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DOE/JPL/954888-79/8

CONTINUOUS CZOCHRALSKI GROWTH. SILICON SHEET GROWTH
DEVELOPMENT OF THE LARGE AREA SILICON SHEET TASK OF THE
LOW COST SILICON SOLAR ARRAY PROJECT

Second Annual Progress Report for October 1, 1978—September 30, 1979

By
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Work Performed Under Contract No. NAS-7-100-954888

Kayex Corporation
Rochester, New York

MASTER

U.S. Department of Energy

Solar Energy

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DRD NO. SE-9
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CONTINUOUS CZOCHRALSKI GROWTH

SILICON SHEET GROWTH DEVELOPMENT
OF THE LARGE AREA SILICON SHEET TASK
OF THE LOW COST SILICON SOLAR ARRAY PROJECT

SECOND ANNUAL PROGRESS REPORT
OCTOBER 1, 1979 - SEPTEMBER 30, 1979
PROGRAM MANAGER: DR. R. L. LANE
PRINCIPAL INVESTIGATOR: E. ROBERTS

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"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DoE."

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PREFACE

This work was performed by the Kayex Corporation Hamco Division Research and Engineering Department, R. L. Lane, Director. Others who participated in this research are: E. Roberts, N. Sarno, F. Merz, and M. Johnson.

Dr. A. R. Kachare is the JPL Project Monitor.

ABSTRACT

The primary objective of this contract is to develop equipment and methods for the economic production of single crystal ingot material by the continuous Czochralski (CZ) process. Continuous CZ is defined for the purpose of this work as the growth of at least 100 kilograms of ingot from only one melt container.

The approach to the project is to utilize a Hamco production CG2000 crystal grower suitably modified to grow large crystals and to permit periodic replenishment of the liquid. Key modifications were a vacuum tight isolation valve to separate the furnace chamber from the pull chamber for recharging, an automatic recharge mechanism, and an enlarged pull chamber to hold a supply of poly material. Other suitable modifications to permit the growth of crystals up to about 35 kilograms each included an optical diameter control system to allow crystals up to 12.5 cm to be grown, and a pull mechanism capable of supporting the large crystal to be grown. Furnace hot zone modifications were designed and built to accommodate 14-inch diameter crucibles having a melt capacity of about 40 kilograms.

During the reporting period (October, 1978 - September, 1979), many positive results have occurred:

- 1) 100 kg of silicon crystal has been grown from one crucible several times - refer to Table 1.
- 2) High quality crystal can be grown after 100 hours of continuous running in a Hamco CG2000 crystal grower.
- 3) Solar cells with an efficiency at AM1 from 14.8% to 16.1% were achieved on high quality material grown during the first 100 kg continuous run (Run No. 30). However, preliminary results indicate that polycrystalline material yields efficiencies 15% to 30% lower than high quality crystal.

4. A system for recharging lump silicon into a hot crucible during continuous runs has been developed. Results to date have been encouraging.

The system is based on a gravity feed hopper mechanism that is lowered into the furnace - refer to Section 2.1.1. The hopper presently being used has the capability to deposit a maximum of 18 kg into a 14-inch diameter crucible at one time. Total recharge time ⁽¹⁵⁾ for this cycle was 2.2 hours.

5. Two 5.9 inch diameter crystals have been grown in the CG2000 grower being used in conjunction with this project.

It is felt that furnace/melt contamination from several different sources has been the biggest deterrent to maintaining the capability to grow high quality material during continuous runs. For this reason, several runs have been terminated or resulted in less than satisfactory percentages of high quality crystal being grown.

Using the SAMICS/IPEG format, economic analysis of continuous CZ suggests that 1986 DoE cost goals can be met by the growth of large diameter (6 inch), large mass crystals from large melts.

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1.0 INTRODUCTION

The purpose of this program is to demonstrate the growth of at least 100 kilograms of mono crystalline ingot from one crucible by the Czochralski (CZ) method.

The approach to the continuous growth process being pursued in this effort relies on conventional CZ technology combined with new equipment designs which allow repeated alternate cycles of crystal growth and hot melt replenishment by methods which are suitable for use in a high volume production facility.

A Hamco Model CG2000 crystal grower was modified with a special chamber for the storage of a supply of polycrystalline silicon and a vacuum-tight isolation valve to permit retrieval of crystals and melt replenishment without contamination. A number of additional modifications to the facility have been completed in the program, and the process study phase is now under way, with a number of multi-ingot runs having been performed.

It is the purpose of this contract extension to describe a program aimed at a more accurate cost analysis of the continuous growth of silicon into material and also an investigative program for the purpose of defining and solving problems which may hinder the development of continuous Czochralski growth.

The proposed work consists of two efforts, the first being to conduct a series of continuous crystal growth runs in a pilot-plant-type operation. This is for the purpose of establishing with more certainty the costs of the process and pushing the technology even farther from the present laboratory operation toward production. The second (and parallel) effort will be to conduct an investigation study in the areas which appear to be related to yield of high quality crystal, specifically the quality of the crucible, the effect of impurities on degradation of the crucible, the introduction of impurities into the silicon, and the effect

of the furnace hot zone parts on the process, specifically in terms of impurities or foreign particles introduced into the silicon melt from its environment.

2.0 PROGRESS

2.1.0 DESIGN AND CONSTRUCTION OF GROWTH FACILITY

In the "First Annual Progress Report" - October 1, 1977 - September 30, 1978, the following areas of growth facility design, construction and modification were discussed as being completed:

- 1) Isolation Valve
- 2) Automatic Diameter Control Optical System
- 3) Poly Weight/Recharge System and Poly Attachment Device
- 4) Dopant Fixture
- 5) Crystal/Poly Transfer Device
- 6) Crystal/Poly Storage Rack

Since the First Annual Progress Report, the following items dealing with growth facility design, construction and modification have been completed:

- 1) Lump Recharging Device (Figures 1 and 2)
- 2) 14-Inch Hot Zone

2.1.1 LUMP RECHARGING DEVICE

The lump recharging device presently being used is based on a self-dumping hopper design that can be seen in Figure 1. Chunks of silicon are loaded into the hopper when it is in the furnace pull chamber. The isolation valve is closed and the pull chamber is at atmospheric pressure. It is necessary to keep the bottom funnel portion of the hopper closed (tight to the bottom opening) so that silicon will not fall through the bottom opening

while loading the hopper. This is accomplished by raising the hopper enough to keep its weight on the funnel. When the hopper is loaded with the desired amount of silicon, it is raised to a sufficient height for the isolation valve to be opened. Before the isolation valve can be opened, however, it is necessary to equalize the vacuum in both the pull chamber and hot zone sections of the grower. This is accomplished by first purging the pull chamber of air by pumping in argon and simultaneously pulling a vacuum on the pull chamber. Once the pull chamber has been purged and the vacuum pressure equalized, the isolation valve is opened and the hopper can be lowered to discharge the silicon into the crucible.

During the loading and purging cycles, the residual melt has been partially frozen on the surface to prevent splashing when the silicon is discharged into the crucible. Also, the crucible has been brought to a position that will minimize the distance the silicon will fall and, at the same time, prevent the silicon from piling up beyond the bottom of the funnel.

The discharge of the silicon is accomplished by stopping the hopper travel with the use of a support ring that rests on the flange of the isolation valve. The rod and funnel portion of the hopper is allowed to travel further, thus creating an opening between the funnel and stationary portion of the hopper. When the desired amount of silicon has been discharged, the rod and funnel are raised, closing the opening. Once the funnel contacts the stationary portion of the hopper, the entire hopper can be raised into the pull chamber past the isolation valve. At this point, you can either prepare for another recharge cycle, if necessary, or move the hopper back out of the way and lower the seed to grow another crystal.

Figure 1

Figure 2

During this reporting period, it was found that the capacity of the present hopper is approximately 18 kg of lump silicon. Since the hopper and its prototype were designed and tested when 12-inch diameter crucibles were being used, the ability to discharge 18 kg of lump silicon into a 12-inch diameter crucible with a residual melt is only possible by the use of a two step method.⁽²⁾ However, this two step method does not require two complete recharge cycles.

Based upon recharge results to date, it appears that particle size for reliable operation will be about 1 inch maximum. It is not known what the minimum acceptable particle size will be, but it has been observed that what we refer to as fines have a tendency to be blown around to a small degree.

A moveable mirror was designed, built and installed on the grower during this reporting period. This moveable mirror eliminates the problem of having to remove the stationary mirror (used in conjunction with the optical system used for diameter control) when lowering the hopper. This was necessitated because of a dimensional conflict between the mirror and the hopper support ring.

2.1.2 14-INCH HOT ZONE

A larger furnace tank was installed at the beginning of this reporting period which would accommodate a 14-inch hot zone set-up.

Initially, a 12-inch hot zone was used in the larger tank for the purpose of thermal comparison of the large tank with the standard smaller furnace tank. Results necessitated better insulation of the lower portion of the furnace.

Power consumption at dip temperature has been decreased from 60 kilowatts to 48 kilowatts with the 12-inch hot zone. Power consumption for the 14-inch hot zone has been decreased from 70 kilowatts to 60 kilowatts at

dip temperature.

The Hamco CG2000 Crystal Grower with the larger furnace tank has now been shown to be capable of growing high quality silicon crystals (suitable for semiconductor use) with a 12-inch hot zone in a production environment as well as an experimental environment.

Since the 14-inch hot zone is not available for production use yet, it has not been proven under these conditions. However, it has been repeatedly shown to be capable of growing silicon crystals (suitable for semiconductor use) at the Hamco-Kayex facility. In addition, it has also been shown to be capable of growing multiple crystals from one crucible which are satisfactory for solar cell use and which meet the specifications of the project goals - as has the 12-inch hot zone.

It is still felt that improvements can be made to both the 12-inch hot zone as well as the 14-inch hot zone and work is continuing to properly develop these hot zones to their maximum capabilities within the furnace design.

2.1.3 OPTICAL PYROMETER

In July, an optical pyrometer temperature sensing system was installed on the grower to replace the thermocouple system for temperature control. Temperature control has been good with the optical pyrometer system. The optical pyrometer system eliminates several shortcomings associated with the thermocouple method of temperature measurement and control.

2.2.0 PROCESS DEVELOPMENT

Even though the goals of growing 100 kg or more of silicon crystals from one crucible have been accomplished several times to date (Table 1), the ultimate goals as stated in the First Annual Progress Report⁽³⁾ can be accomplished by growing fewer crystals.

Date	Run No.	Total Melted (kg)	Total Pulled (kg)	No. of Crystals	Diameter (cm)	Average Pull Speed (cm/hr)	Run Time (hr)	Throughput (kg/hr)	Pulled Yield (%)	High Quality Crystal (%)
2/22/78	5	25.0	22.0	1	11.0	9.1	18	0.82	88	100
4/17/78	9	31.2	27.1	3	11.2	8.7	39	0.70	87	85
6/78	11	48.7	42.5	4	10.7	9.1	44	0.97	87	88
10/31/78	19	63.9	57.2	6	13.3	8.9	64	0.89	90	56
11/28/78	21	55.0	53.4	5	13.3	8.4	44	1.21	97	62
12/4/78	22	52.4	46.3	5	13.3	9.0	50	0.93	88	91
1/29/79	30	100.5	99.1	6	12.7-13.3	8.7	79	1.25	99	27
3/27/79	33*		50	3		Seed Broke				
5/15/79	41	50.4	48.7	3	12.7	7.6	42.5	1.15	97	70
6/26/79	47	65.1	60.2	5	12.7-13.5	6.8	51.6	1.17	92.5	88.3
7/17/79	49*	114.5	108	9	13.3	7.0	85.5	1.26	94.3	84.8
10/8/79	55*	106.1	100.6	10	12.7-16.0	7.2	91.0	1.11	94.8	74.6
10/22/79	2* **	104.5	100.3	9	12.7	7.7	109	0.92	96.0	63.7

* 14-inch crucible/hot zone

** New Hamco CG2000 grower with a 12-inch hot zone

Table 1

Initially, it was not possible to grow five 20 kg crystals without losing crystal structure⁽⁴⁾ with eventual polycrystalline growth before all five 20 kg crystals could be grown. Progress has been made in improving the percentage of high quality crystal grown during the 100 kg continuous runs as evidenced by Table 1. However, for various reasons (including structure loss), it has been necessary to grow more than five crystals to achieve a high percentage of high quality crystal. Growing more crystals does not significantly affect the amount of silicon available for solar cell production, but it does affect the amount of time necessary to grow an equal amount of silicon, which, in turn, affects the economic analysis. To offset some of the increased run time brought about by growing more crystals, time savings have been accomplished in the area of hot melt replenishment which are discussed in that section.

The 14-inch hot zone results have progressed to the point of growing a 28 kg crystal from a 30 kg melt. More than 100 kg have been grown from one 14-inch crucible during a continuous run with the largest individual crystal being 22.4 kg from a 29.7 kg melt. Several other one-crystal runs have resulted in crystal from 24 kg - 28 kg being grown from 30 kg melts.

Moreover, numerous crystals have been grown with a diameter exceeding 12.5 cm (5 inches) with some very near to, and slightly exceeding, 15.2 cm (6 inches). (See Figures 3 and 4).

2.2.1 HOT MELT REPLENISHMENT

Hot melt replenishment has evolved from the first attempts at melting off a virgin poly rod into molten silicon to the present two step method of recharging up to 18 kg of lump silicon in one recharge cycle⁽⁵⁾ ⁽⁶⁾.

During this reporting period, a hopper capable of discharging chunks of silicon into a hot crucible with varying amounts of residual melt was

Figure 3

Figure 4

developed (Figures 1 and 2). A complete explanation of its operation has been described in Section 2.1.1 of this report. It is felt that the advantages of using this system of hot melt replenishment outweigh the disadvantages associated with the poly rod method (melting off a polycrystalline rod). During this reporting period, all monthly and quarterly reports have dealt with the development of the hopper system of recharging lump silicon and its comparison with the polycrystalline rod method. A brief comparison of the poly rod and lump methods is presented in Table 2.

Preliminary results have also indicated that the amount of lump silicon recharged is not a significant factor in the amount of time necessary to melt the silicon, e.g. 5 kg of lumps requires approximately the same amount of time to melt as does 10 kg of lumps. A slightly more significant factor is the amount of residual melt in the crucible - the more residual melt, the less time needed to melt the silicon recharged.

2.2.2 100 KG CONTINUOUS RUNS

To date (9/30/79), eleven attempts have been made to grow multiple crystals using hot fill replenishment methods (Table 1). Of these eleven attempts, nine have used a 12-inch crucible/hot zone. Two other attempts involved the use of a 14-inch crucible/hot zone. In addition to these runs, two more successful 100 kg runs were made in October, 1979 (Table 1).

Initial attempts in 1978 did not achieve the 100 kg goal. However, early in 1979, the first successful 100 kg run was completed. Three more successful 100 kg runs have been completed since that time. One of these successful 100 kg runs (Run No. 2*) was accomplished in a new standard Hamco CG2000 grower which had previously grown only one crystal (Figure 5). Figure 6 shows the crystals grown during Run No. 2*.

COMPARISON OF LUMP VS ROD RECHARGING

	<u>ROD</u>	<u>LUMP</u>
Recharge Time	Relatively slow - about 4 hours to recharge because rod must be heated slowly at first.	Faster than rod. 18-22 kg can be recharged to seed dip in 2 hours.
Contamination of Melt	None, except for handling rods.	Lumps contact metal feeding mechanism. To date, we have seen no contamination of hopper material in crystal impurity analysis.
Effect on Crucible	The biggest single disadvantage to the poly rod method. High heater temperatures necessary to keep the center of the melt hot enough to melt the poly rod tend to increase devitrification of the crucible, thus decreasing the crucible life.	Crucible temperature remains lower, prolonging the life of the crucible. Particles may stick to crucible wall.
Convenience	Rod must be notched to hold it.	Convenient. Hopper can remain in furnace during the entire run. Simply load hopper with bagged silicon.
Capacity of Recharge Mechanism	20 kg rods (18-20 kg recharge capacity).	18 kg per cycle. Unlimited number of cycles.
Miscellaneous	5-inch diameter poly rods are not crack free. The possibility always exists of a rod breaking apart and falling into the crucible. From experience, it appears that partial rods being used over increases the possibility of the rod breaking apart considerably. Therefore, it is felt that partial rods left over should not be reused for recharging.	No thermal cracking problems with the hopper.

Table 2

Figure 5

Figure 6

It should be noted that the first three attempts listed in Table 1 were never intended to continue through 100 kg. These runs were intended to learn more about the parameters involved in growing multiple crystals from one crucible and also to develop the poly rod recharging method.

Details of most runs in Table 1 can be found in previous monthly, quarterly, and the last yearly reports.

The problem of loss of structure has been improved tremendously, but has not been completely eliminated. Possible sources of crystal structure loss have been categorized and explained by Dr. Richard Lane⁽⁷⁾. We are beginning to better understand the possible causes of structure loss (previously a mystery) through the use of impurity analysis results and continued study and development of the thermal parameters of the 12-inch and 14-inch hot zones. Melt contamination⁽⁸⁾ has always been a possible cause of structure loss. Present efforts are being directed toward defining the causes and results of different types of furnace/melt contamination. Preliminary data indicate that most contaminants are not absorbed by the crystal to any degree. They appear to attack the quartz crucible instead. There is so little data to corroborate this theory that we will not try to elaborate on these findings until more data is received. However, one axiom that always seems to reappear is that a clean, tight crystal grower will produce high quality crystals.

A future goal of this project was accidentally achieved when a 5.9 inch diameter crystal was grown when a test run was made (Run No. 51). The crystal which is shown in Figure 3 is slightly over 25 inches long and weighs 25.9 kg. The next test run (Run No. 52) also produced a 5.9 inch diameter crystal 23 inches long weighing 23.8 kg. Both crystals were grown from 30 kg melts.

2.2.3 CRYSTAL QUALITY

Crystal quality, a distinct problem during the first 100 kg run (Run No. 30) has improved from a low of 27% to a high of 85% during Run No. 49. Run No. 47 resulted in an even higher yield of high quality crystal, 88%, before the crucible failed.

Mechanisms of structure loss in silicon crystals have been thoroughly explained by Dr. Richard Lane⁽⁹⁾. Dr. Lane has also elaborated on several melt contaminants that are known to cause structure loss⁽¹⁰⁾.

During the time interval between Run No. 30 and Run No. 47, efforts were made to eliminate, to the best of our ability, all possible causes of structure loss.

1. Mechanical problems which might cause vibrations or shocks were looked for and eliminated.
2. Thermal parameters were studied and reviewed to improve thermal gradients and develop the best possible growth conditions of the furnace. In so doing, numerous hot zone changes were attempted. Some were for the better and some made conditions worse. Work is still being carried on to improve the hot zone characteristics even further.
3. Finally, a great deal of time has been spent identifying possible sources of furnace/melt contamination and eliminating them. The Seventh Quarterly Progress Report⁽¹¹⁾ listed the possible areas of furnace/melt contamination. Any of the six areas of furnace/melt contamination considered in that report can cause the loss of high quality crystals.

We feel that we have eliminated the possibility of volatile matter contamination by removing all vacuum grease from sealing areas where the grease would be in the vacuum portion of the grower or could leak into the vacuum side of the grower.

We are more aware of the possible contamination from carbon parts in the furnace and pay special attention to proper baking out of those parts.

Our etching procedures have been improved to the extent of our present equipment, which include a new water purification system, clean room techniques in handling etched silicon, and special bagging of all cleaned silicon.

The two areas of furnace/melt contamination which have been improved but not eliminated involve air leaks and water leaks. O rings and lip seals have a certain average life under normal operating conditions. We have studied many sealing areas of the grower and have located those which experience the hardest service and therefore tend to lose their sealing effectiveness after a certain amount of use. A preventative maintenance program was prepared to try and eliminate the possibility of any seals failing during a run. We feel that these efforts along with the substitution of a new top plate on the furnace have enabled us to accomplish our goals of growing 100 kg or more of silicon from one crucible with a large percentage of high quality crystal. The reason for replacing the original top plate was the continual problem with pin hole water leaks developing on weld areas. The new top plate was installed the first week in June prior to Run No. 43. Our best results have been accomplished since that time - refer to Table 1. Further development is being done to improve sealing areas with the shortest lifetime. Alternative type seal assemblies are being investigated.

It is felt that, if a residual gas analyzer was incorporated into the system in the near future, we would be able to identify contaminants in the furnace environment, tell when contaminants appear in the furnace environment, relate types of contaminants to crystal quality and further develop process parameters of the grower.

2.2.4 CRUCIBLE PERFORMANCE

At this time last year (October, 1978), our knowledge and practical

experience with crucible performance during long recharge runs was very limited. Since that time, we have concentrated on recording observations of crucibles used before and after continuous recharge runs as well as single ingot growth runs. Based upon these observations and data involving impurity analysis, it is felt that crucible devitrification may be the single most detrimental factor to long term continuous growth of high quality crystals. Results have shown that severe devitrification can degrade the original smooth glassy inner surface of the crucible to such an extent that relatively large bubble holes appear on the surface, many being filled with solidified silicon. When this type of devitrification occurs, it is highly probable that solid particles of quartz (SiO_2) are released from the crucible surface into the melt. Most of these particles are held against the walls of the crucible by the centrifugal force of the crucible rotation. However, it is always possible for some particles to somehow be swept out into the melt where they can come in contact with the growth interface, causing the crystal to lose structure. The possibility exists that the faster the growth of the crystal (pull speed), the greater the probability of sucking particles of quartz from the crucible walls into the melt. We have observed during our continuous runs that, when the crucible becomes devitrified to the degree where particles may come off the inner walls of the crucible, fast pull speeds many times result in structure loss. However, slower pull speeds tend to result in a higher percentage of high quality crystal late in a continuous run when devitrification is marginal. For this reason, it was decided not to attempt fast pull speeds on several of the latest 100 kg continuous runs.

Several examples of crucible devitrification are shown in the pictures on the succeeding pages.

Figures 7 and 8 show relatively severe devitrification on the inside

Figure 7

Figure 8

surface of a crucible after forty four (44) hours of run time. Devitrification is spotty, but covers a majority of the crucible surface below the melt level. Deep bubble holes are visible, several filled with solidified silicon. Figure 8 is a close-up view of the same crucible as Figure 7, showing the relative depth of one bubble blow hole.

Figure 9 shows the crucible used in Run No. 47 that failed after approximately fifty (50) hours of run time. The outside of the crucible is shown. It is difficult to tell from the picture that the clear area on the wall of the crucible is a void where the crucible ballooned out on the interior surface of the crucible. Oddly enough, the inner surface of the crucible does not exhibit severe devitrification. Patches of devitrification occupy less than a majority of the inner surface. Moreover, very few open bubble holes are visible (Figure 10). At the time the crucible failed during Run No. 47, 88% of the 60 kg of crystal grown was high quality crystal.

Figure 11 shows the crucible from Run No. 49. The inner surface (melt side) is shown on the left side. The outside surface (graphite side) is shown on the right and a cross section is shown in the middle. As can be seen, the devitrification is more severe on the outside surface of the crucible (thicker and frothy) than on the inner surface. Even though we would classify the inner surface devitrification of this crucible as severe, we were still able to grow high quality crystals at the end of this run after more than eighty hours of continuous run time and more than 100 kg of silicon crystals had been grown. Close examination of the inner surface reveals a fused appearance with a relatively small amount of bubble holes.

Figure 12 shows the crucible used for Run No. 2*. This crucible was run for a total of 109 hours. Refer to Table No. 3 for information concerning impurities of new and used crucibles. Further explanation will be included in future reports.

Figure 9

Figure 10

Figure 11

Figure 12

2.3.0 SAMPLE PREPARATION AND ANALYSIS

During the first yearly reporting period which ended September 30, 1978, there was a limited amount of data concerning impurity analysis and solar cell analysis. Moreover, since there had been no continuous recharge runs totalling more than forty three (43) kg pulled, there was no data available for a one hundred (100) kg run.

During this second yearly reporting period, much more data has become available, including results from several one hundred (100 kg runs.

2.3.1 IMPURITY ANALYSIS

A great deal of time and effort has been placed on trying to solve structure loss problems based on the theory that furnace/melt contaminants are the cause.

Table No. 4 presents the resulting data from Run No. 30 - a 100 kg run, Run No. 47 - a 60 kg run, and Run No. 49 - a 108 kg run. These results, while by no means conclusive, tend to indicate two things:

1. Impurities tend to increase only slightly in the grown ingots as the run progresses. The residual melt may or may not contain more of one or more contaminants depending on the amount of contaminants in the furnace environment during the run. This is evidenced by Run No. 30 where it is felt that the furnace atmosphere during the run contained considerably more contaminants than during Run No. 47 or Run No. 49. A significantly higher percentage of high quality crystal was grown during Run Nos. 47 and 49 than during Run No. 30.
2. Furnace/melt impurities tend to affect the crucible to a much greater degree than they affect the silicon melt and the resulting crystal being grown. The impurity levels of samples taken from the crucibles used in Run No. 47 and 49 indicate a significantly higher concentration than impurity levels of the crystal samples or the residual melt

CRUCIBLE IMPURITIES
(Concentration in PPM by Weight)

1	2	3	4	5	6	7
Impurity	Amersil	Quartz Products	General Electric	Corning	Run #47 Amersil	Run #49 Toshiba Cruc.
Al	12	20	28	5	6	7
B	1	NR	1	0.5	0.1	0.4
Ca	4	3	3	1	33	410
Cu	1	NR	1	0.05		
Fe	3	1	4	5	11	12
Li	1	1	0.5	NR	Int	Int
Mg	1	1	1	0.1	6	0.4
K	2	3	3	0.1	35	80
Na	3	1	3	2	66	41
Ti	1	2	2	10	7	16
Cr	NR	NR	3	NR	Int	Int
Zn	NR	NR	2	NR	0.9	5
Mn	NR	NR	2	NR	0.1	0.4
Cl					29	41
Br					9	28
F					20	11
I					6	7
S					2	8
P					6	25
Mo					6	15 /
Zr					9	0.9
Se					13	32

Table 3

1	2	3	4	5	6	7
Impurity	Amersil	Quartz Products	General Electric	Corning	Run #47 Amersil	Run #49 Toshiba Cruc.
Ba					6	35
Pb					2	3
Ge					0.6	6

NR: Not Reported
Int: Interference

Maximum impurities in Fused Quartz (vitreous SiO₂) crucibles provided by vendors. Expressed as parts per million by weight.

Table 3

IMPURITIES (CONCENTRATION IN PPM WEIGHT)

Sample I.D.	Na	Mg	Ca	K	Zn	Cu	Fe	Cr	Ta	Cs	Ti	Al	P	F	Cl	S	Ba
Virgin Poly	1	0.1	2	0.4			5	1			≤0.2	0.1	0.9		0.3	≤0.04	
1-A	0.9	0.2	4	1			3	0.3			0.09	0.07	0.4	0.06	0.2	0.2	
30-1 Top	0.5	0.3	0.2	0.04	0.2		6	3	0.8		0.2	0.09	1	0.02	0.3	0.03	
30-1 Bottom	0.7	0.2	0.2	0.4	0.4		3	0.8	2		0.1	0.05	0.9	0.04	0.2	≤0.04	
30-6 Top	3	4	0.4	0.3	8		4	0.6			≤0.1	0.07	2	0.2	0.2	≤0.06	
30-6 Bottom	4	4	0.7	0.6	0.2	1	6	0.7	2	0.02	0.4	0.3	0.6	0.6	0.4	≤0.03	
30 Residual Melt	3	2	150	12	1	3	Int.	≤0.5	1		1	2	0.9	≈30	5	1	0.9
47-1 Top	7	0.3	<0.1	0.1			Int.	≤0.1	≤0.5			<0.1	0.7	<0.1	0.7	0.2	
47-3 Bottom	0.8	0.3	<0.1	0.1	0.1	0.1	Int.	<0.1	≤0.4		0.1	<0.1	0.8	<0.1	0.3	0.2	
47 Residual Melt	1	0.3	<0.1	0.1	0.1	2	Int.	<0.1	≤0.3		0.1	<0.1	0.4	<0.1	0.6	0.1	
47 Crucible	66	6	33	35	0.9	2	11	Int.		0.5	7	6	6	≈20	29	2	6
49-1 Top	0.4		<0.1	<0.1	<0.1		Int.	0.2			0.1	<0.1	0.4		0.3	<0.1	
49-5 Top	4		<0.1	0.2		0.2	Int.	<0.1	≤0.4				<0.1		0.6	<0.1	
49-9 Top	7	0.5	0.1	0.6	0.2	0.7	Int.	≤0.2	≤0.6		0.1	<0.1	0.8	<0.1	0.3	<0.1	
49-9 Bottom	1	0.5	0.1	0.1		<0.1	Int.	0.2	≤0.6		0.1	<0.1	0.8	<0.1	0.7	0.2	
49 Crucible	41	7	410	80	5	4	12	Int.	2	0.1	16	7	25	11	41	8	35

Table 4

from those runs. The crucible from Run No. 30 was not tested for impurities, but will be sent out for analysis in the near future. However, samples of new crucibles and crucibles used for Run No. 55 and Run No. 2* have been sent out for analysis. These results will be available for the next report.

2.3.2 SOLAR CELL RESULTS AND EVALUATION

Solar cell results have run similar to those in the past with high quality crystal yielding the highest efficiency levels and polycrystalline material resulting in significantly lower efficiency levels. Table No. 5 contains information concerning samples taken from Run No. 9, Run No. 11, Run No. 30, Run No. 47, and Run No. 49. Run No. 9 and Run No. 11 were reported in the First Annual Report⁽¹²⁾. However, Run No. 30, the first 100 kg run accomplished, resulted in the two extremes of solar cell efficiency being realized up to that time. Solar cells fabricated from high quality silicon crystal material taken from the tops of all crystals grown during Run No. 30 yielded efficiencies at AM1 from 14.8% to 15.9%. Moreover, a cell fabricated from the middle of the first crystal grown (high quality material) resulted in an efficiency rating at AM1 of 16.1%. Solar cells fabricated from polycrystalline silicon samples from Run No. 30 resulted in efficiencies at AM1 as low as 10.3%. Control samples for Run No. 30 ranged from 14.7% to 14.8% AM1.

Run No. 47 and Run No. 49 resulted in efficiencies of all samples in excess of 15% AM1. A wafer taken from the top portion of the third crystal grown during Run No. 47 resulted in an average efficiency of 13.7% AM1 due to excessive polishing. The wafer was seven mils thick, causing the efficiency to be low. The bottom of the same crystal resulted in an average efficiency of 16.0% AM1. Efficiencies of solar cells made from Run No. 47 and Run No. 49 ranged from

SOLAR CELL ANALYSIS
Data Taken at AMO (Converted to AM1)

Run No.	Ingot No.	Sample Description	Resistivity ohm-cm	Navg AMO	Navg AM1
9	2	Top - OD	5.75	10.1	14.1
9	2	Middle - OD	6.00	9.5	13.3
9	2	Bottom - OD	5.6	9.9	13.9
9	2	Bottom - Dislocated	5.6	9.9	13.9
9	3	Top - OD	5.2	9.0	12.6
9	3	Top - Dislocated	5.2	9.1	12.7
9	3	Bottom - Poly	4.4	9.4	13.2
11	1	Top - OD	2.99	10.4	14.6
11	2	Top - OD	2.74	9.7	13.6
11	2	Bottom - OD	2.57	10.1	14.1
11	3	Top - OD	3.69	10.2	14.3
11	4	Top - OD	3.52	9.3	13.0
11	4	Bottom - OD	3.62	9.3	13.0
11	4	Bottom - Dislocated	3.62	9.6	13.4
30	1	Top - OD	2.30	11.4	15.9
30	1	Middle - OD	1.86	11.5	16.1
30	1	Bottom - Dislocated	1.82	8.4*	11.7
30	2	Middle - Poly	1.72	7.8	10.9, 11.3
30	2	Bottom - Poly	2.94	8.7	12.2
30	3	Top - OD	2.47	11.1	15.5
30	3	Bottom - Poly	2.78	8.2	11.5
30	4	Top - OD	2.34	11.3	15.8
30	4	Middle - Poly	3.12	8.7	10.8, 12.2
30	4	Bottom - Poly	1.95	8.6	12.0
30	5	Top - OD	2.20	11.1	15.5
30	5	Bottom - Poly	2.48	7.8	10.9
30	6	Top - OD	2.16	10.6	14.8
30	6	Middle - Poly	2.97	7.4	10.3
30	6	Bottom - Poly	1.90	9.0	12.6
47	1	Top - OD	Not	11.4	16.0
47	3	Top - OD (Thin wafer 7 mils)	Completed	9.8	13.7
47	3	Bottom - OD		11.4	16.0
49	1	Top - OD	2.67	11.6	16.3
49	1	Bottom - Single	1.95	11.5	16.1
49	6	Top - OD	1.80	11.6	16.3
49	9	Top - OD	2.06	11.5	16.1
49	9	Bottom - Single	1.73	11.1	15.5

Table 5

15.0% to 16.9% AML. Single crystal material yielded results similar to zero dislocation material. No polycrystalline material was tested from Run No. 47 or Run No. 49. Fill factors were satisfactory, with most samples averaging between 73% and 75%. A more detailed analysis will be included in the next quarterly report at the end of December, 1979.

The tendency for efficiencies to decrease slightly throughout the run as previously reported⁽¹³⁾ was not readily evident in the results of Run No. 30, Run No. 47, and Run No. 49.

It must be remembered that there is a standard error involved in these efficiency results as can be evidenced by our own control sample results for the middle of crystal number two and the middle of crystal number four from Run No. 30. Control tests will be done in the future on high quality material.

2.4.0 ECONOMIC ANALYSIS

A detailed analysis of projected cycle times, growth methods and conditions, and SAMICS/IPEG Input Data and Cost Calculations can be found in the First Annual Progress Report⁽¹⁴⁾. This information will not be repeated in this report. Instead, a table relating the actual run time for Run No. 49 will be compared to the original projected time analysis for the CZ-2 method and the corresponding add-on costs (Table 6). A third column relates information gathered from Run No. 49 to the original projected and add-on costs.

In the first column, the projected time cycles from our earlier cost analysis, the CZ-2 process is based on pulling four 25 kg ingots out of a 35.5 cm diameter crucible. The time cycles are broken into four major operations: melt down, seed and crown growth, recharge, and straight growth.

The next column is the breakdown of Run No. 49. The updated projection values were arrived at in the following way:

COST UPDATE FOR CZ NO. 2*

<u>OPERATION</u>		<u>PROJECTED TIME (HR)</u>	<u>ACTUAL TIME (RUN #49) (HR)</u>	<u>UPDATED PROJECTION (HR)</u>
Melt Down		4	2	2
Seed and Crown Growth		10.6 (4 ingots)	23 (9 ingots)	14.6 (4 ingots)
Straight Growth		30.4 (10 cm/hr)	50 (6.8 cm/hr)	30.4 (10 cm/hr)
Recharge		12.5 (3 times)	11 (5 times)	9.0 (3 times)
		—	—	—
		57.5	86	56.0
Add-on CZ	1975 Dollars	17.91	22.16	16.61
Cost	(1980 Dollars)	(25.07)	(31.0)	(23.25)
*CZ No.2:	14 inch crucible 100 kg 13.3 cm diameter 10 cm/hr			

Table 6

- 1) The best times of the previously projected time values were used where possible.
- 2) Updated practical estimates were made for the operations of "Melt Down", Growing Preparation, and Recharge Cycle times based on data from Run No. 49 and other continuous runs. This data was compared with the previously projected time cycles and weighted in favor of the actual time data.

It should also be noted that Run No. 49 produced 108 kg of crystal, not 100 kg.

The resultant add-on cost for the projected was \$16.97 and the actual cost from Run No. 49 was \$22.16 for 108 kg production. The updated projection points out a dramatic improvement in the initial melt down time and the recharge cycle time (using lump silicon). A more conservative estimate has been made for growing preparation due to the possibility of structure loss during the initial stages of growing a crystal. The neck growth, crown growth, and rounding over procedures are important from an operator standpoint. If melt backs are necessary, this lengthens the "Growing Preparation" time cycle. Using this data, we arrive at an add-on cost in 1975 dollars of \$16.61, slightly less than the add-on cost of the previously projected time.

Based on actual continuous run data, the best results from achieved time cycles would drastically reduce the add-on costs if it were necessary to grow only four ingots in succession.

3.0 DISCUSSION

The objective of growing 100 kg of silicon crystal from one 12 inch diameter crucible has been achieved. To date, several continuous recharge runs have produced at least 100 kg of silicon crystal from one crucible (Run No. 49 - 108 kg). It has been shown that high quality crystal can be grown after eighty (80) hours of continuous run time. Several crystals of 5.9 inch diameter or greater have been grown in the Hamco CG2000 grower used for this project. A system of recharging lumps of silicon has been developed using a hopper gravity feed method. The results using this method have been satisfactory and are felt to be the best method for recharging lump silicon during our continuous growth process presently available.

Preliminary solar cell efficiency results indicate that efficiencies do not decrease during the entire continuous growth run. The biggest detriment to solar cell efficiencies appears to be the loss of high quality crystal structure (polycrystalline growth).

A satisfactory percentage of high quality crystal has been grown during these continuous runs (84% and 88% - refer to Table 1). However, it is felt that a satisfactory percentage of high quality crystal can only be grown with a grower that has a clean growth environment. Furnace/melt contaminants are felt to be detrimental to the continuous growth of high quality crystals. Therefore, considerable effort is being put into identifying types of furnace/melt contaminants and their sources. The effects of these contaminants is being studied with the goal of identifying specific causes of structure loss in crystals.

Growth of large diameter (5.9 - 6.0 inch) has been accomplished. It is felt that the goals of this project can be achieved provided a clean furnace environment can be maintained throughout the run.

4.0 PLANS

Efforts are continuing to complete a total of six 100 kg continuous runs by the end of this contract extension (December 31, 1979). Emphasis is being placed on improving the percentage of high quality crystal. We are stressing the maintenance of a clean furnace environment in order to grow fewer high quality crystals to achieve the same 100 kg goal.

REFERENCES

- (1) R. L. Lane, "Continuous Czochralski Growth", First Annual Progress Report. DOE/JPL 954888 October 1, 1977 - September 30, 1978.
- (2) R. L. Lane, "Continuous Czochralski Growth", Seventh Quarterly Progress Report. DOE/JPL 954888 April 1 - June 30, 1979.
- (3) R. L. Lane, First Annual Progress Report, Op. Cit.
- (4) R. L. Lane, "Continuous Czochralski Growth", Fifth Quarterly Progress Report (Appendix). DOE/JPL 954888 October 1 - December 31, 1978.
- (5) R. L. Lane, Seventh Quarterly Progress Report, Op. Cit.
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- (7) R. L. Lane, Fifth Quarterly Progress Report (Appendix), Op. Cit.
- (8) R. L. Lane, Seventh Quarterly Progress Report, Op. Cit., Section 2.2.1.
- (9) R. L. Lane, Fifth Quarterly Progress Report (Appendix), Op. Cit.
- (10) R. L. Lane, First Annual Progress Report, Op. Cit.
- (11) R. L. Lane, Seventh Quarterly Progress Report, Op. Cit.
- (12) R. L. Lane, First Annual Progress Report, Op. Cit.
- (13) Ibid.
- (14) Ibid.
- (15) R. L. Lane, Twenty Second Monthly Progress Report, Op. Cit., Table 2.