DRD NO. SE-7
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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

FIFTH QUARTERLY PROGRESS REPORT
OCTOBER 1 - DECEMBER 31, 1978
PROGRAM MANAGER: R. L. LANE
PRINCIPAL INVESTIGATOR: F. MERZ

KAYEX CORPORATION
1000 MILLSTEAD WAY
ROCHESTER, NEW YORK 14624

"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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ABSTRACT

The JPL Continuous Czochralski Growth Facility is now essentially complete and is functional. In this reporting period, a silicon lump recharging device was designed, and a prototype was built which performed well in simulated recharge tests. The large chamber (designed to accommodate a 14-inch hot zone) was put into operation initially with the standard hot zone in order to compare performance with previous experience. Some modifications had to be made to the hot zones in the larger chamber due to considerably larger radiative heat losses.

Several short (one-ingot) runs were performed and four continuous runs were attempted. The largest continuous run lasted 64 hours and produced 57 kilograms of ingot.

The major problem in achieving the 100 kg goal has been difficulty in maintaining high quality (zero dislocation) ingot growth for long periods of time. This may be related to particulate contamination of the melt from the crucible or the hot zone.

The previously reported SAMICS analysis was compared with actual experience with regard to recharging. Cost analyses of four possible methods of continuous CZ are included.

Spark source mass spectrographic analyses were performed to determine the level of impurity build-up in continuous CZ runs.

CONTENTS

ILLUSTRATIONS

1.0 INTRODUCTION

The purpose of this program is to demonstrate the growth of at least 100 kilograms of single crystal 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.

2.0 PROGRESS

2.1.0 DESIGN AND CONSTRUCTION OF GROWTH FACILITY

The program plan (Figure 1) for design and construction of the growth facility is nearly complete. Remaining unfinished portions of the program are (1) melt level control via weight and (2) the lump recharge device.

2.1.1 MELT LEVEL CONTROL VIA WEIGHT

The weight signal is available in the control circuitry. A circuit has been designed, and is ready to build and install on the grower. Further activity in this area has been postponed so that emphasis can be placed on recharge runs.

2.1.2 LUMP RECHARGING DEVICE

A preliminary concept for lump recharging was developed which utilizes a self-dumping hopper. The hopper is loaded with silicon and lowered (using the recharge system) into the crucible. The residual melt is partially frozen to prevent splashing and the silicon is released into the crucible. Ten kilograms can be handled in one cycle. Additional loads can be added to the crucible while the first load is melting.

An experimental prototype was fabricated and a series of simulated recharge experiments was performed to establish an optimum configuration (Figure 2). It appears that particle size for reliable operation will be about 1 inch maximum. It is not known what the minimum particle size will be, and no powdered material is presently available for such a test.

PROGRAM PLAN - CONSTRUCTION OF CZ GROWTH FACILITY

	MILESTONES
1	DESIGN SPECIFICATION, JPL APPROVAL
2	ADC OPTICAL SYSTEM
3	POLY WEIGHT/RECHARGE SYSTEM
4	POLY ATTACHMENT DEVICE
5	MOD. BEAD CHAIN/CABLE MECHANISM
6	DOPANT FIXTURE
7	CRYSTAL/POLY TRANSFER DEVICE
8	MELT LEVEL CONTROL VIA WEIGHT
9	14" HOT ZONE
10	RECHARGE DEVICE - POWDER OR LUMP

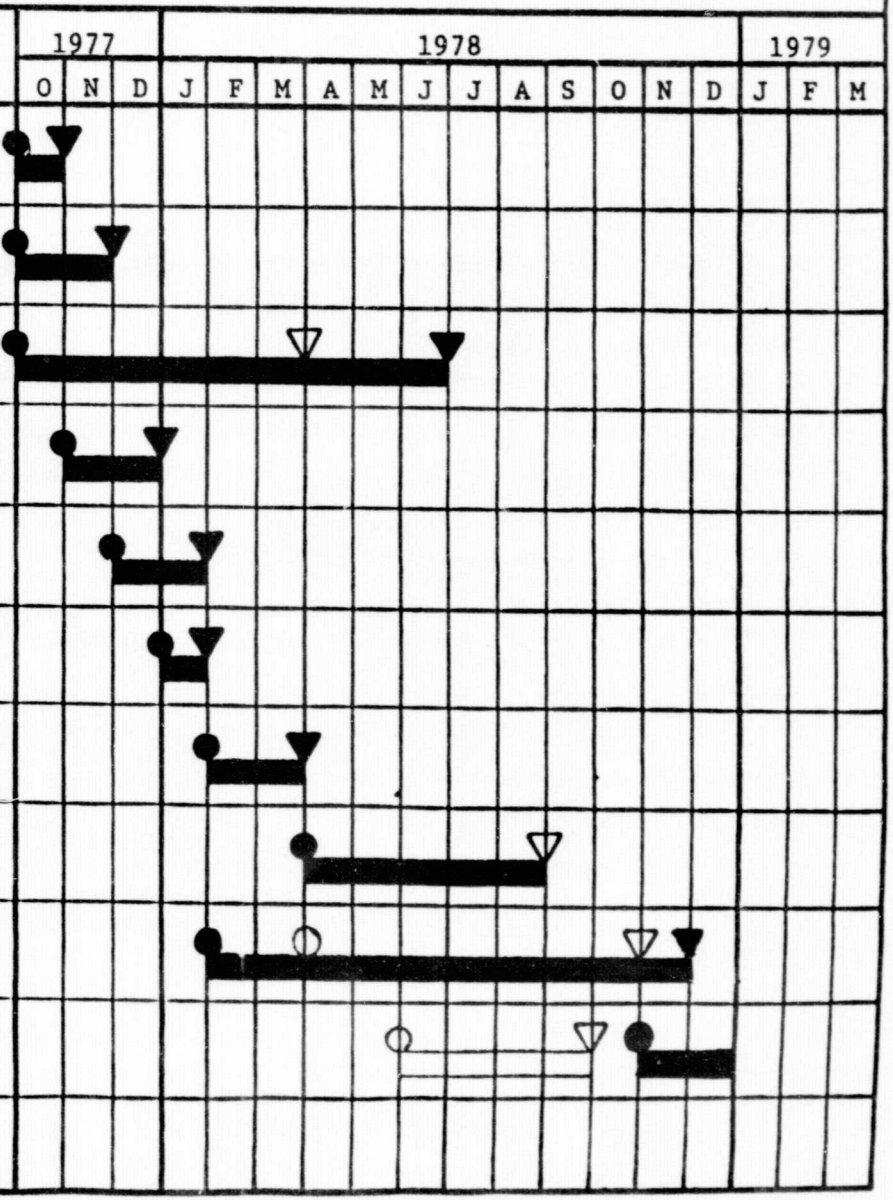


FIGURE 1

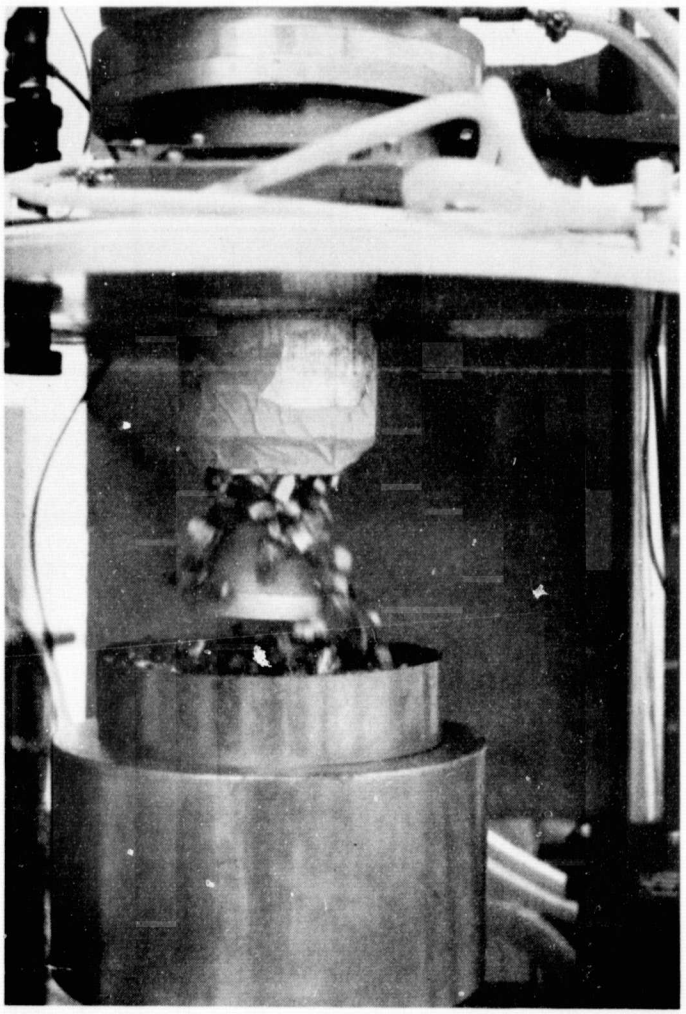


FIGURE 2

SIMULATED RECHARGING USING EXPERIMENTAL

LUMP RECHARGING DEVICE

2.1.3 14-INCH HOT ZONE

The installation of the larger furnace tank was completed. After vacuum leak checking, thermal tests were performed. A standard 12-inch hot zone was placed in the larger chamber to obtain comparative data with earlier runs in the smaller chamber.

It was found that power input was too high in relation to actual temperature. In fact, on the first crystal growth run, melt-down time was much longer than expected. The normal melt-down time for 20 kg is about 2 hours, and the new chamber system required 3-1/2 hours.

This situation was improved by heat shielding and insulation in the lower portion of the furnace. A reflecting shield under the heater and additional base plate insulation reduced melt-down time back to normal. Apparently, the reflectivity of the chamber top and bottom are reduced significantly when the larger chamber is used, resulting in increased heat losses to the chamber walls.

2.2.0 CRYSTAL GROWTH DEVELOPMENT

2.2.1 14-INCH HOT ZONE

As stated above, excessive heat loss problems occurred when the standard 12-inch hot zone was placed in the larger furnace chamber. Therefore, it was decided to postpone 14-inch development work until the growth of 100 kg from a 12-inch crucible was demonstrated. Additional shielding and insulation corrected the 12-inch hot zone problem, and several zero dislocation crystal runs were made with the larger chamber during this reporting period.

2.2.2 RECHARGE RUNS

Table 1 is a summary of the significant runs that have been made on the project. Three recharge runs were attempted in the reporting period, runs No. 19, 21, and 22. Run No. 19 was the largest and most productive run. It lasted 64 hours and produced 57 kilograms of ingot. Recharge material was polyrod feed stock. Although the pulled yield was high, the quality of the crystal ingot was disappointing. Only 56% of the ingot was dislocation free. All crystals turned to polycrystalline growth shortly (within one hour) after dislocating.

Run No. 21 produced 57.2 kilograms of ingot, and, again, structure loss was a problem. Additionally, a water leak developed in the chamber which resulted in excessive silicon monoxide deposits. The run was terminated because the viewports became covered with SiO.

Run No. 21 was terminated on Thursday, November 30, and Run No. 22 was started the following Monday, after cleaning and repairing the furnace. This run showed good promise of achieving the 100 kilogram goal. However, after three recharge cycles and five ingots, the run had to be aborted due

PROGRAM PLAN - CRYSTAL GROWTH DEVELOPMENT

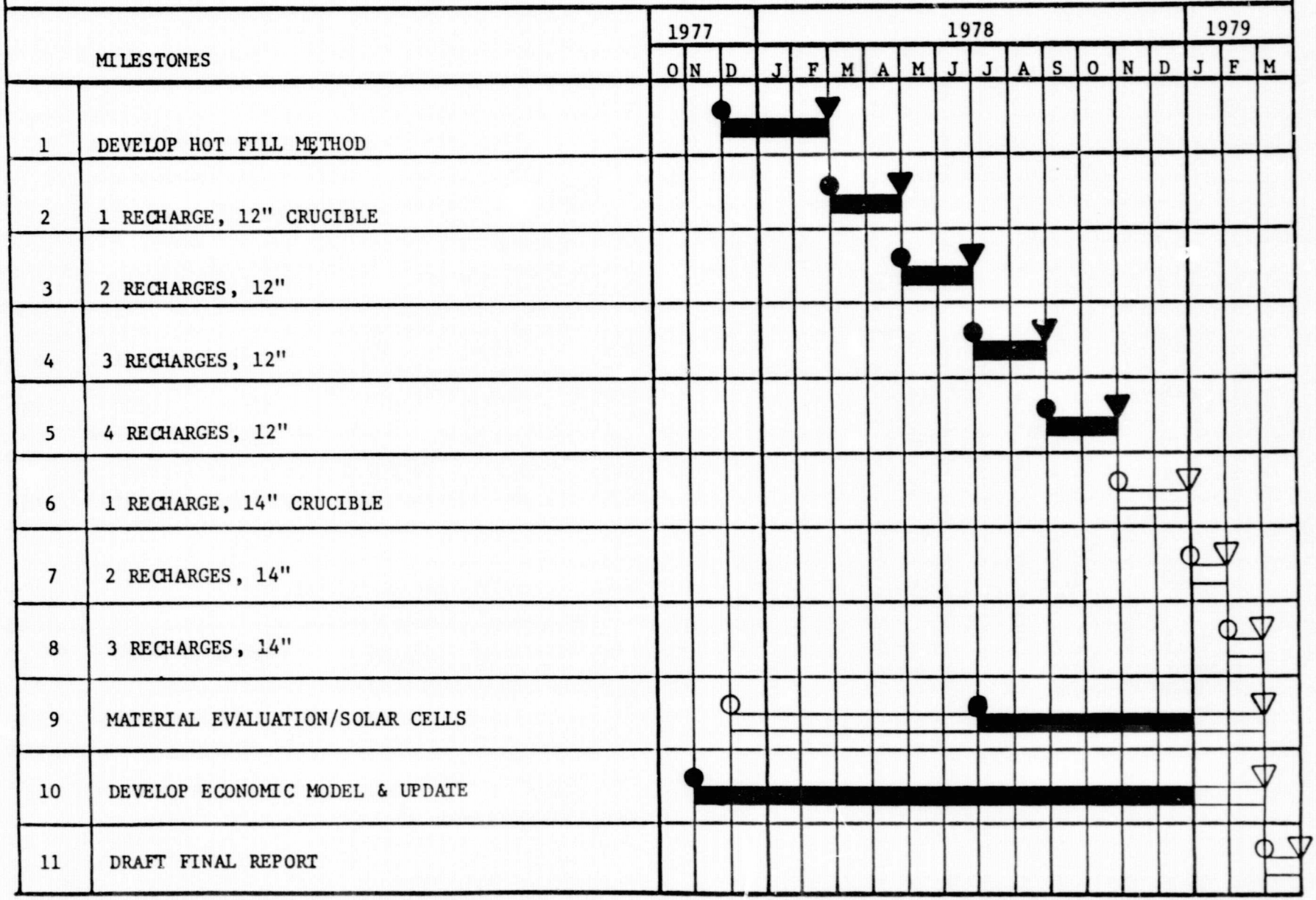


FIGURE 3

CONTINUOUS CZ GROWTH SUMMARY

RUN NO.	TOTAL MELTED (kg)	TOTAL PULLED (kg)	NO. CRYSTALS	DIAM. (cm)	AVG. PULL SPEED (cm/hr)	RUN TIME (hr)	THROUGHPUT (kg/hr)	PULLED YIELD (%)	ZERO DISLOC. (%)
5	25.0	22.0	1	11.0	9.1	18	0.82	88	100
9	31.2	27.1	3	11.2	8.7	39	0.70	87	85
11	48.7	42.5	4	10.7	9.1	44	0.97	87	88
19	63.9	57.2	6	13.3	8.9	64	0.89	90	56
21	55.0	53.4	5	13.3	8.4	44	1.21	97	62
22	52.4	46.3	5	13.3	9.0	50	.93	88	91

TABLE 1

to failure of the cable supporting the recharge feedstock rod. 46 kilograms of high quality ingot were produced in 50 hours.

2.2.3 COST ANALYSIS

The recharge cycle was timed during continuous runs to compare actual experience with the cost estimates in the economic model. The following table illustrates this comparison.

	Estimated	Actual
Cool and remove crystal	40 min.	10 min.
Install new polyrod	5	12
Preheat and lower polyrod	5	14
Meltback	65 (10 kg/hr)	80 (8.1 kg/hr)
Stabilize temperature & seed melt	40	65
Total	155	181

Table 2
Comparison of Economic Model with Actual Experience

Approximately 10 minutes extra were required for the installation of a polysilicon rod during the run because the recharge device was not functioning at the time. This required the pull chamber door to be opened one extra time for each recharge.

The estimated values appear to be a reasonable goal considering the fact that we are still gaining experience with the continuous mode of operation.

The SAMICS format was applied to four methods for continuous CZ growth. Comparisons among these four methods of growth are indicated in Table 3, with the major differences circled. Method No. 1 corresponds to that being presently studied and the details of the calculations and input data were presented in a previous report[1].

SAMICS ANALYSIS OF FOUR METHODS OF CONTINUOUS CZ

CONDITIONS	CZ NO. 1 1979	CZ NO. 2 1980	CZ NO. 3 1982	CZ NO. 4 1986
CRUCIBLE SIZE, DIA. x HT. (in)	12 x 9	14 x 10.5	14 x 11.5	15 x 12
CRYSTAL DIAMETER (cm)	10	12.5	15.2	17.8
GROWTH RATE (cm/hr)	10	10	10	11
NO. CRYSTALS/CRUCIBLE	5	4	4	5
TOTAL POLY MELTED (kg)	105	144	170	260
TOTAL INGOT PULLED (kg)	100	134	160	250
PULLED YIELD (%)	95	93	94	96
USABLE AFTER GRINDING (kg)	87	117	140	219
USABLE INGOT YIELD (%)	83	81	82	84
TOTAL CYCLE TIME (hr)	75	73	75	80
THROUGHPUT (kg/hr), (m^2/hr)	1.2	1.6	1.86	2.74
ADD-ON COST, 1975 \$/m^2	19.24	14.63	12.97	8.56

Table 3

Methods 2, 3, and 4 were developed by assuming an approximately constant run time for each method, i.e. 75 to 80 hours, which seems to be a safe duration, taking into account crucible degradation and equipment maintenance requirements. Increases in diameter and growth rate account for the increase in throughput as one progresses from CZ-1 to CZ-4.

It is further projected that CZ-4 can be achieved by 1986, and utilizes a 15-inch diameter crucible holding approximately 60 kilograms of silicon.

Figure 4 shows the add-on cost of crystal growth for each method versus the number of crystals grown from a crucible. It is evident that the major cost saving occurs when going from one to two crystals. It is also apparent that more than 4 or 5 crystals from one crucible would have little impact on reducing the cost. In fact, one should consider the cost of yield losses due to the additional risk of crucible failure or low quality ingots when doing such a cost analysis. The data suggest also that once 100 kilograms capability has been achieved, then efforts should be directed toward other cost reducing possibilities such as increased growth rates.

The effect of increased growth rate on CZ costs is shown in Figure 5. If the growth rate is increased from 10 to 12 cm/hr, then cost will be reduced from $19.24 to $17.70 for CZ No. 1.

2.2.4 IMPURITY ANALYSES

The question of impurity build-up in the residual melt is often brought up in relation to the growth of multiple crystals from a crucible with periodic melt replenishment.

Run No. 11 was selected for study and samples were sent to JPL for solar cell and impurity analyses. Solar cells were prepared and tested by OCLI. Spark source mass spectrographic analyses were performed by a commercial

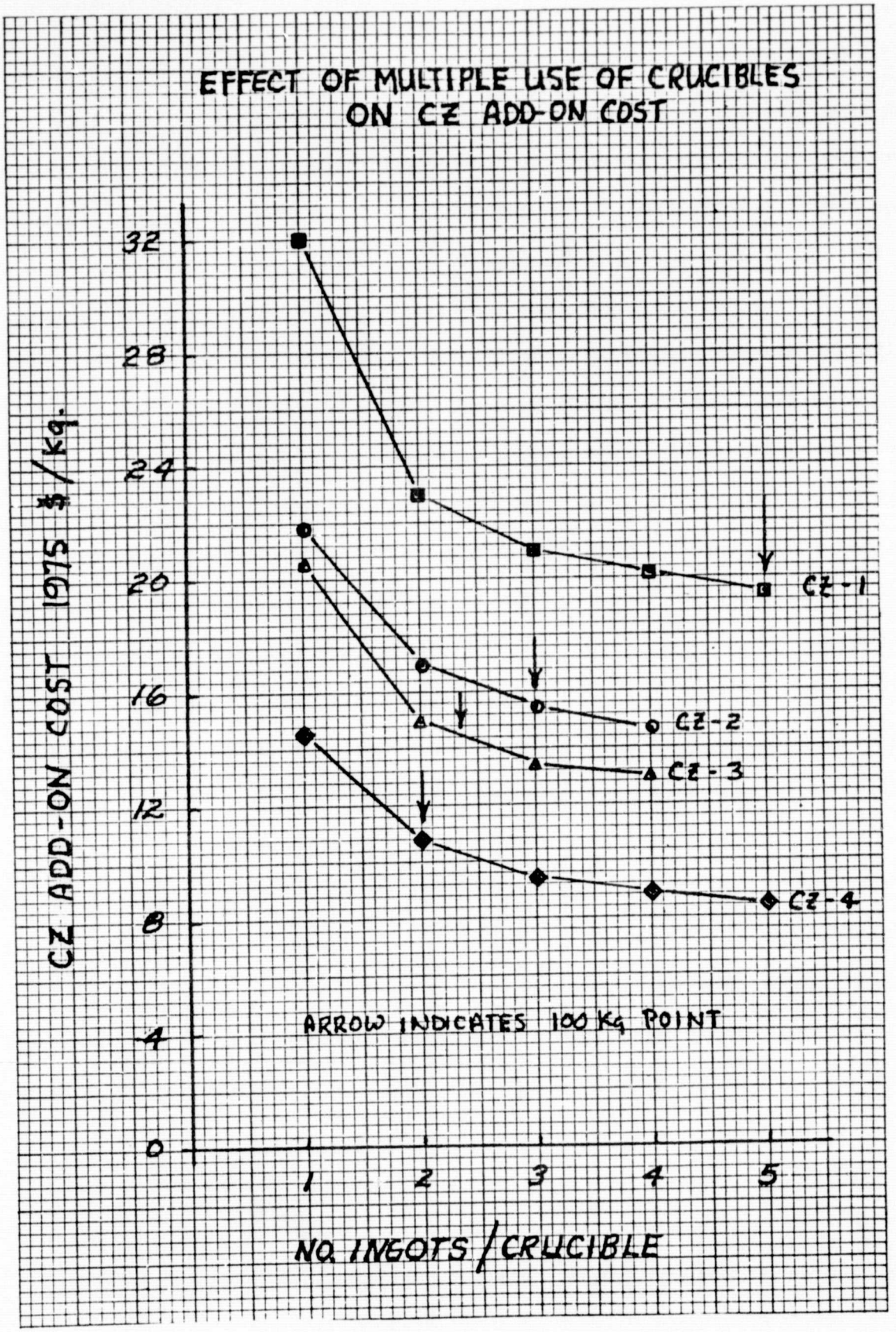

EFFECT OF MULTIPLE USE OF CRUCIBLES
ON CZ ADD-ON COST
CZ ADD-ON COST 1975 $/Kg.
32
28
24
20
16
12
8
4
0
CZ-1
CZ-2
CZ-3
CZ-4
ARROW INDICATES 100 Kg POINT
1
2
3
4
5
NO. INGOTS / CRUCIBLE

Figure 4

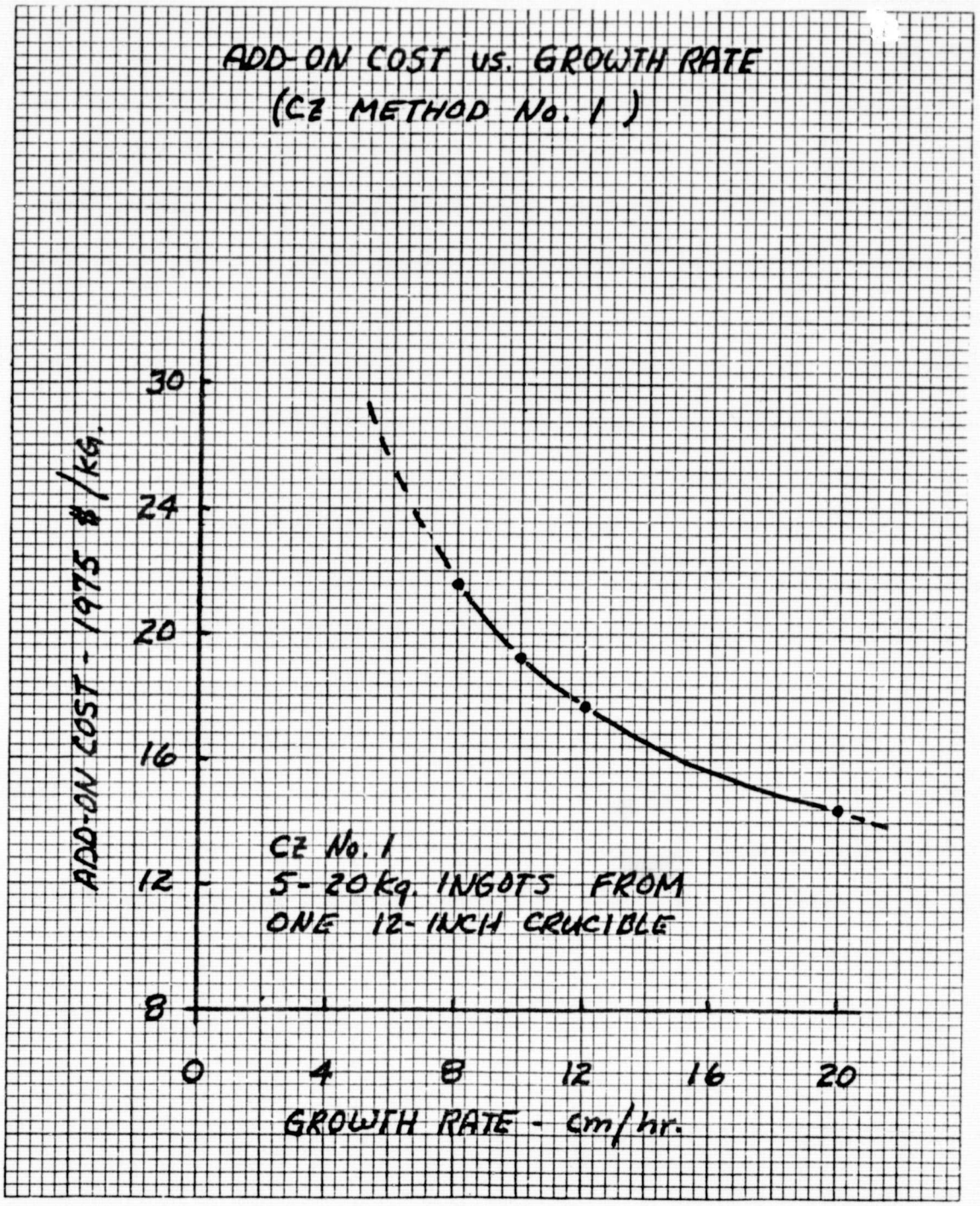

ADD-ON COST vs. GROWTH RATE
(CZ METHOD No. 1)
ADD-ON COST - 1975 $/kg.
30
24
20
16
12
8
CZ No. 1
5-20 kg. INGOTS FROM
ONE 12-INCH CRUCIBLE
0
4
8
12
16
20
GROWTH RATE - cm/hr.

Figure 5

testing laboratory on the raw material and the residual melt, as well as the grown ingots. The results are given in Tables 4 and 5.

A small but consistent reduction in solar efficiency is evident from the first to the last ingots grown in the run. This may be due to the build-up of impurities in the melt as they are segregated at the crystal growth front.

The impurity levels in the grown ingot did, in fact, increase as expected, although more measurements should be made to establish correlations with solar cell efficiency and the segregation coefficients of the metallic impurities. Also, carbon, an element not detected by spark source mass spectrography, should be measured, as it may relate to the structure loss problem.

Analyses of the residual material left in the crucible were erratic, presumably because of the segregation of impurities as the melt solidified. Two fused silica sampling devices were fabricated (Figure 6), one with a U-shaped tube, the other with a shallow boat. These were dipped into the melt before the furnace was shut off. The high surface tension of liquid silicon prevented any liquid from entering the closed tube; however, the boat has been successfully used to sample a small (approximately one gram) sample of the residual melt. Hopefully, this will permit more accurate impurity measurements on the residual melt.

SAMPLES FROM RUN NO. 11 SELECTED FOR
SOLAR CELL AND IMPURITY ANALYSES

SAMPLE NUMBER	DESCRIPTION	RESISTIVITY Ω-CM	SOLAR CELL EFFICIENCY (%) AT AM-0
101	First Ingot, top section All single crystal	2.99	10.4
103	Second Ingot, top section All single crystal	2.74	9.7
104	Second Ingot, bottom section All single crystal	2.57	10.1
105	Third Ingot, top section All single crystal	3.69	10.2
106	Fourth Ingot, top section All single crystal	3.52	9.3
107	Fourth Ingot, bottom section Dislocated material	3.62	9.3

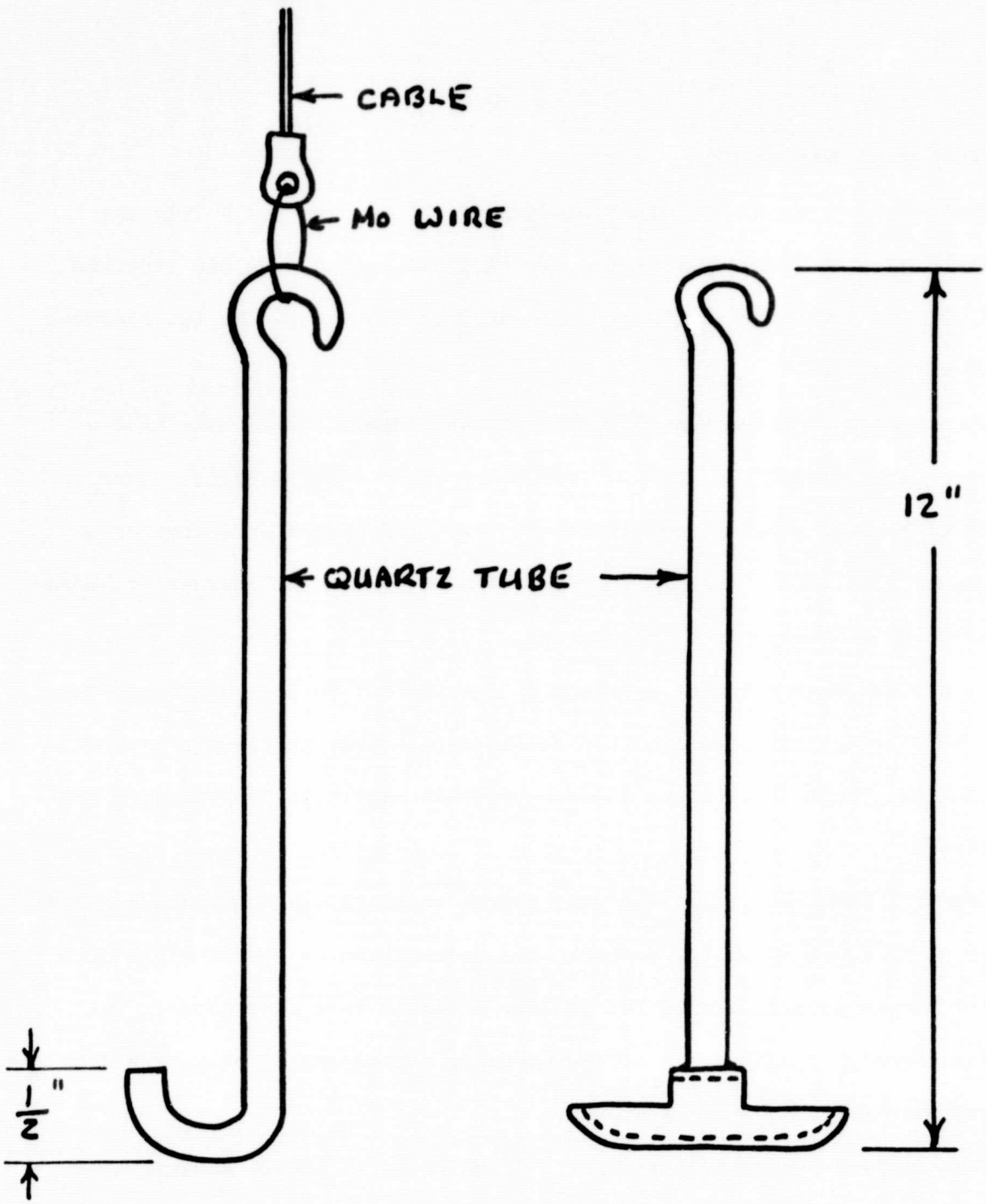
TABLE 4

SPARK SOURCE MASS SPECTROSCOPY IMPURITY ANALYSIS
(ATOMS/CM^3) FOR FEEDSTOCK AND SAMPLES OF RUN NUMBER 11

MAJOR IMPURITY	SEGREGATION COEFFICIENT(2)	FEED-STOCK	SAMPLE NUMBER				
			103	104	105	106	107
		($x10^{15}$)	($x10^{15}$)				
Ag	-	7.67	-	-	-	-	-
Al	2.8×10^{-3}	1.53	0.30	1.03	1.54	10.26*	11.36*
Mn	1.3×10^{-5}	5.10	0.26	0.76	0.50	1.01	1.89
Zn	1×10^{-5}	1.27	-	0.42	-	-	-
Cu	8×10^{-4}	1.95	1.31	2.18	4.36	4.86	9.86
Fe	6.4×10^{-6}	22.2	17.36	24.80	49.59	49.59	50.37
Cr	1.1×10^{-5}	2.39	1.07	2.66	2.66	7.99	8.93
Ti	3.6×10^{-6}	0.86	< 0.58	< 1.16	< 1.45	< 2.60	< 5.76
Mg	3.2×10^{-6}	5.10	1.71	5.69	5.69	11.08*	11.30*
Mo	$\sim 10^{-6}$	-	< 1.15	2.89	2.89	5.77	7.38
Ta		0.15	2.30	4.59	3.06	7.65	8.73
V		-	< 0.05	< 1.54	< 1.54	< 3.08	< 5.69

*Heterogeneous distribution

Table 5



LIQUID SILICON SAMPLING DEVICES

Figure 6

3.0 DISCUSSION AND CONCLUSIONS

There are two major concerns relating to the project goals: (1) the demonstration that 100 kilograms can, in fact, be pulled from one crucible, and (2) the production high quality zero-dislocation ingot. The two concerns are closely related.

The throughput (less than 1 kg/hr) in the longest run to date is low because a large effort was made to grow the highest quality ingot. There appears to be a decreasing probability of zero-dislocation structure as a function of time into a run. Most runs have been terminated because it became impossible to grow high quality material.

It appears that the best approach to the project is to concentrate the effort on solving these two problems utilizing the familiar 12-inch system and delay the conversion to the 14-inch crucible until the 100 kilogram goal is achieved.

Crucible devitrification does not appear to be severe enough to preclude runs of up to 70 or 80 hours. However, the degradation of the crucible wall may play a role in determining the quality of ingot that is produced. The appendix contains a discussion of the possible mechanisms of structure loss as it relates to continuous CZ growth.

Cost analyses of several methods of continuous CZ growth suggest that the cost saving is marginal when more than 100 to 150 kilograms of silicon are grown from a crucible.

4.0 PLANS

The major effort will now go toward achieving the 100 kilogram target.

A study of the causes of structure loss will be initiated in order to improve the quality of the produced ingot.

5.0 COSTS AND MAN HOURS

	Prior Reported	Current Period	Total
Man Hours	5833.0	1612.5	7445.5
Costs	$ 219,719	$ 47,606	$ 267,325

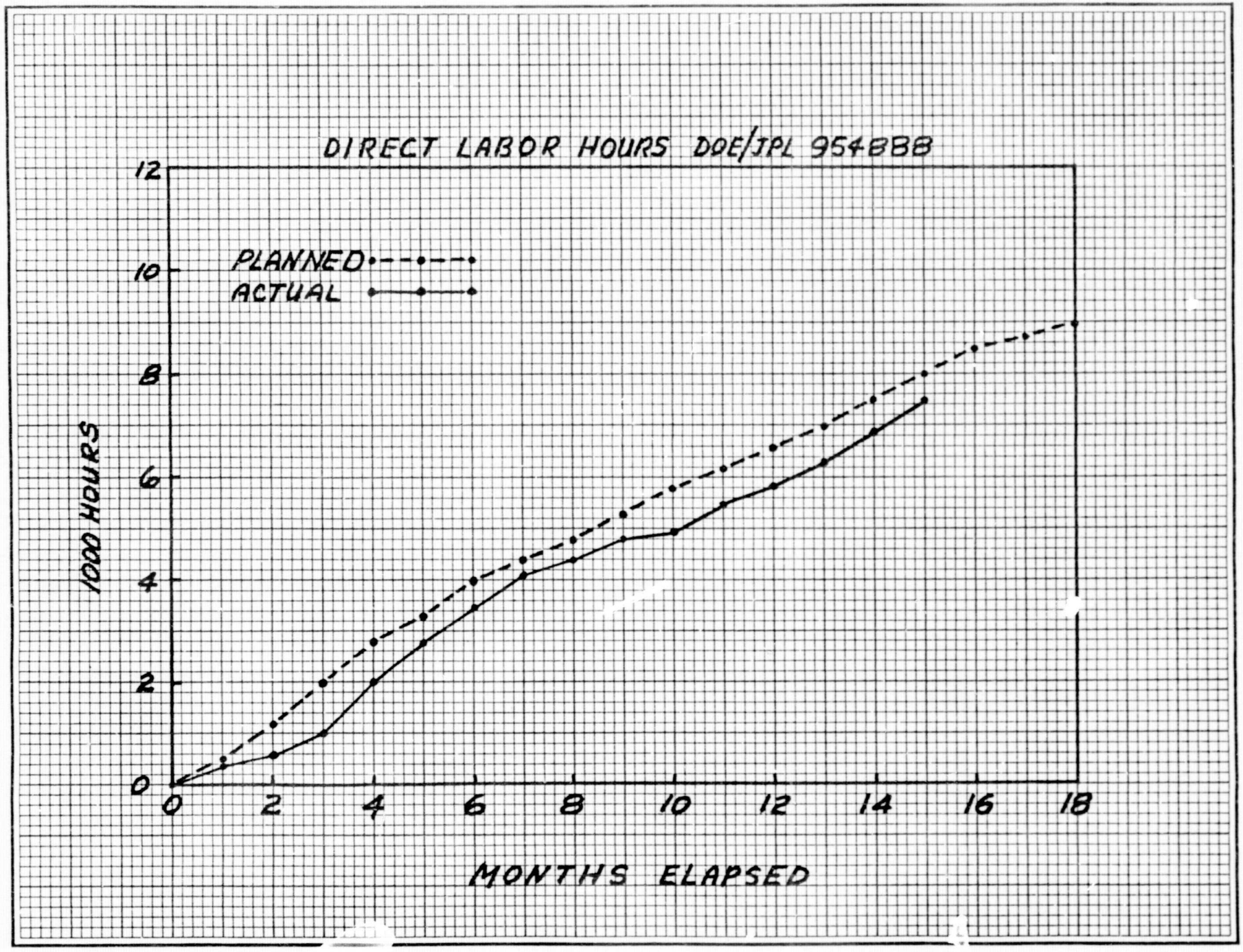

DIRECT LABOR HOURS DOE/JPL 954888
PLANNED
ACTUAL
1000 HOURS
0
2
4
6
8
10
12
0
2
4
6
8
10
12
14
16
18
MONTHS ELAPSED

Figure 7

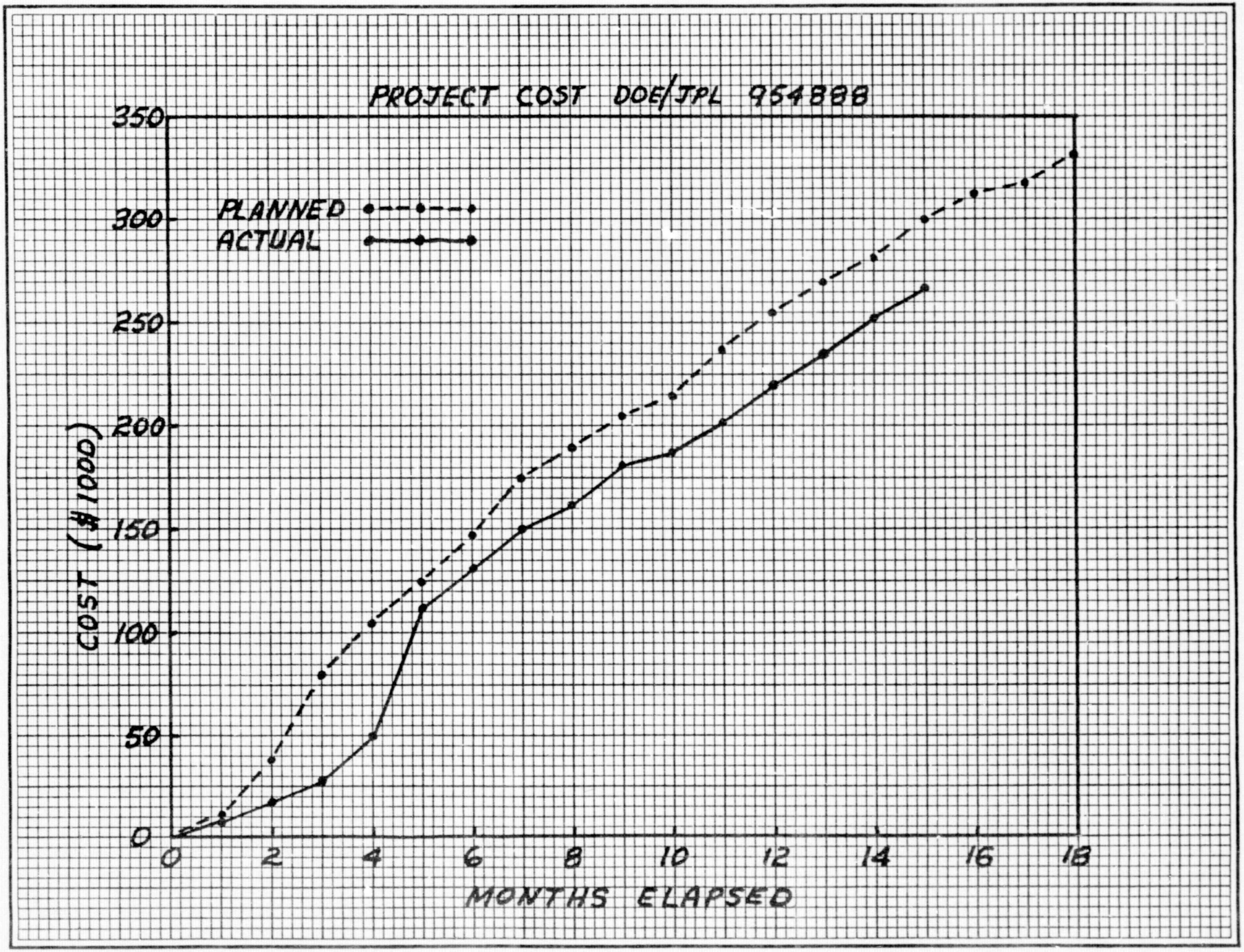

PROJECT COST DOE/JPL 954888
PLANNED
ACTUAL
COST ($1000)
350
300
250
200
150
100
50
0
0
2
4
6
8
10
12
14
16
18
MONTHS ELAPSED

Figure 8

REFERENCES

(1) Lane, P. L. "Continuous Czochralski Growth", First Annual Progress Report DOE/JPL 954888, September 30, 1978.

(2) Hopkins, R. H., et. al., J. Crystal Growth, 42 493 (1977).

APPENDIX

STRUCTURE LOSS IN CZ SILICON CRYSTAL GROWTH

1.0 INTRODUCTION

Silicon single crystals are grown in high purity vitreous silica (commonly called fused quartz) crucibles, in a CZ furnace having an inert atmosphere to prevent oxidation of the silicon. The technology has advanced to the point where large single crystal ingots can be grown with relative ease having no dislocations discernible by etch-pit count. The only defects present in such a crystal are point defects brought about by the thermal equilibrium vacancies or by impurities in the lattice.

By structure loss is meant the loss of this zero dislocation (O-D) structure. When an O-D crystal loses structure, the shock is nearly always severe enough to subsequently cause twinning and eventually polycrystalline growth.

It is considered highly desirable in CZ growth to produce O-D crystals, because the growth is stable and easily controlled, and the resulting material produces the highest efficiency solar cells.

Attempts to grow 100 kilograms of high quality CZ ingots by the "continuous" process (e.g. growth with periodic melt replenishment) have been limited to about 50 kilograms by structure loss problems, and at this point it is not clear what mechanisms are causing the problem, although there are a number of known structure loss mechanisms.

2.0 CAUSES OF STRUCTURE LOSS

Structure loss mechanisms can be categorized into three general areas, (1) mechanical or equipment perturbation such as vibration or shock, (2) thermal perturbation, and (3) melt contamination, especially particulate contamination.

2.1 MECHANICAL PERTURBATIONS

Loss of structure by mechanical upset to the growth process can be caused by poorly working mechanisms, improper design or construction of the grower, or the effects of external shock or vibration on the equipment. Although this is occasionally observed, it is not considered to be a problem with the growth runs on the project. Proper maintenance of the equipment is the best way to avoid mechanical problems.

2.2 THERMAL PERTURBATIONS

Large thermal changes are likely to cause structure loss as they affect the profile of the crystal growth front and the growth rate. Suitable design and maintenance of the hot zone and control systems is sufficient to avoid structure loss by this mechanism. Thermal upset can also be caused by argon flow rate changes, cooling water flow or temperature changes, and, of course, a momentary power loss. Thermal problems are not believed to represent a problem for continuous CZ.

2.3.0 MELT CONTAMINATION

It is well established that a foreign particle in the silicon melt will cause at least the loss of O-D structure, and most likely will cause twinning or polycrystalline growth. Silicon monoxide and quartz particles cause loss of structure, the effect being easily observed by the operator. Silicon carbide particles behave in a similar way in EFG growth. The possibility exists, in CZ growth, that SiO, SiO_2, or SiC could enter the melt. Thus, all are possible causes of structure loss and should be investigated.

2.3.1 Silicon Monoxide (SiO) - This material is formed by vaporization from the melt and subsequent condensation as a submicron powder on cooler surfaces in the furnace. The oxygen that is required for its formation

comes from the crucible or from other sources such as air or water leaks, or impure argon. Although considerably more care must be taken on recharge runs to have a leak-tight system, it is believed that normal SiO deposition as a result of this reaction between liquid silicon and the crucible can be tolerated. Gas turbulence in the furnace must be minimized to prevent dislodging particles from the inner walls. To some extent, gas flow can be controlled in the furnace, directing the deposits to areas that are away from the growth region.

2.3.2 Silica (SiO_2) - Occasionally, silica particles are seen floating on the melt. These are probably due to chips from the crucible produced during the loading or melt-down. Silica is distinguishable from silicon monoxide because it does not evaporate, and the operator waits until the particle lodges against the wall of the crucible before starting a crystal.

Assuming proper care is exercised in loading the crucible and that the crucibles are high quality, then visible silica particles appearing on the melt initially should be very rare.

During long runs, however, microscopic particles of silica may be released from the crucible, which could float to the surface and destroy the crystal structure. Defects in the inner wall of the crucible such as unfused areas, pinholes, blisters or gas bubbles near the surface are potentially sources of particles.

The crucible is also subject to crystallization from the glassy form of SiO_2 to quartz by a process generally called devitrification This occurs at high temperature and is accelerated (or catalyzed) by alkalis, alkaline earths, halides, and, to a lesser extent, a number of

other metallic ionic species. A small amount of devitrification is often observed on the inner surface of crucible walls with no apparent deleterious effect. If devitrification is severe, however, it seems plausible that quartz particles could be released into the melt. There is no direct evidence of this mechanism. However, the degree of crucible devitrification is not predictable and occasionally severe. More investigative work should be done.

2.3.3 Silicon Carbide (SiC) - Little is known about carbon control in CZ melts. Carbon contamination in CZ furnaces occurs, but the mechanism of its production is not clear, and the level of contamination is below saturation in semiconductor grade wafers.

Silicon carbide "scum" can be produced easily in the crystal grower by the use of improperly "baked out" graphite parts. Presumably, vaporized hydrocarbons from the graphitization process react with the melt surface.

In investigating this mechanism, consideration should be given primarily to the crucible as a source of oxygen. Oxygen is then transported to the graphite via direct contact or via SiO production and deposition on the graphite. The carbon monoxide produced would diffuse back to the melt surface.

If the production of CO is unavoidable, the control of gas flow in the furnace should minimize melt contamination by controlling both the transport of SiO and CO.

If there is a CO or CO_2 phase present in the furnace atmosphere due to oxygen from chamber leaks or from the crucible, then gaseous transport of carbon to the melt would appear to be feasible. In long

recharge runs, saturation could occur, leading to precipitation of SiC particles at the growth interface in the supercooled region.

3.0 CONCLUSION

The important structure loss mechanisms, in order of decreasing probability appear at present to be as follows:

(1) Silicon carbide precipitation from the melt.

(2) Release of particles from the crucible.

(3) Silicon monoxide particles falling in the melt.

(4) All other processes, e.g. mechanical, thermal, leaks, etc.