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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

SIXTH QUARTERLY PROGRESS REPORT
JANUARY 1 - MARCH 31, 1979
PROGRAM MANAGER: R. L. LANE
PRINCIPAL INVESTIGATOR: F. MERZ

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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

During the reporting period, a successful 100 kilogram run was performed. Six ingots of 13 cm diameter were grown, ranging in size from 15.5 kg to 17.7 kg. Melt replenishment methods included both poly rod and lump feed material.

Samples from each ingot were prepared for solar cell fabrication and analyses, impurity analysis, and structural studies.

The furnace was converted to the 14-inch hot zone and preliminary heat runs were performed. Two successful runs were demonstrated, by growing 25 kg ingots from 30 kg melts. Also, a 100 kg run was attempted, utilizing the 14-inch crucible hot zone, but was prematurely terminated due to excessive monoxide which accumulated on the viewports and a seed failure.

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, with a number of multi-ingot runs having been performed.

2.0 PROGRESS

2.1 Hot Melt Replenishment--several runs were performed by hot filling the crucible using the lump feeding mechanism to establish the reliability of the method. The method consists of lowering a hopper through the isolation valve and automatically releasing the polysilicon into the crucible.

In order to prevent splashing of liquid silicon, the residual melt was allowed to freeze over partially before recharging. It was learned subsequently, however, that splashing was not a problem, even if the poly is released directly into the liquid, provided the distance from the hopper to the melt is controlled. A method was devised to control this distance by proper positioning of the crucible height prior to recharging. The position of the crucible depends upon the amount of residual melt left in the crucible.

A minor problem that arose was the tendency of fine particles of silicon to scatter and attach to the crucible wall or to fall in other parts of the hot zone. This problem was due to the relatively large quantity of fine particles in the recharge material, most of which was prepared by hand methods from previously grown ingots. Commercial "nugget" or "niblet" polysilicon has very few fine particles, and thus the problem was minimized when commercial lump material was used. Solar grade silicon, if in granular or lump form, would preferably have fine particles removed. Of course, a small quantity of fines will be generated in shipping, handling, and feeding lump material and therefore this problem should be considered in production equipment design.

A comparison between the poly rod and lump methods is presented in Table 1. A general conclusion that one may make is that the poly rod method has less tendency to add contaminants to the melt because the silicon does not contact or abrade a metal container. The lump feeder is faster and allows the crucible to remain cooler during recharging. If a combination of the two methods is used, the lump material is added first and, while this is melting, the rod is preheated, thus speeding up the recharge process.

2.2 100 Kg Run Results--Tables 2 and 3 summarize the results of the 100 kg run (Run No. 30). Table 2 lists the general conditions of crucible size, ingot size, throughput and yield. Table 3 is a summary of the relative amounts of time used in melting, recharging, growth, reseeding, etc.

It is interesting to note that only 50% of the total time is devoted to actual crystal growth at full diameter. About one fourth of the run time was used for the recharge operation. The balance was used in crown growth and final crystal taper.

Although the throughput of 1.2 kg/hr as predicted in the economic model(1) was achieved, it is apparent that, not only increased growth rate should be attempted, but that faster recharging will be very effective in reducing the cost of crystal growth.

The yield of zero dislocation material from Run No. 30 was disappointing. The growth of high quality ingot material was difficult to achieve throughout the run. Several attempts had to be made on the first ingot to achieve a zero dislocation structure. This problem became worse as the run progressed, with all subsequent crystals dislocating part way through the growth cycle.

It is not clear why the dislocation problem was encountered, especially on the first ingot, because that operation was essentially the same as the state of art crystal growth process being used for semiconductor materials. The exceptions to the standard process are: (1) hot filling to about 25 kg in

COMPARISON OF LUMP AND ROD RECHARGING

	Rod	Lump
Recharge Time	Relatively slow - about 4 hours to recharge because rod must be heated slowly at first.	Faster than rod. 2 hours to recharge 18-20 kg.
Contamination of Melt	None, except for handling rods.	Lump contacts metal feeding mechanism.
Effect on Crucible	More reactive with crucible due to higher temperature. Crucible walls remain clean and particle-free.	Crucible temperature lower. Particles may stick to crucible wall.
Convenience	Rod must be notched to hold it.	Convenient.
Capacity of Recharge Mechanism	20 kg rods (18-20 kg recharge capacity).	10 kg hopper must be filled at least twice to recharge.

TABLE 1

SUMMARY OF RUN NO. 30

CRYSTAL INGOT DIAMETER	13.3 cm
AVERAGE GROWTH RATE	8.7 cm/hr
RUN TIME	79 hrs
THROUGHPUT	1.2 kg/hr
PULLED YIELD	99%
ZERO DISLOCATION	27%
TOTAL INGOT PULLED	99.1 kg

TABLE 2

RECHARGE AND INGOT GROWTH TIME (RUN 30)

MELT NO.	RECHARGE TIME (HR)(1)	COMMENTS	CRYSTAL GROWTH(3) TIME (HR)
1	3.5(2)	6.5 kg lump hot filled	5.5
2	4.0	Rod material only, 12.1 kg	7.5
3	3.0	5.0 kg lump plus 11.7 kg rod	7.0
4	3.4	5.0 kg lump plus 11.0 kg rod	7.0
5	3.0	6.2 kg lump plus 10.4 kg rod	6.5
6	2.0	15.8 kg lump	5.7
	TOTAL 18.9 Hr		39.2 Hr

(1) Recharge Time includes: Removal of grown crystal

Insertion of poly

Hot fill

Melt down

Seed preparation up to seeding the melt

(2) Includes cold fill and hot fill time on first melt

(3) At 125 mm diameter

NOTE: Total Run Time = 79 hours

TABLE 3

a 12-inch diameter crucible and (2) the growth of 130 mm diameter ingots.

The formation of dislocation and structure loss mechanisms were discussed in more detail in the last quarterly report(2).

2.3 Sample Preparation and Analyses--Samples were taken from all ingots grown for the purpose of measuring the following:

a. resistivity

b. dislocation density

c. grain size (in poly crystalline ingots)

d. solar cell efficiency and related parameters.

Resistivity measurements as well as dislocation densities and grain size were made at Kayex. Solar cells were prepared and measured at Optical Coating Laboratory, Inc. in City of Industry, California.

A 2-inch section was cut from the top, center, and bottom of each ingot. These cylindrical sections were then quartered by two vertical cuts in the direction of growth (see Figure 1).

2.3.1 Resistivity--Dopant was added to the melt through the dopant fixture after each recharge was complete. The dopant was in the form of silicon/boron alloy pellets. The resistivity of the ingots remained fairly constant throughout the run varying from 2.02 ohm-cm to 2.59 ohm-cm.

2.3.2 Dislocation Density (Table 4)--All ingots had a zero dislocation count at the top. Dislocation density increased as expected, toward the bottom, eventually causing grain boundaries to form and poly crystalline growth. In the poly crystalline material, dislocations seemed to accumulate near

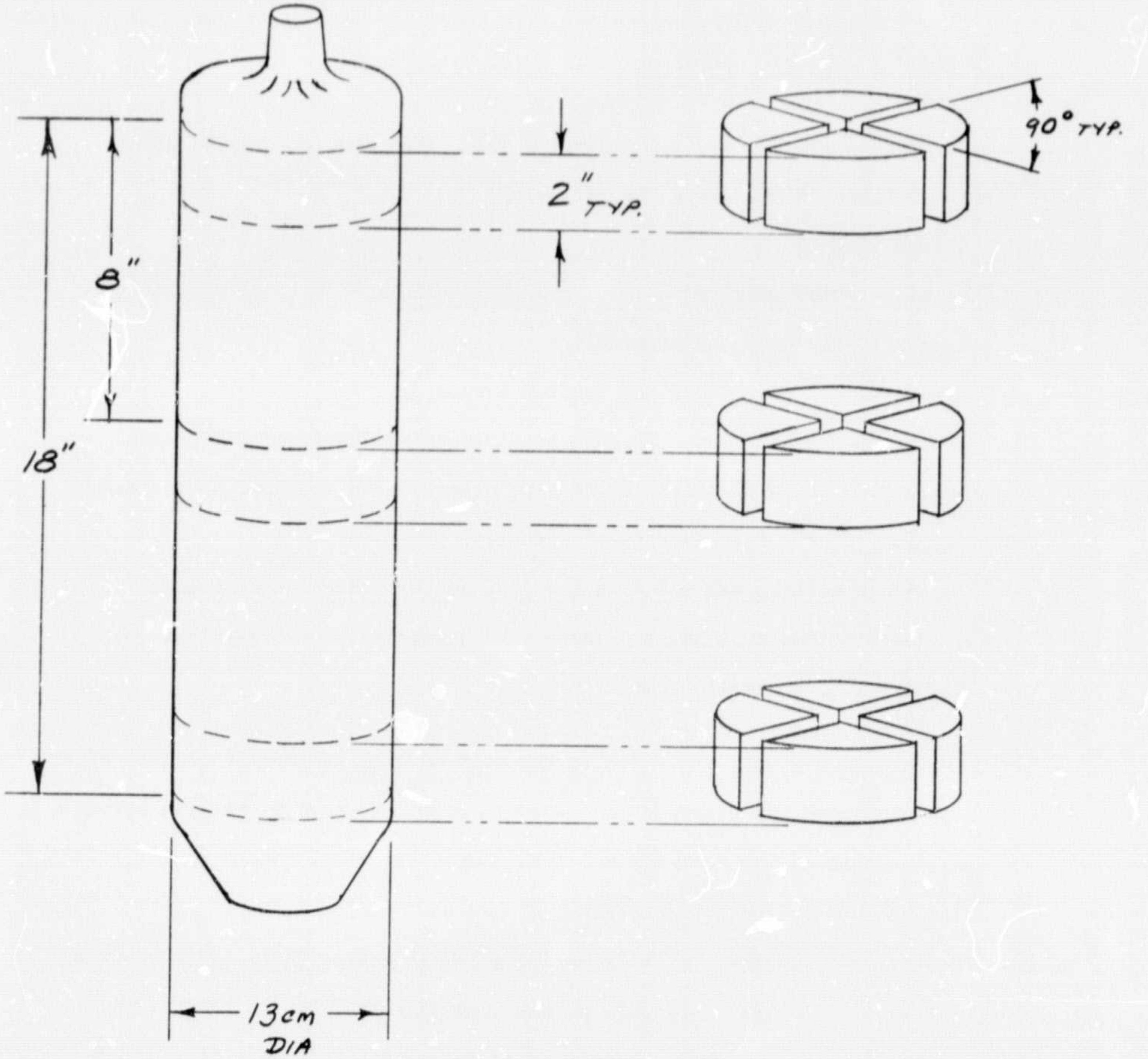


FIGURE #1

DISLOCATION DENSITIES, RUN NO. 30

Ingot No.	1	2	3	4	5	6
Top	0	0	0	0	0	0
Middle	0	Poly	Poly	Poly	Poly	Poly
Bottom	$20 \times 10^3/\text{cm}^2$	Poly	Poly	Poly	Poly	Poly

All poly crystalline samples had irregular dislocation concentrations. Dislocation clusters near grain boundaries were typically separated by areas of low dislocation count within the grains.

TABLE 4

grain boundaries, leaving the centers of grains often nearly dislocation-free.

Ingot No. 1 remained high quality throughout with only some dislocations near the bottom and had no grain boundaries.

2.3.3 Grain Size--Ingots 2 through 6 were single crystal at the top but gradually degraded to poly crystalline growth. Grain size became smaller as ingot growth progressed. Grain size distribution was wide and quantitative measurements were very difficult to determine.

2.3.4 Solar Efficiency and Related Parameters--Table 5 gives the solar efficiency at AM-0 of the ingots grown on Run 30.

Table 6 shows measured diffusion lengths on samples from the top of ingots 1, 3, 5 and 6. Diffusion length was measured using the short circuit response at long wavelength (.8-1.0μm) method. Cell thickness was .015" ± .002" (0.38 mm ± .05).

The highest solar efficiency (11.5% AM-0) ever achieved in this program was measured on a cell prepared from the center of the first ingot of the 100 kg run. This is approximately equivalent to 16% AM-1.

Solar efficiencies of cells made from the 100 kilogram run stayed essentially constant from ingot to ingot throughout the run. This is encouraging, as it indicates that degradation of solar efficiency due to the expected impurity build-up will probably not be sufficient to degrade cell performance. This conclusion is supported also by the fact that the bottom of the last ingot had significantly higher solar efficiency than any of the other ingot bottoms.

Solar efficiency degraded from 15% to 30% from the top to the bottom of each ingot. This would seem to be due to the steadily degrading crystal

AM-0 SOLAR CELL EFFICIENCY, RUN NO. 30

Ingot No.	1	2	3	4	5	6
Top	11.4		11.1	11.3	11.1	10.6
Center	11.5	7.8	7.7	8.7	8.1	7.4
Bottom	8.4	8.7	8.2	8.6	7.8	9.0

Control Samples: 10.5
10.6
10.5

TABLE 5

DIFFUSION LENGTH MEASUREMENTS

Ingot No. Top	Diffusion Length (μm)
1	160
3	80
5	70
6	40

Method: Short Circuit Current Response at long (.8-1.0μm)

Cell Thickness: .015" ± .002"

TABLE 6

structure.

Ingot 1 maintained high quality single crystal zero dislocation structure nearly to the bottom where it dislocated. Thus, the bottom samples had approximately 20×10^3 dislocation per cm^2. This appears to explain the lower efficiency for this sample. All of the other ingot tops were zero dislocation single crystal. The centers and bottoms were large grain poly crystal material, and accordingly very dislocated, especially near grain boundaries. This would appear to explain the lower solar efficiency, although the mechanism of efficiency loss (grain boundaries, dislocations, impurity traps, etc.) cannot be determined easily.

2.4 14-Inch Crucible/Hot Zone--The furnace was converted to the 14-inch hot zone after the 100 kg run was completed.

After a number of test runs utilizing up to 30 kg melts, a 100 kg run was attempted. Some difficulty was encountered with SiO build-up on the viewports; however, the run was terminated when a seed broke on the third ingot. It was concluded that a better seed holding design was needed for growing > 25 kg ingots.

3.0 Conclusions and Discussion

The feasibility of growing 100 kg from a 12-inch diameter crucible has been demonstrated. Solar cell efficiency goals have been met for the ingots grown that have good crystal structure. Efficiency degrades from 15 to 30%, however, if the ingot crystallinity degrades by dislocating or polycrystalline growth.

Thus the major problem is to improve the yield of high quality material.

A number of possibilities have been identified as structure loss mechanisms(2). These all relate primarily to contaminants entering the melt and therefore future work will include investigation in these areas.

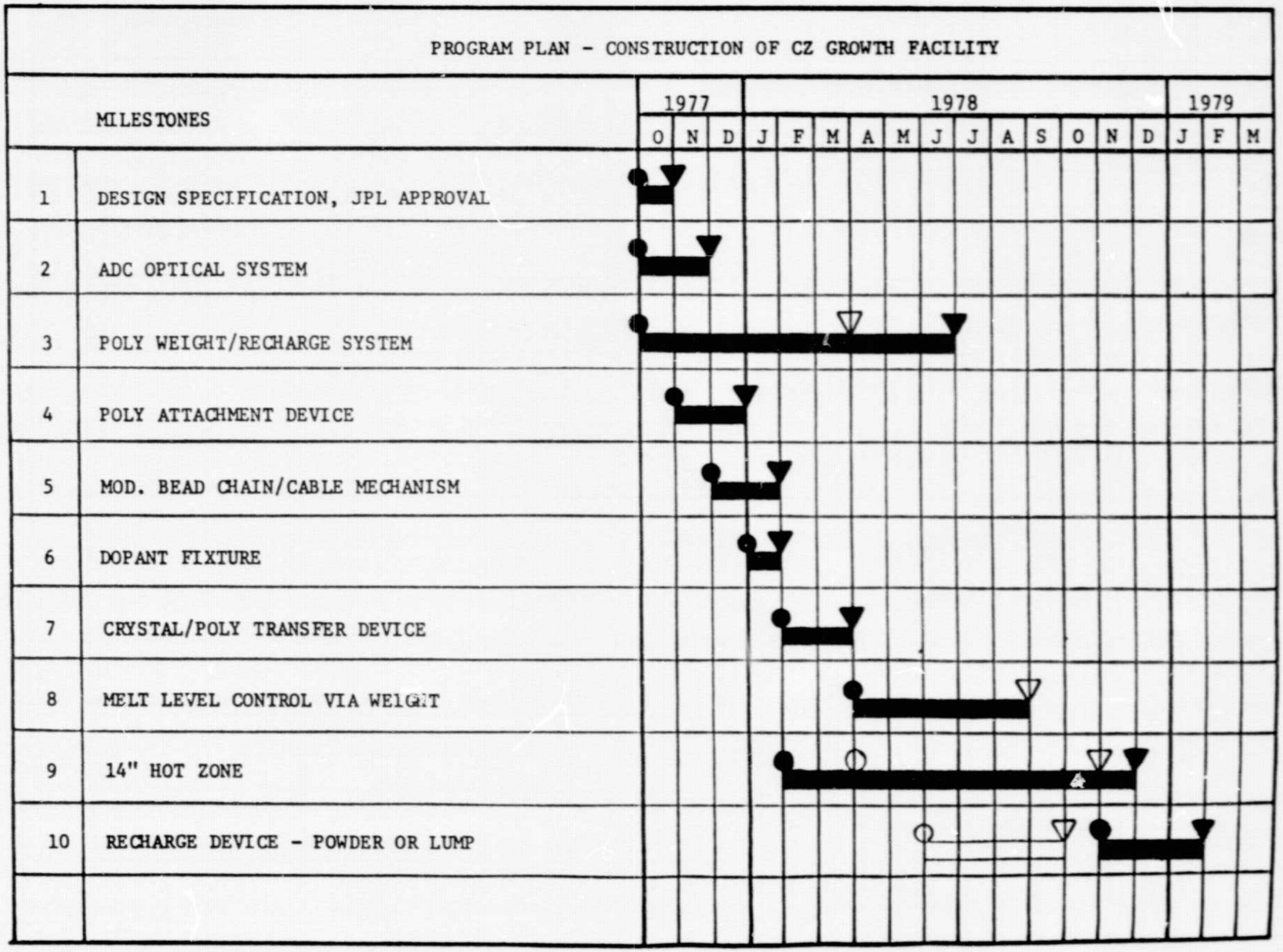
4.0 Plans

The original 18-month program is concluded with this report; however, JPL has granted an extension of the work. The goal of the continued effort is to develop and optimize the process parameters for the growth of 100 kg of high quality ingot from a single melt container.

5.0 Program Plan, Costs, and Man-Hours

The updated Program Plan is shown in Figures 2 and 3; Cost and Direct Labor are shown in Figures 4 and 5.

	Prior Reported	Current	Total
Man-Hours	7,445.5	1,670	9,115.5
Costs	$ 267,325	66,643	$ 333,968


PROGRAM PLAN - CONSTRUCTION OF CZ GROWTH FACILITY
MILESTONES
1977
1978
1979
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N
D
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M
J
J
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S
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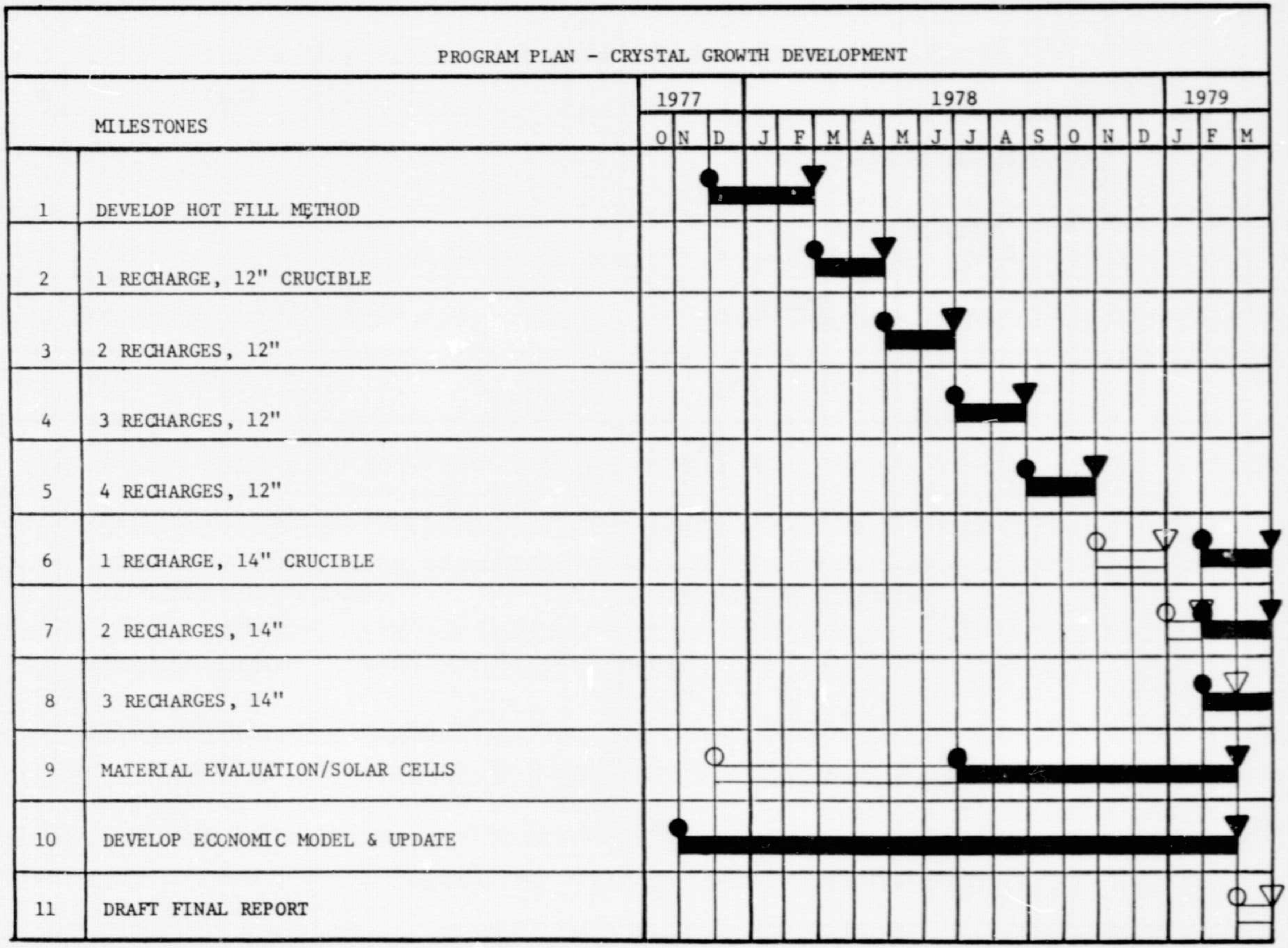
M
1 DESIGN SPECIFICATION, JPL APPROVAL
2 ADC OPTICAL SYSTEM
3 POLY WEIGHT/RECHARGE SYSTEM
4 POLY ATTACHMENT DEVICE
5 MOD. BEAD CHAIN/CABLE MECHANISM
6 DOPANT FIXTURE
7 CRYSTAL/POLY TRANSFER DEVICE
8 MELT LEVEL CONTROL VIA WEIGHT
9 14" HOT ZONE
10 RECHARGE DEVICE - POWDER OR LUMP

Figure 2


PROGRAM PLAN - CRYSTAL GROWTH DEVELOPMENT
MILESTONES
1977
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1 DEVELOP HOT FILL METHOD
2 1 RECHARGE, 12" CRUCIBLE
3 2 RECHARGES, 12"
4 3 RECHARGES, 12"
5 4 RECHARGES, 12"
6 1 RECHARGE, 14" CRUCIBLE
7 2 RECHARGES, 14"
8 3 RECHARGES, 14"
9 MATERIAL EVALUATION/SOLAR CELLS
10 DEVELOP ECONOMIC MODEL & UPDATE
11 DRAFT FINAL REPORT

Figure 3

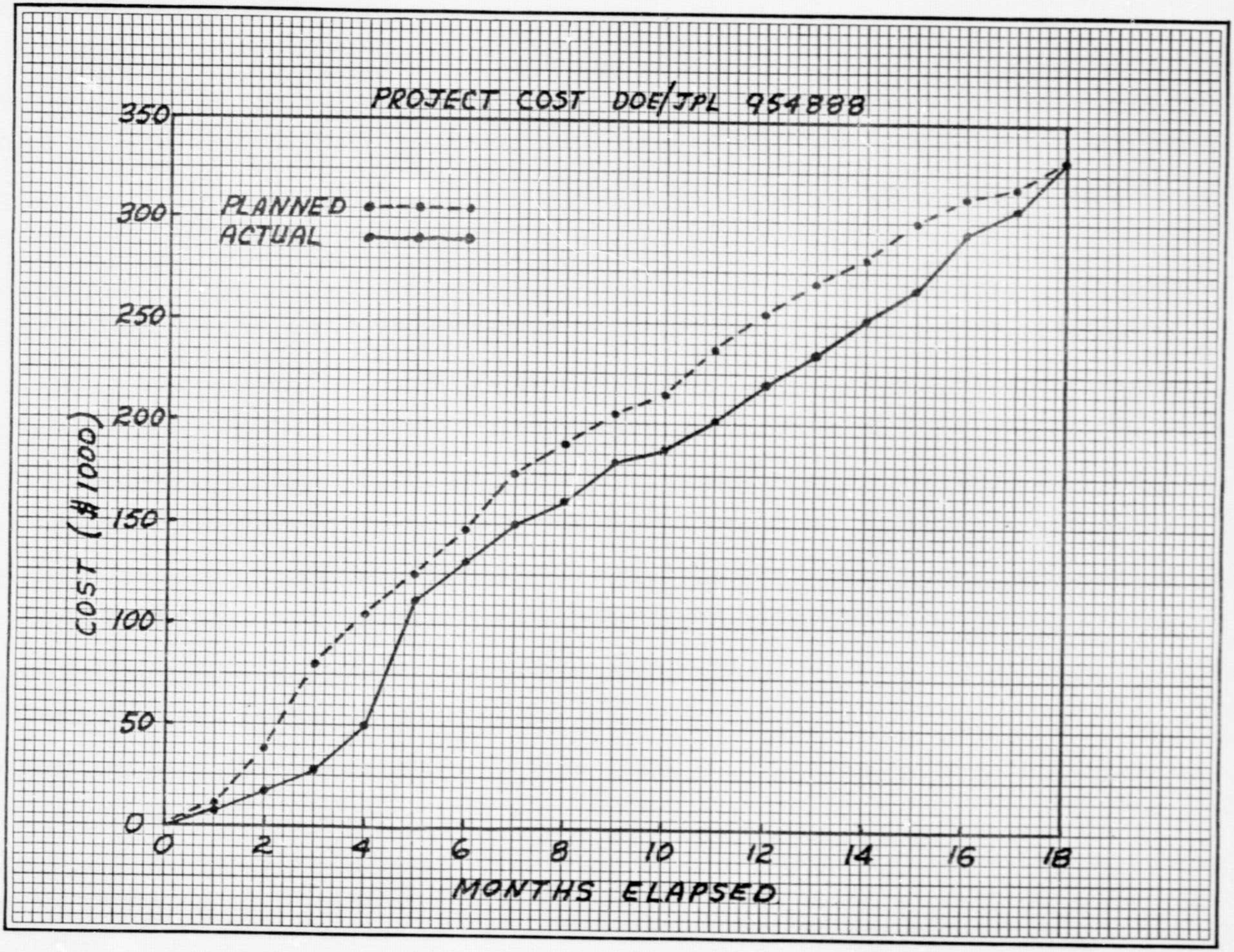
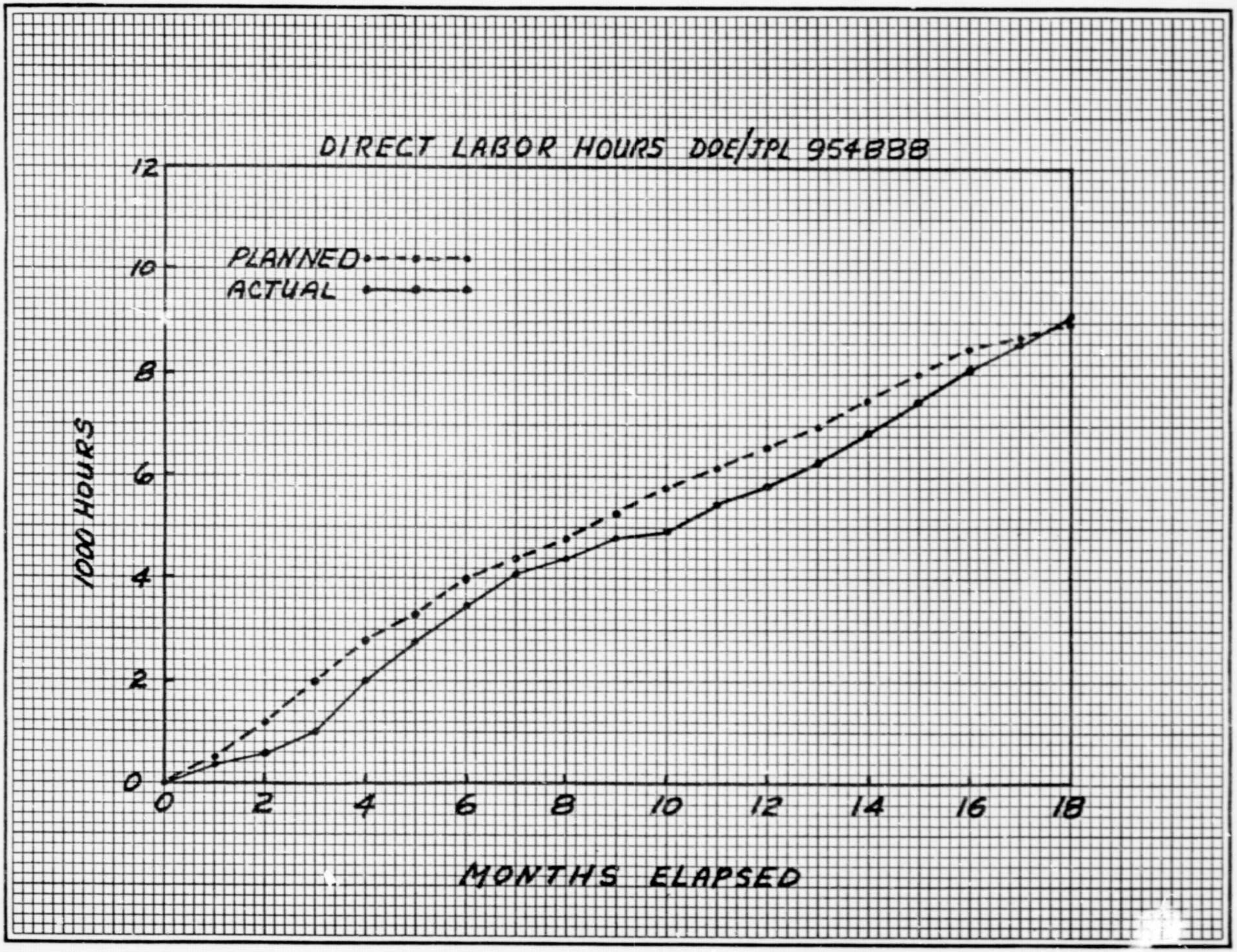

PROJECT COST DOE/JPL 954888
PLANNED
ACTUAL
COST ($1000)
0
50
100
150
200
250
300
350
0
2
4
6
8
10
12
14
16
18
MONTHS ELAPSED

Figure 4


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

Figure 5

REFERENCES

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

(2) R. L. Lane and F. Merz, "Continuous Czochralski Growth", Fifth Quarterly Progress Report DOE/JPL 954888, December 31, 1978.