a combination of evolutionary refinement of existing components and additional automation.

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