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LOW COST SOLAR ARRAY PROJECT TASK I—SILICON MATERIAL
GASEOUS MELT REPLENISHMENT SYSTEM

Annual Report for April 1979—April 1980

By
D. N. Jewett
H. E. Bates
D. M. Hill

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Energy Materials Corporation
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Task I - Silicon Material

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JPL Contract 955269

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D.N. Jewett
H.E. Bates
D.M. Hill

Energy Materials Corporation
Ayer Road
Harvard, Massachusetts 01451

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photo-voltaic 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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1. ABSTRACT

1.1 Intent

This 18 month contract is intended to research and develop an innovative method of low cost silicon production from known technology, deposition of silicon from a hydrogen-chlorosilane mixture.

1.2 Task Specifics and Milestones

The contract is divided into four major Tasks and a subcontract for evaluation of silicon produced. Planned time frames are shown in the Milestone Chart on page 2. Month zero is April of 1979.

The goal of Task I is to produce $\frac{1}{2}$ kg/hr. silicon for 24 hours with at least 18% conversion of trichlorosilane to silicon. The Task II goal is to improve the reactor to produce $\frac{1}{2}$ kg/hr. at a minimum conversion of 18% for 96 hours. The goal of Task III is to deliver liquid silicon from the reactor through a tube to a Czochralski crystal puller. Task IV is to operate the production system simultaneously with the Czochralski unit continuously for one week. Silicon produced will be evaluated by solar cell fabrication by Applied Solar Energy Corporation.

PROGRAM PLAN - Milestone Chart - (JPL Contract 955269)

Revised
4-17-80.

1.3 Innovative Reactor

The innovative reactor is a resistively heated quartz vessel; the chlorosilane-hydrogen mixture will flow through the inside of the vessel where silicon will deposit. The deposit will be melted and then drained from the vessel.

1.4 Support Systems

Support equipment will: 1) deliver to the vessel and heat a known trichlorosilane mixture, 2) efficiently insulate the hot vessel therefore reducing power consumption, 3) recover and recirculate hydrogen gas, 4) melt the silicon deposit and allow it to flow from the vessel to a collection box or a delivery tube, 5) monitor gas composition at various points, 6) maintain a slight positive pressure inside the vessel to prevent collapse and 7) collect particles that do not deposit in the vessel.

2. INTRODUCTION

2.1 Gaseous Melt Replenishment - Intent and Status

This contract is expected to provide a near term, low cost source of solar grade silicon; 90% of the first year has been used to design, procure and build a system to test and develop the innovative production vessel design. Equipment procurement caused some unexpected delays and consequently, a re-evaluation and adjustment of the program plan shown on page 2. Four test runs have been completed using inexpensive cylindrical test vessels. Primarily, these runs have allowed familiarization of run procedures and have pointed to major problems which must be solved before larger, more expensive reactors are used.

In anticipation of approval of Tasks III and IV, we have ordered and received a Czochralski unit, and we have begun the design of the silicon delivery tube.

3. INNOVATIVE REACTOR

3.1 Basis for Design

The reactor is based upon known 1) experiments showing silicon deposition in quartz tubes, 2) the Siemens process, and 3) data by Hunt, Sirtl, and Sawyer on SiHCl_3 equilibrium. Predicted benefits and improvements of the design will allow a production rate of $\frac{1}{2}$ kg/hr. silicon at 20% conversion, a dense silicon product, an energy efficient system, and an extended reactor life compared to quartz tube experiments.

3.2 Basic Design and Operation

A schematic cross-section of the reactor system is shown in Figure 1. Polycrystalline silicon is deposited on the inside walls of a resistively heated, multi-walled fused silica reaction chamber by H_2 reduction of SiHCl_3 . After sufficient silicon has been produced, the reactor is flushed with argon and the silicon melted out of the reactor into a Czochralski crystal growth crucible or any other desired container. The reactor is then returned to the deposition stage. The reaction chamber

Figure 1.

Schematic Diagram of
"Poly" Reaction Chamber

(Scale $\approx 5:1$)

and the crystal growth system are separated by a heated delivery tube. The "U-tube" acts as a valve, when the temperature is adjusted above or below the melting point of silicon. A more detailed description of a process cycle is given below:

1. The reactor is brought up to temperature under inert gas flow.

2. A small amount of silicon is melted in the "U-tube" to form a positive gas seal. The "U-tube" temperature is dropped to about 1200°C.

3. At the selected reaction temperature SiHCl_3 and H_2 are introduced into the chamber and their flow rates set to optimize the maximum mass deposition of silicon.

4. The reaction is allowed to run for several hours until the desired amount of silicon has been deposited. This is determined by the desired cycle time and the reactor vessel size.

5. At this point the reactant gases are flushed out of the reactor with Ar.

6. Keeping the "U-tube" at 1200°C, the reactor is raised to about 1450°C to melt down the silicon produced.

7. The gas pressure between the reactor and the delivery tube is equilibrated.

8. The "U-tube" and delivery tube are raised to about 1415°C. When the silicon is melted in the "U-tube", the reactor

will empty due to gravity, causing liquid silicon to flow out through the delivery tube to either the Czochralski crucible or an intermediate replenishment crucible. Due to the equilibrated pressures and a vent to prevent siphoning, the "U-tube" will remain full after the reactor has been emptied.

9. The reactor is returned to reaction temperature and the "U-tube" and delivery tube are returned to 1200°C.

10. The reactant gas flow is then re-admitted to the chamber to start the cycle again.

3.3 Specific Vessel Designs

A square quartz reaction vessel was designed and manufactured.

It is a 10 inch square box of 0.135" thick quartz plates. The bottom is sloped five degrees toward the centered silicon drain tube.

The internal walls are 0.135" thick vertical plates. There are fourteen internal walls; each is 10" high. Some of the internal walls have notches at the bottom for silicon drainage to the bottom center tube. The total internal surface area is 15.28 ft.²; 3.6 ft.² comprise heat exchange surface between the incoming gas and the outgoing gas. The four central walls that comprise most of the heat exchange surface are shown in

Figure 5a to 5b, on page 17 of the First Quarterly Report.

The silicon drainage tube is 6mm I.D. quartz tube with a 6mm I.D. "anti-siphon" vent tube located at the top of the spill-over side of the "U-tube". For a clear description of how the reaction vessel functions with respect to the deposition/melt-down cycle, see the Process Description section on page 3 of the Third Quarterly Report.

The innovative design feature of this reaction chamber is large surface area per volume of reactor (26.4 ft.² surface area per cubic foot) with internal heat exchange capabilities. The reactor is described in the Equipment section of the First Quarterly Report on page 16.

The internal path of the square vessel is a long or "serpentine" path. A short path with parallel walls and an impaction oriented path were also considered. Due to the expense of the first serpentine vessel that was made, alternatives were considered. A six-inch cylindrical tube, 10 in. long with a single baffle down the center was made at considerably lower cost. This is representative of a parallel flow path. Problems occurred securing the center baffle and therefore a similar 6" diameter tube was used with baffles perpendicular to the tube axis. These were simple to make and represent the serpentine or long flow path as well as showing areas of impaction.

4. NECESSARY SUPPORT SYSTEMS

4.1 Description

The five necessary support systems are: 1) the materials handling system, 2) the vessel pressure equalization system, 3) the vessel support system, 4) the material sampling system and 5) the waste treatment system. All of these systems are directly or indirectly connected.

The materials handling system 1) supplies a known pressure and volume of trichlorosilane and hydrogen to the reactor vessel, 2) heats the inlet gases by heat transfer from the hot outlet gases, 3) removes particles from and cools the by-product gases, 4) condenses the chlorosilane by-products from the gas stream and pumps them to storage, 5) removes by-product HCl from the hydrogen gas by means of activated charcoal adsorption and 6) recycles the clean hydrogen back to the reactor as a reactant.

The pressure equalization system continually adjusts the pressure outside of the quartz reaction vessel to about 2" H₂O less than the pressure inside the vessel, therefore preventing the vessel from sagging or collapsing.

The vessel support system is broken into three subsystems:

1. The physical support of the vessel.
2. The power control and heaters.
3. The temperature monitoring instruments.

The outside physical support system is a steel double walled water cooled chamber. Inside, the quartz vessel is surrounded by a graphite box, the main heating elements, another graphite box, 2" of insulation, and a thin stainless steel box which holds the insulation in place. In addition, a water-cooled silicon trap extends below the support chamber. Silicon which is melted from the reaction vessel will drop from the "U-tube" into the trap.

Two power supplies, 24kva and 6kva, heat the Grafoil^R main heating elements and the Grafoil "U-tube" heating elements, respectively. Automatic controllers increase or decrease power according to thermocouple feedback.

Other thermocouple junctions are placed at various places in the support system. Thermocouples approximate the inlet gas, the vessel gas and the outlet gas temperatures.

A Varian 921 gas chromatograph is used to monitor the reactant, the by-product, the post condenser and the recycle gas streams. The sample lines are heated to prevent internal

condensation. Percent conversion can be determined by comparing chromatograph analysis of the reactant and by-product gases.

The waste treatment system is gas-liquid adsorption of any vented chlorosilanes or hydrochloric acid gases into a 10% sodium-hydroxide solution. The HCl from the materials handling system's activated charcoal scrubber is the major source of HCl gas. The purge gas from the chlorosilane storage drum is the major source of chlorosilanes that are scrubbed.

4.2 Operation Results

With few major changes, all the support systems have functioned as designed on the first four runs.

The primary heat exchanger which was intended to heat the inlet gas by heat exchange from the outlet gas has been only slightly effective because the existing gas has not reached the high temperatures expected. This is partly due to the smaller test vessels used which reduces the amount of heat transferred into the gas passing through the hot vessel.

5. DISCUSSION OF RESULTS AND PLANS

After one year we have built the reactor and its five support systems. We have tested four cylindrical vessels that have a single baffle parallel to the axis of the tube.

The first two vessels yielded no deposition results. In both tests hydrogen leakage was detected, but the exact location was not discovered. Operational procedures were familiarized and support systems tested.

The third and fourth runs yielded silicon deposits of less than 20gms. The runs were terminated because of slight hydrogen leakage. The leakage was from the primary heat exchanger because of thermal expansion differences between the graphite body and the S.S. rods which hold the plates of the exchanger together. In future runs moly rods will provide a tightening of the heat exchanger seals as temperature rises rather than the loosening which occurred in runs 1 through 4.

In runs three and four, plugging occurred in the outlet tube of the vessel. The material seems to be a silicon/silicon-oxide mixture. Our next vessel will test two schemes of collecting

the mixture, 1) a trap which includes baffles and additional volume on the hot outlet section of the reactor chamber, and 2) a similar trap in the colder section of the reactor support chamber. If these traps prove ineffective, the primary heat exchanger may be revised or removed because plugging limits batch cycling.

During the first four runs, the initial silicon charge that fills the "U-tube" valve was successfully melted. The materials handling, pressure equalization, and the waste treatment systems worked as designed. More work is needed on the gas chromatograph sampling system.

We are considering the smallest reactor size that will yield $\frac{1}{2}$ kg/hr. silicon at 18% conversion to be the optimum size. The following factors influence the volume and surface area needed to achieve the production rate and conversion percent.

1. Gas temperature
2. Wall temperature
3. Reactor geometry
4. Reaction kinetics
5. Gas phase nucleation
6. Diffusion of by-products from boundary layers
7. Rate of chemical vapor deposition

8. Concentration of reactants
9. Gas flow regime Laminar/Turbulent
10. Particle size
11. Reaction initiation
12. Reaction termination
13. Residence time/average time a small volume of gas is in the reactor

We do not intend to investigate each of these factors. We do intend to investigate the influence of temperature, reactant concentrations and reactor geometry, surface area, volume, and length of flow path.

Some of the influencing factors can be determined by previous experiences. The etching of quartz by HCl at temperatures above 1250°C is documented. We have observed quartz etching in experiments three and four which were run at wall temperatures approaching 1350°C. Therefore, the upper reactor wall temperature will be 1200°C. Data by Hunt, Sirtl and Sawyer predict that at 1200°C at a Cl/H ratio of 0.03 (a large excess of hydrogen) 72% of trichlorosilane could be converted to silicon if equilibrium is reached. For this set of conditions limits become imposed by the necessity of getting a large volume of hydrogen to 1200°C. The theoretical residence time of a small volume of gas in the reactor becomes very short.

This could cause particles that are formed to be blown from the reactor. At high Cl/H ratios, such as 1.0, a maximum predicted conversion efficiency 24% could possibly be reached.

6. CONCLUSION

Our first years work has yielded an operable system to test and monitor silicon production reactors. Four inexpensive reactors were used; all four runs were terminated due to hydrogen leakage. The leak problem has been found and eliminated. We expect to make six cylindrical reactor test runs in the next three months. The results should provide design data for reactors able to produce $\frac{1}{2}$ kg/hr. silicon at better than 18% conversion.