LOW-COST THIN-FILM POLYCRYSTALLINE
SILICON SOLAR CELLS

QUARTERLY PROJECT REPORT NO. 2
FOR THE PERIOD
JULY 1, 1979 to OCTOBER 31, 1979

Gerard A. van der Leeden

November 1979

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SUMMARY

During this second quarter the following tasks were accomplished;

- a method for the purification of silicon by acid leaching was established;
- a method for an even recrystallization of silicon-on-graphite on a large graphite substrate ($7.6 * 27 \text{ cm}^2$) was developed;
- the epitaxial deposition system was calibratorated;
- a system for depositing contacts was put in operations;
- a system for the evaluation of dark and illuminated (AM1) I-V characteristics of solar cells was made;
- a solar cell was completed to establish remaining laboratory scale production problems.

CHAPTER I: INTRODUCTION

During this period the systems needed to produce polycrystalline thin films solar cells on a routine basis were further developed and some procedures were standardized. At the end of the period a solar cell was made although this was done more in an effort to identify laboratory line production problems than in an effort to make a first generation solar cell.

To better understand the problems involved in the production of these solar cells a schematic diagram of the process steps is given in Figure I. 1. With the number of major process steps involved (thirteen when the grinding of the silicon and the sandblasting are included) it is felt that a reproducible process, and thus a standard procedure, has to be available for each step. Written procedures were not available from the originators of this solar cell process (the solar cell group at Southern Methodist University) and therefore had to be developed at Poly Solar. On the other hand acid-leached, P_2O_5 gettered and etched metallurgical silicon was provided by the S.M.U. group at the start of the program which made it possible to recrystallize silicon without even having bought ground silicon. However all process steps had been carried out previously at S.M.U. in one way or another and thus information on most steps was available on a verbal level.

Some of the procedures that were originally used have already been changed not on the basis of final solar cell efficiency but on the basis of productivity. It is felt that to obtain our goal within the given "Statement of Work" for this contract it will be necessary to produce about 200 solar cells in batches of approximately twenty per batch; this made it necessary for example to bake two graphite blocks in one run.

In Chapter II the purification of the metallurgical silicon will be described. Chapter III deals with the procedures presently being used to prepare the graphite substrates in Chapter IV the recrystallization of silicon is described. Chapter V contains a description of the growth of the epitaxial layers. The other processes are discussed in Chapter VI.

Figure I-1: Process and evaluation steps involved in producing and evaluating thin film epitaxial polycrystalline silicon solar cells.

CHAPTER II: PURIFICATION OF METALLURGICAL SILICON

II. 1 Starting material

So called high purity metallurgical silicon is obtained from KBI, Inc. in Pennsylvania. It contains 0.2% iron (maximum). It is ground by S-G metals in Kansas to -10 to +35 mesh, with the remaining grindings being shipped seperately.

II. 2 Acid Leaching of the Ground Silicon

The first batch of metallurgical silicon to be acid leached at Poly Solar consisted of 3 kg of ground silicon to which 2 liters of aqua regia (a mixture of three parts of hydrochloric acid and one part of nitric acid) were added. This mixture was boiled for about 8 weeks (with acid changes every 5 days) in a spherical 5 liter flask. After this period the remaining liquid was still greenish in color, and since information supplied by SMU stated that a completely colorless liquid should remain further leaching was needed. Since the result still was not satisfactory after 8 weeks it was decided that this might be caused by a difference in the proportion of aqua regia to silicon:

at SMU the ratio used was 0.6 kg of silicon per liter of acid. The silicon was therefore split in two batches of 1.5 kg which were boiled with 2.5% of silicon. After another 5 weeks of boiling the liquid still was not colorless and the process was stopped. A rough test is now used to determine the amount of iron in the remaining liquid:

a sodium hydroxide solution is added to the acid residue and is checked for a ferric hydroxide precipitate.

In the second batch to be acid leached it was found that there wasn't any precipitate after the second 100 hour boiling period and the present procedure calls for a total of four times a hundred hours. Samples of the remaining acid are preserved to be used in the future for analysis of the iron content.

CHAPTER III: PREPARATION OF THE GRAPHITE SUBSTRATE

III. 1 Starting Material

An essential part of the program is the use of graphite as a substrate. Although in principle a 2 to 5 mm thick graphite substrate would be enough, a 15 mm thick substrate is used at present: in that way the graphite can be used both as a substrate and as a susceptor for RF heating. This is the same method as used at SMU.

The graphite used is obtained from POCO graphite in Decatur, Texas. The quality is PLC-1, dimensions are 7.6 cm by 28 cm with a thickness of 15mm. The blocks are band-sawed.

III. 2 Sandblasting

It has been found that a band saw finished surface is too smooth to be wetted completely by molten silicon. By sandblasting about 0.5 to 1 mm of the graphite block this problem can be solved. Early experiments showed that molten silicon will drop off the side of the graphite block during the recrystallization process and although it was found that eliminating any tilt along the width of the susceptor will prevent this to a certain extent, it still occurs. Therefore a small strip with a width of about 1 to 2 mm along the length of the susceptor on both sides is kept covered during the sand blasting. This area will not be wetted during the recrystallization process and thus spills are prevented.

III. 3 Low Temperature Cleaning

To remove particles and oil that contaminate the graphite blocks after the band sawing and the sandblasting the blocks are ultrasonically cleaned with perchlorethylene, methanol and deionized water. The blocks are dried at a temperature of about 100°C in air.

III. 4 Baking

POCO PLC-1 graphite is not high purity graphite. A high temperature baking step is included as part of the graphite preparation. The graphite blocks are simply baked for about 30 minutes at a temperature of 1500°C or higher in a hydrogen atmosphere. A contaminant that is definitely removed is sulphur which redeposits on the cold tube wall during baking and can be identified by its smell. The baking is carried out in a 100 cm diameter quartz

tube with a hydrogen flow rate of about 20ℓ/min. The blocks are heated with an RF generator.

III. 5 Carbon Coating

Graphite is in its industrial form a rather porous material. To prevent the molten silicon from sinking in the graphite the graphite blocks are coated with carbon. The carbon coating is carried out at a temperature of about 1100°C in a quartz tube. Higher temperatures usually result in an increased volume reaction. The gas used is 1.5 percent propane by volume in helium: hydrogen suppresses the pyrolysis of propane. This process takes about 20 minutes, excluding the heating up and cooling down step. After this process step the graphite blocks are ready for the recrystallization of silicon.

III. 6 Discussion of the Graphite Block Preparation

All the process steps described here were essentially developed by the SMU group. Changes made at Poly Solar mainly were directed at a higher throughput. A major difference is the size of the graphite block: at Poly Solar a 7.6 by 27 cm² rather than a 3.8 by 15 cm² block is used. The influence of baking time and carbon coating time on the final solar cell efficiency can obviously only be investigated after a complete solar cell preparation process has been developed.

CHAPTER IV: RECRYSTALLIZATION OF METALLURGICAL SILICON

IV. 1 Starting Materials

The silicon that was used in the recrystallization process described here was metallurgical grade silicon supplied by the Southern Methodist University group. Both acid leached silicon and P_2O_5 gettered material were used. The graphite blocks used were the 7.6 by 27 cm blocks that have been described in Chapter III.

IV. 2 Experimental Set-up

The experimental set-up used for the recrystallization of silicon is given in Figure IV. 1

The RF coil can move over a distance of approximately 30 cm, the quartz tube remains in one position. The graphite block with the silicon on top is mounted in a quartz liner.

IV. 3 Early Experiments

In the first experiments a number of problems were encountered. Major problems were:

- 1) The molten silicon spilled over the side of the graphite block during the recrystallization process;
- 2) The silicon was initially distributed evenly over the graphite block but ended up mostly on the side of the susceptor that recrystallized last;
- 3) A radiation screen that was placed around the quartz liner was locally heated up to too high a temperature once the coil started moving.

The third problem was the first to be solved: the radiation screen was taken out and the coil spacing was adjusted in such a way that initially the silicon melted over a length of about 10 cm while the last part of the graphite was at a temperature only slightly above 900°C . The silicon could be melted and recrystallized over the whole length of the graphite block.

Figure IV. 1. Experimental set-up for the recrystallization of silicon-on-graphite.

RECRYSTALLIZATION OF SILICON-ON-GRAPHITE

- The susceptor is mounted under an angle of 2.8 degrees.
- The coil moves at a velocity of about 1 cm/min.
- A molten zone with a length of 5 to 10 cm is maintained.
- The temperature in the middle of the zone is kept at approximately 1470°C.
- Hydrogen flow rate is 15ℓ/min.

The second problem was more complicated. Although it was quite clear that the graphite block should be mounted under an angle (see Figure IV. 1) establishing the correct angle was rather difficult since the silicon kept spilling off the block. In the end it was decided that rather than sandblasting the silicon over the whole area a 1 mm strip should be left over the total length on each side of the block (see section III. 2). Even after this the silicon kept spilling off but this now usually happened during the end of the process. The spilling problem was finally solved by keeping the temperature in the middle of the molten zone constant during the recrystallization process. Previous to that the power output of the RF generator was set with a variac on the saturable reactor which acts as the power control for the RF generator. After this it was fairly simple to establish the proper value of the angle. With the temperatures and the quantity of silicon (60 grams) used now an angle of $\arctan 0.038$ is used. It is rather difficult to establish the exact temperature in the middle of the molten zone since the temperature is measured with an optical pyrometer and the real temperature is at least 140°C off. However, by measuring the temperature at the recrystallization front and comparing it with the temperature in the middle of the zone it was established that the temperature is approximately 50°C above the melting point of silicon i.e. approximately 1470°C . It should be noted that previously the temperature of the silicon would go as high as 1550°C , at which temperature apparently both the viscosity and the surface tension of the silicon decrease rapidly, which causes the spillovers.

In order to obtain a reasonably flat surface it was found to be necessary to level the graphite substrate accurately prior to the recrystallization. The velocity of the recrystallization front was kept at approximately 1 cm per minute during all experiments. If this velocity is increased dendritic growth immediately results. Although there is no reason to assume that dendritic growth will decrease the final solar cell efficiency, the initial goal is to obtain a flat surface since the highest efficiency obtained at SMU to date was a solar cell with a flat rather than a dendritic surface. It should be noted that the reason for trying to get a flat surface was that it is easier to evaporate contacts through a mask on a flat surface.

IV. 4 Current Problems

At present there are only two easily identified problems left. In the first place the last part of the silicon to solidify "bubbles" up; at the end of the recrystallization the molten zone length can obviously not be kept constant and neither, as it turns out, can the temperature. This causes the silicon to recrystallize at the end from two sides resulting in a silicon "hill" or "bubble" which is approximately 3 to 5 millimeters higher than the rest of the surface. It has also been found that part of the "silicon" must be extremely heavily contaminated with other materials, since the melting point of the "hill" is less than 1300°C . This is not surprising since all the metallic impurities left after the purification steps described in Chapter II will remain in the molten part of the silicon due to the high segregation coefficient of metals in silicon.

The second problem is that the recrystallization front has a peculiar shape which seems to make foreign particles (presumably silicon carbide) move to a position about 10 mm from the side of the susceptor. (see figure IV. 2).

The curved arrows in Figure IV. 2 show the approximate move of particles floating in the molten silicon. They usually end up in the area that is shaded in Figure IV. 2. It would obviously be better if the particles were trapped at the side of the susceptor, since cutting off one or two millimeters after solar cell processing would then remove all particles. It is felt that a different shape of the recrystallization front (such as the one given in Figure IV. 3) might result in the trapping of foreign particles on the side of the susceptor.

Figure IV. 2. Shape of the recrystallization front.
The curved arrows show the movement of foreign particles. The shaded areas show where the foreign particles usually end up.

Figure IV. 3. Preferred shape of recrystallization front.

CHAPTER V.: Epitaxial Deposition of Silicon Layers on Recrystallized Silicon

V. 1 Introduction

The best solar cell made by the Southern Methodist University group (AMI efficiency = 9.75%) had a heavily doped metallurgical silicon substrate. On top of this a substrate a 20 to 25 micron thick, 0.2 ohm. cm layer of n-type silicon and a 2 micron thick graded p-layer was grown. Phosphine and diborane were used as doping gases and trichlorosilane as the silicon source gas. High purity hydrogen is used as the carrier gas. Since the system used at Poly Solar is considerably larger than the one at SMU, deposition rates and resistivity had to be calibrated. This is especially important since the top layer is graded and since future efforts to improve solar cell efficiency will also contain the incorporation of a back surface field or a graded base layer in order to improve apparent minority carrier lifetimes and thereby collection efficiency.

V. 2 Deposition Rate

In the present system (a 100 mm internal diameter quartz tube is used) it is not possible to obtain a constant thickness over the total surface of the $7.6 \times 27 \text{ cm}^2$ susceptor. The front part has a deposition rate which is approximately 20% higher than the middle and the end. The usual solutions to this problem did not work: tilting the susceptor to its maximum possible tilt within the tube dimensions did change the deposition rate but did not have a large influence on the ratio between the front part and the back part. The hydrogen flow rate was limited by the purifier capacity to about 40 l/min. However, it is felt that 20% thickness variation is acceptable at this time. Thickness variations due to doping concentration difference were not observed within the experimental accuracy (about 10%).

V. 3 Doping Calibration

In a single crystal it is in principle possible to measure a doping profile, either by capacitance-voltage measurements or by angle lapping and spreading resistance measurements. The polycrystalline material used by Poly Solar is not suitable for these measurements because the

surface is not flat enough. Of course, C-V measurements could be performed but not in the doping levels (up to 10^{20} cm^{-3}) that are used here. Therefore calibration curves were established for the two doping gasses (phosphine and diborane in hydrogen) giving the resistivity (or doping level) as a function of the doping gas flow rates. Rather than measuring the profile a, presumably reproducible, continuous change in gas flow rates was used. This should in principle lead to a reproducible doping profile which can then be adjusted to obtain the desired spectral response and sheet resistance. It was realized that a redistribution of the doping profile would occur even during the deposition, considering the high temperature (about 1100°C) and the time involved.

The dopant calibration curves are given in figure V. 1 for diborane and in figure V. 2 for phosphine. All experiments were carried out at a hydrogen flow/rate of 40ℓ/min and a substrate temperature of about 1100°C . The flow/rate through the trichlorosilane bath was kept at 15.5°C and the hydrogen flow/rate through this bath was adjusted so as to give a deposition rate of 0.5 to 1.5 micron in the middle of the 7.6 by 27 cm^2 susceptor. Within the experimental accuracy the resistivity was found to depend only on the ratio of the doping gas flow rate and the hydrogen flow rate through the trichlorosilane bubbler.

V. 4 Conclusions

In order to improve the thickness of the deposited layer it will probably be necessary to change the size of the reactor tube: a 120 mm tube may be sufficiently large since this would provide the same ratio of tube diameter to graphite width as used at SMU. However the H_2 flowrate will then have to be about 80 liters per minute which is outside our present capabilities.

Figure 7. 1.

Calibration curve for diborane

Figure V. 2.

Calibration curve for phosphine

VI.: OTHER PROCESSES

VI. 1 Contact Deposition

Titanium-silver contacts are at present deposited. A facility to measure the thickness of the deposited layer will become available in November. Annealing is carried out by heating the susceptor to 525°C for about 10 minutes.

A major problem in this process is that the contacts are deposited through a grid. Since the substrate is not flat the gridfingers seem to be much wider than they are supposed to be: in the order of 0.5mm rather than 0.1mm. It is difficult to see how this can be prevented using any method outside a photo resist method.

VI. 2 Anti-Reflection Coating

Anti-reflection coatings have not yet been applied. The evaporation of silicon monoxide will be used initially.

VI. 3 Evaluation of Solar Cells

The I-V characteristics are measured by driving the solar cell with a bi-polar power supply (Hewlett Packard Model 6825A). This method has the advantage that the voltage and current can be measured in all three applicable quadrants for the illuminated I-V curve. A Hewlett-Packard X-Y recorder is used to draw the I-V curves.

The solar simulator consists of four 150W quartz-halogen lamps with cold light mirrors. The position of the lamps is adjusted in such a way that an area of about 50 cm² is available in which the intensity changes less than 2%. An area of more than 100 cm² is available in which the intensity is constant within 5%. A system for the measurement of spectral response curves has been designed but has not yet been set-up.

VII. First Solar Cell

A solar cell was completed in an effort to check any remaining technical and evaluation problems. The cell characteristic is shown in figure VII 1.

From the characteristic it is clear that the series resistance is too high. At the low current level used the series resistance was not caused by the contact but by the sheet resistance which was too high. The cell area was 280 cm^2 of which approximately 40 cm^2 was covered by a contact grid.

Figure VII. 1. Air mass 1 and dark I-V characteristic of first solar cell.

VIII. Plan for the Next Period

In the next three months the following tasks will be performed:

- A standard solar cell deposition condition will be established.
- An effort will be made to obtain a better temperature profile for the recrystallization of silicon.
- A silver plating method will be developed to reduce contact series resistance.
- An effort will be made to analyze the problems that lead to the low shunt resistance that seems to be normal in this type of solar cell according to information provided by the Southern Methodist University Group.
- The analysis of grain boundary effects at Southern Methodist University will be continued with a view towards passivating them.

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