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INVESTIGATION OF THE IMPURITY
TOLERANCE OF SEMICRYSTALLINE
SILICON SOLAR CELLS
SILICON IMPACT PROGRAM

Quarterly Technical Progress Report No. 1

October 1, 1979 - December 31, 1979

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Sponsored by the Solar Energy Research Institute
Photovoltaic Program Office
Contract No. XS-9-8272-1

FIRST QUARTERLY PROGRESS REPORT

(Covering the Period October 1, 1979 to December 31, 1979)

on

INVESTIGATION OF THE IMPURITY TOLERANCE
OF SEMICRYSTALLINE SILICON SOLAR CELLS SILICON IMPACT PROGRAM

SERI Contract No. XS-9-8272-1

to

Solar Energy Research Institute
Golden, Colorado

from

Solarex Corporation
1335 Piccard Drive
Rockville, MD 20850

ABSTRACT

This First Quarterly Progress Report on SERI Contract No. XS-9-8272-1 covers the work during the period October 1 to December 31, 1979. A Veeco resistance heated Czochralski crystal growing furnace was redesigned to allow for the in-situ casting of semicrystalline silicon ingots. The casting technique that is being employed in this program is based upon the Bridgeman technique of crystal growth.

Samples of metallurgical grade silicon have been obtained from Ohio-Ferro Alloys Corporation and preparation of this material has begun for incorporation into the experimental castings.

Initial casting experiments have commenced using pure semiconductor grade silicon to establish a base line process for later experiments which will employ metallurgical grade silicon.

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I. INTRODUCTION

It has been shown that cast semicrystalline silicon is suitable for use in photovoltaic devices with efficiencies up to 16% (AM1) being reported in the literature.^{1,2,3} To date semiconductor grade silicon has been produced using only pure semiconductor grade silicon which has been developed for the semiconductor industry. The cost of this highly refined silicon is about \$80 per kilogram. By contrast, metallurgical grade silicon is very inexpensive, approximately \$1 per kilogram. It is, therefore, apparent that the cost of photovoltaic sheet material would be lowered if it were produced from a silicon feedstock containing only a fraction of metallurgical grade silicon.

It is the purpose of this current program to provide a scientific basis for understanding the relationship between the key parameters for the formation of semicrystalline sheet material cast from material with a variety of impurity levels, and the resulting crystallographic and photovoltaic cell characteristics. Silicon ranging from pure semiconductor grade to 90% semiconductor, 10% metallurgical grade will be cast into ingots under various thermal conditions which will vary the growth rate and resultant crystal structure.

A necessity in establishing this type of controlled experimental program is a well-characterized source of silicon starting material of known impurity. To achieve this, high

quality semiconductor grade polysilicon will be used throughout the program, with metallurgical grade silicon added in increasing amounts.

Several approaches will be evaluated for deriving a homogeneous metallurgical source. The most likely approach to be taken consists of melting the metallurgical grade silicon in a crucible, allowing it to mix, and pulverizing the resulting material after solidification. An impurity analysis will then be carried out on the crushed material to check for impurity content and uniformity of distribution.

The silicon casting will take place using in-situ directional solidification. This method is based upon the Bridgeman technique of crystal growth. In this technique, silicon will be melted in a resistance furnace, then cooled from the bottom. This will set up a vertical thermal profile, with the solidification front moving from the bottom to the top of the melt. The velocity of this movement (anticipated to be in the range of one to ten centimeters per hour) will be one of the key parameters varied in the experiments.

Various analytical techniques will be applied during the program in order to derive the maximum degree of understanding of the correlation between the process, impurity levels, and the experimental results. The major elements planned are:

- a) Thermal Model: A mathematical model will be developed to describe the thermal environment of the casting parameters such as the thermal gradient and the solidification rate. This model will be used to set the initial experimental conditions, and refined until it corresponds closely to measurements made during experimentation.
- b) Bulk Material Analysis: Bulk material will be characterized for impurities by Spark Source Mass Spectrometry (SSMS) or Neutron Activation Analysis (NAA). This will be applied to the metallurgical grade source material used in casting, and to wafers removed from ingots. An important result of this program will be the measure of the impurity distribution from bottom to top of the ingot as compared to the impurity levels of the original starting material.
- c) Visual Evaluation: Following preferential etch, selected wafers will undergo a visual evaluation and features such as grain size will be recorded as a function of position within the ingot.
- d) Solar Cell Evaluation: Solar cells fabricated will be evaluated for:
 - o light and dark current-voltage characteristics
 - o leakage current temperature-dependence
 - o junction capacitance
 - o quantum yield
 - o light emission pattern

These tests will be performed using standard Solarex techniques, and will be the basic criteria used to judge the applicability of a particular set of experimental conditions to the formation of useable photovoltaic sheet material.

II. TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

1. Experimental Assembly and Calibration

Most of the work in this quarter has centered around redesigning a Veeco, resistance heated, Czochralski crystal puller to allow for the in-situ casting of polycrystalline ingots. The casting technique employed is based upon the Bridgeman method of crystal growth. In this method, the crucible, usually of cylindrical geometry is lowered out of the furnace hot zone in such a manner that the solidification front travels normal to the axis of the cylinder. This produces a well defined directional solidification within the ingot.

In order to obtain the proper thermal characteristics within the furnace it was necessary to redesign the entire heater assembly. The original furnace design employed a graphite "picket fence" heater situated at the bottom of the furnace chamber. This was to allow room for baffles and heat shields above the furnace so the proper thermal gradients for Czochralski growth could be maintained. This arrangement did not leave enough room below the heating element to establish the proper thermal profile for Bridgeman growth. Thus, it was necessary to raise the heater. This could not be done without sacrificing some of the heater height. As this loss of height reduced the hot zone it was necessary to reduce the heater diameter

to maintain a cylindrical hot zone having a height to diameter ratio of 2:1.

These changes in geometry necessitated a change in the thickness of the heaters to keep its resistance within specified limits. This was necessary to match the impedance of the power supply.

The final design is capable of employing three inch diameter, six inch high crucibles. There is enough room below the furnace for heat shields to change and modify the thermal profile plus enough room to lower the crucible completely out of the furnace hot zone to ensure that solidification will occur long before the crucible has reached the end of its travel.

Figure 1 is a schematic representation of the inside of the furnace showing the relative positions of all the major components. The molybdenum heat shields are moveable to allow modification of the casting parameters. Both the rotational and vertical motions of the lower head in this crystal puller are controlled by a chopper stabilized power supply. The power to the drive motors is digitized giving very precise and reproducible control. The vertical motion can be varied in both the plus and minus Z-directions from 99.9 to 0.1 millimeters per minute in steps of 0.1 millimeters per minute, while the rotational motion can be varied in both the clockwise and counterclockwise directions from 99.9 to 0.1 rpm in steps of 0.1 rpm.

FIGURE 1. SCHEMATIC DIAGRAM OF THE INSIDE OF THE SEMICRYSTALLINE CASTING FURNACE

In this particular machine the crucible support rod is water cooled. This is a particular advantage in the present work, for, by varying the material and construction of the crucible support structure, it is possible to vary the heat sinking directly at the bottom of the crucible.

During the casting process the most important thermal parameter to monitor is the thermal profile within the furnace. The temperatures will be monitored through the use of Platinum-6% Rhodium vs. Platinum-30% Rhodium (Type B) thermocouples placed at various heights within the furnaces. The Type B thermocouples were chosen since they do not require any temperature compensation at the cold junction and uncompensated copper wire can be used for lead-in wires. Quartz sheathed thermocouples can be inserted into the melt to obtain a temperature profile within the solidifying ingot. This will enable us to determine the rate of solidification under various thermal conditions. In the colder parts of the furnace Chromel vs. Alumel (Type K) thermocouples can be employed. A multi-point chart recorder will be used to simultaneously record all the inputs.

In addition to using the thermocouples to control and monitor the temperature of the furnace the crystal puller makes use of an Ircon IR temperature sensing system to control the furnace temperature. The output of the detector, as well as its deviation from a set point, is displayed directly

on a chart recorder. Since the output of this IR sensor is not calibrated a Leeds and Northrup model 8632-C optical pyrometer will be used to measure the temperature of the heating elements. This temperature reading can then be correlated to the melt temperature, temperature profile of the furnace, and the power used by the heaters. The change in power needed to maintain a specific furnace temperature over a period of time will be used to indicate the aging of the heating elements.

2. Impure Silicon Starting Material

There are about seven manufacturers of metallurgical grade silicon in the United States. The primary use for this material is in alloying steels and aluminums in foundry type operations. In this type of environment, slight differences in impurity content from one lot to another of metallurgical grade silicon will not be noticed. However, in establishing this controlled experimental program, a well-characterized source of silicon starting material of known impurity is a necessity. To achieve this, high quality semiconductor grade polysilicon will be used for each run, with metallurgical grade silicon that has all the impurity species known and impurity concentrations well established, added in increasing amounts.

Metallurgical grade silicon is very inhomogeneous owing to the way in which it is manufactured. Thus, to ensure

uniformity throughout the course of this investigation it will be necessary to prepare the impure silicon feedstock for the entire program at one time. Two methods of preparing this material have been considered. The first consists of simply pulverizing and mechanically mixing the material. The second method consists of melting the metallurgical grade silicon in a crucible, allowing it to mix well, and pulverizing after solidification.

Typical impurity levels found in metallurgical grade silicon are presented in Table 1.⁴ Except for boron and phosphorous with segregation coefficients of 0.8 and 0.32, respectively,⁵ the segregation coefficients of all the other elements listed are less than 2×10^{-3} .⁵ Thus, after melting and resolidifying metallurgical grade silicon one would still have a significant impurity gradient inside of the ingot. Thus it was decided to simply grind the metallurgical grade silicon starting material so that the particle weight is small compared to the weight that will be added to the castings.

Samples of metallurgical grade silicon were ordered and obtained from Ohio-Ferro Alloy Corporation, Hanna Mining Company, and Union Carbide Corporation (Metals Division). These samples were evaluated for suitability as a source of metallurgical grade silicon for the experimental casting runs. The silicon from Ohio-Ferro Alloys Corporation was found to be the most suitable for the task, since out of

Element	Impurity Concentration (ppma)
Al	4,000
B	40
Cr	< 50
Fe	3,000
Mn	80
Ni	80
P	< 50
Ti	200
V	200

Table 1. Typical Impurity Levels Found in
Metallurgical Grade Silicon

the samples received it contained the least amount of iron.

The task of preparing the metallurgical grade silicon feedstock has begun. In order to minimize extraneous contamination, the impure silicon chunks, which are about four centimeters in diameter, are being ground against anvils made from semiconductor grade silicon. The powder is being graded using a one millimeter mesh sieve. It is anticipated that we will need about five kilograms of impure feedstock to complete this program. Upon completion of preparing the metallurgical grade silicon feedstock samples will be analyzed for impurity content and concentration. This will be used as verification that a uniform feedstock of impure material has been produced.

3. Experimental Casting

As stated above, the casting will take place using in-situ directional solidification based upon the Bridgeman technique of crystal growth. In this technique, silicon will be melted in a resistance furnace, then cooled from the bottom. This will set up a vertical thermal gradient within the ingot. The solidification front will then move from the bottom to the top of the melt as the ingot is lowered from the furnace. The velocity of this movement (anticipated to be in the range of one to ten centimeters per hour) will be one of the key parameters varied in the experiments. The furnace has been designed to accommodate crucibles approximately six

inches high and three inches in diameter. Argon will be used as the ambient gas in order to protect the graphite heating elements and minimize contamination of the melt.

In recent years there has been an extensive search for materials that are compatible with molten silicon for ribbon processes and substrate dipping.⁶ The most relevant candidates for crucible use in the present experiments are quartz and graphite.

Graphite, while available in high purity form, is very expensive in sizes required for these experiments. Quartz, on the other hand, is relatively inexpensive, is in ready supply from a number of sources, and is available in a highly pure form which will not appreciably dope the contained silicon. For these reasons, fused quartz was chosen as the primary crucible material.

Actual experimentation began during the last two weeks of the quarter. A summary of these experiments made during this period is presented in Table 2. It can be seen that none of the runs have been successful. Only two of the failures, runs 1 and 5, can be attributed to system problems, the others have been due to severe fracturing of the ingot due to the differential thermal expansion between the quartz and the silicon.

Ciszek has been successfully employing Union Carbide's CMB graphite as a crucible material using an approach similar

Run #	Date	Silicon Composition	Rate (cm/hr)	Crucible Composition	Remarks
1	12-14-79	SG		Quartz	System Failure
2	12-18-79	SG		Quartz	Crucible Failure
3	12-19-79	SG	2	Quartz	Ingots Shattered upon cooling
4	12-21-79	SG	2	Quartz	Ingots Shattered upon cooling
5	12-27-79	SG		Quartz	System Failure
6	12-29-79	SG	1.33	Quartz	Ingots Shattered upon cooling

Table 2. Summary of Crystal Growth Efforts

to the methods adapted in this study.⁷ CMB graphite is a relatively dense graphite, 1.76 gm/cm^3 , having a maximum grain size of 76 mm. The coefficient of linear thermal expansion of this material closely matches that of silicon in the range of 20-600°C, which appears to be the critical range in which the shattering of the ingot occurs. This material has been ordered and experiments using it as a crucible material will begin next quarter.

Thermocouples have been used to monitor temperatures within the furnace. A Leeds and Northrup model 8690 potentiometer has been employed to measure the thermocouple EMF. This is a single input instrument and, as it is desirable to monitor the temperature at several locations within the furnace simultaneously, taking the data has become cumbersome.

We are planning to obtain a multipoint chart recorder which will greatly facilitate data taking. All inputs can be simultaneously monitored and any slight variations in the thermal conditions can be correlated back to the crystal growth. This new system should be ready during the next quarter.

4. Summary

A resistance heated Czochralski crystal growing furnace has been redesigned to accommodate the in-situ casting of semicrystalline ingots. The necessary modifications have been made and experimental casting has begun. Thermocouples

have successfully been employed in the system to measure furnace temperatures. During the second quarter it is anticipated that the temperature monitoring system will be significantly upgraded to allow more data to be easily obtained.

We are experiencing difficulty with our choice of crucible materials. The ingots are shattering due to the differential thermal expansion that occurs between silicon and quartz. It is hoped that this situation will be remedied by employing crucibles fabricated from Union Carbide's grade CMB graphite.

Samples of metallurgical grade silicon have been obtained from several sources. After an evaluation of suitability, the material from Ohio-Ferro Alloys Corporation was found to be the best due to its lower iron content. Preparation of this material as a feedstock has commenced using a grinding method. It is anticipated that this task will be completed next quarter and a detailed chemical analysis of the material carried out.

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