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HIGH VELOCITY CONTINUOUS-FLOW REACTOR FOR THE
PRODUCTION OF SOLAR GRADE SILICON

Second Quarterly Report

By
L. Woerner

MASTER

March 1978

Work Performed Under Contract No. NAS-7-100-954914

J. C. Schumacher Company
Oceanside, California

U.S. Department of Energy

Solar Energy

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HIGH VELOCITY CONTINUOUS-FLOW REACTOR FOR THE PRODUCTION OF SOLAR GRADE SILICON

SECOND QUARTERLY REPORT

L. WOERNER
MARCH, 1978

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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FOREWORD AND ACKNOWLEDGMENTS

This is the second Quarterly Progress Report on a program which began on October 24, 1977. It covers the period December 25, 1977, to March 24, 1978.

During this period, the following individuals made significant contributions to the program:

Mr. E. Moore, Chemical Engineer

and

Dr. J. Schumacher, Project Manager

ABSTRACT

The objective of this program is to determine the feasibility of a high volume-high velocity continuous reduction reactor as an economical means for producing solar grade polycrystalline silicon. Preheated streams of hydrogen and bromosilanes are used as feed to the reduction reactor. Nucleation and deposition sites are provided by the additional feed of preheated silicon particles to the reactor.

During this quarter, the thrust of our efforts has been directed at studying the chemistry taking place in the reactor, determining the factors which influence its course, and making necessary reactor modifications as dictated by observed results. The initial reactor design as described in the first quarterly report⁽¹⁾ has been extensively changed. Energy losses due to gas expansion in the nozzle/mixer section of the reactor dictated these design changes. A "Tee" configuration, in which the two preheated gas streams are merged at right angles without any expansion, has replaced the nozzle/mixer.

The hydrogen reduction of tetrabromosilane with and without the use of silicon deposition substrate particles has given interesting results. Three conditions of thermal energy input to the system have been found to produce these

results, 1) energy from preheated reactants only; 2) energy from a hot reactor wall as well as preheated reactants and substrate particles; and 3) energy from preheated reactants and hot reactor walls. When the preheated gas streams are the sole source of energy input to the mixing area (case 1), an incomplete reduction has been found to take place. The main reaction products isolated in this case are HBr and what is suspected to be hexabromodisilane, Si_2Br_6 . When heated silicon particles are introduced into the reaction and hot reactor walls used (case 2), some silicon deposition has possibly been noted on the particles. In addition, extensive reactor wall deposition of silicon has occurred and a finely divided coating of homogeneously nucleated silicon observed throughout the collection system. The condensate captured in the cold traps is composed of HBr and what is thought to be HSiBr_3 . If silicon particles are omitted from the reaction (case 3), the same homogeneously nucleated Si coating is noted; however, the amount of HSiBr_3 that is found in the condensation traps is very small.

It should be noted that:

- 1) Measurable weight gain (1-2%) of deposition substrate particles could have resulted from either a "scrubbing" of wall deposits or by actual particle growth. Actual particle growth would indicate very favorable kinetics (deposition rate) for the reaction. This possibility

is being evaluated by microscopy studies of the product particles.

2) Homogeneous nucleation does occur.

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I. INTRODUCTION

This is the second quarterly report for a program being carried out by the J.C. Schumacher Company for the purpose of evaluating a continuous high volume - high velocity reduction process for meeting the objectives of the JPL Low-Cost Silicon Solar Array Project. The rationale underlying the approach being pursued in this work was described in the first quarterly report.⁽¹⁾

The reduction reaction being studied in this program can be described by the following idealized reaction:

Both gaseous reactants are first separately preheated to above the reaction temperature. They are then merged and mixed so as to allow reaction (1) to take place. Silicon particles, which have been preheated, are introduced into the mixed gas phase to serve as nucleation and deposition sites. The heated particles also provide a means of delivering more thermal energy into the reaction zone. Two bromosilanes, tetrabromo and tribromosilane, are being used in the program.

In writing this report, it has been assumed that the reader will have the background information given in the first

quarterly report concerning system design, materials of construction, and the initial experimental studies on preheating and thermal stabilities of the bromosilanes. This report concerns itself mainly with Task-3, Reaction Chemistry Studies, as defined in the original program.

II. TECHNICAL DISCUSSION

A. Reactor Modifications and Additions

1. Nozzle/Mixer Subsystem

The initial design of this subsystem was described in detail in the first quarterly report. Its design was based on the known physics and dynamics of gases in ejector-type systems. Although the design promoted excellent mixing of the two preheated gas streams, little or no reaction was noted between the two streams. Five experimental runs were carried with the nozzle/mixer. These runs are labeled L-1 through L-5 in Table 1.

One of the first problems noted with the nozzle/mixer configuration was the inability to attain the desired temperatures in the mixing or reaction chamber. A temperature differential in excess of 200°C was found to exist between the preheated gas streams entering the nozzle chamber and that measured in the chamber. Because the design is dependent on gas expansion to promote mixing, idealized calculations assuming adiabatic conditions were carried out using input pressures and reaction chamber pressures. The calculations predicted a large temperature drop would be sustained due to the adiabatic expansion of the hydrogen stream. The calculations were verified by experimental measurements which were made by

disassembling the reactor and inserting a thermocouple at various locations within the nozzle chamber.

Since the mixing or reaction chamber was run under conditions where no thermal energy was introduced into the reaction area other than that present in the two streams, the rapid expansion caused the mixed streams to cool to the point where the free energy for reaction (1) is no longer favorable. The results given in Table 1 for runs L-1 through L-5 verify this theoretical conclusion.

A design utilizing a Tee configuration has replaced the nozzle/mixer. It has been reported that the Tee configuration provides an excellent mode of mixing two gas streams.⁽²⁾ Complete mixing is usually achieved within three pipe diameters of the point of merging of the two streams.

The initial Tee configuration that was used consisted of an eight millimeter quartz tube, which was the exit end of the hydrogen preheater, and a four millimeter quartz tube exiting the tetrabromosilane preheater. (All diameters are internal.) The tetrabromosilane stream was merged at a right angle to the hydrogen flow. The combined streams were then allowed to mix and react in an eight millimeter tube 13 centimeters in length. Following the 13 centimeter segment, the gas stream was allowed to expand into the remainder of the reactor tube which had a 15 mm internal diameter.

During the initial experiments with the Tee gas mixer, the SiBr_4 preheater was constructed totally from the 4 mm I.D. tubing to equilibrate the individual stream pressures at mixing. This concept was eventually abandoned due to the fragile nature of the 4 mm tubing. (Average lifetime for a preheater constructed of 4 mm tubing was found to be about 2.5 experimental runs.) The current design utilizes 8 mm tubing for both the "Tee" and mixing area. Both preheaters were constructed from the same diameter tubing.

The final Tee design now being used has allowed the attainment of $1,345^\circ\text{K}$ at the point where the two preheated gas streams are merged. This temperature was attained with the Tee being outside of the hot zone of the furnace; that is, no thermal energy was being delivered to the mixing point other than that contained in the two gas streams. Part 3 of this section will discuss the subsequent effect of placement of the mixing Tee on the reaction and reaction products.

2. Substrate Feeder

Several methods were investigated as a means of introducing particles of various sizes into the mixing area. The first method investigated involved heating of the particulate matter in an external furnace, fluidizing and transporting them with a stream of hydrogen to the mixing area, and injection of this stream into the mixing area. Particulate material of -325 mesh and 50 mesh size was used.

Experimental studies showed that material of the -325 mesh size was quite difficult to control with respect to the rate of transport of the material to the mixing area. A large amount of thermal energy was also lost in the transfer process. Use of 50 mesh particles required hydrogen flows that were prohibitively large; that is, nearly 80% of the hydrogen required in the reaction was needed to transport material to the mixing area. With this scheme, large heat losses were also incurred. The fluidizing method was thus abandoned in favor of a gravity feed to the last pass of the hydrogen preheater. Gravity feed precluded the use of the -325 mesh material as this size did not give a freely flowing material. The 50 mesh material, although free flowing, required an excessive volume of hydrogen to sweep the particles into the last pass of the preheater. In addition, the particle containing hydrogen stream excessively lowered the temperature of the

total hydrogen/silicon stream entering the gas mixer.

The system currently being utilized, which has been found to work quite satisfactorily, consists of the following: Silicon particles are allowed to flow by gravity, from a hopper and through a valve which is used to control their rate, into the hydrogen stream which feeds the preheater. The hydrogen stream carries the particles through the complete length of the preheater. This provides a heated path of about 4.5 meters. To insure against plugging of the hopper valve mechanism, the complete hopper unit is vibrated by a small solenoid.

Experiments have shown that this system allows the introduction of an easily controlled, uniform rate of particles to the gas mixer. Little, if any, particle retention in the preheater has been noted. The addition of particles to the hydrogen stream entering the preheater has not presented any problems in heating the particle-laden stream as it has been possible to attain the same temperature for a given flow rate with or without the particles. It has not been possible to determine the exact temperature of the particles; however, it is thought to be near the temperature of the gas stream.

3. Gas Mixer and Particle Input Locations

Figure 1 shows the locations, which have been studied, for the gas mixer and injection of particles. Silicon particles, from the substrate feeder, have been introduced at point (a), which is the inlet to the hydrogen preheater. This location provides a heating path of slightly greater than four meters.

The Tee or gas mixer has been located at points (b) and (c). At point (b), the thermal energy input to the gas mixer is due only to the preheated gas streams and the heated silicon particles. Point (c) allows for the input of thermal energy from the furnace to the gas mixer and reactor tube. The heated reactor tube length is about 0.9 meters, while its total length is about 1.15 meters.

B. Experimental Observations

As noted in the first quarterly report, some silicon deposition was detected in the preliminary runs. During this past quarter, a number of experimental runs, which are tabulated in Table 1, were carried out. The results of these runs were found to differ with respect to energy input into the system and the presence or absence of substrate material. Each case studied and its results are given below. All experiments described were carried out utilizing a Tee configuration for gas mixing and tetrabromosilane as the silicon bearing material.

1. Energy Input From Only The Preheated Gas Streams

This configuration had the Tee and reactor area located totally outside the hot zone of the furnace, point (b), shown in Figure 1. In this configuration, the energy delivered to the mixing and reactor areas is contained completely within the two preheated gas streams. The mixing and reactor areas can be considered to be adiabatic with respect to heat transfer into these areas from any external source. Several different temperatures and compositions were investigated. These are summarized in Table 1 and are designated as runs L-6 through L-10.

A large amount of unreacted tetrabromosilane was collected in the system cold traps; two were maintained at 0°C and two at -78°C. Each of the runs produced a heavy, dense, white fog or smoke which could not be captured by the cyclone separators. Part of this finely divided white material coated the interior of the collection tubes. Heating some of the delivery tubes coated with this material showed that it melted in the neighborhood of 100°C. The material also appeared to be quite soluble in the unreacted tetrabromosilane.

Within the reactor section, that is, prior to expansion of the mixed gas stream, a finely divided cream-to-brown colored coating was detected on the reactor walls. This material

reacted violently with a standard HF-HNO_3 etch solution with the liberation of NO_2 . It has tentatively been identified as amorphous silicon.

In the liquid nitrogen traps of the collection system, a large amount of HBr was captured. The volume of HBr collected could not be accounted for by assuming that it originated from the reduction of tetrabromosilane to silicon. However, if the finely divided white material is assumed to be hexabromodisilane, Si_2Br_6 , then the volume of HBr becomes more realistic. (Hexabromodisilane is a
(3)
white solid melting at 95°C .)

It is probable that the material assumed to be hexabromodisilane originates as the result of an incomplete reaction of tetrabromosilane with hydrogen. The incomplete reaction could result from the following reasons or a combination of them: 1) The two preheated gas streams do not contain sufficient energy to effect the complete reduction of tetrabromosilane to elemental silicon, or 2) the kinetics of the reaction. In the latter case, it is possible that the residence time in the reactor is too short to allow the reaction to go to completion. In summary, this experimental arrangement produced HBr and two solid materials which have tentatively been identified as amorphous silicon and hexabromodisilane.

2. Energy Input From Preheated Gas Streams and Heated Silicon Particles

The position of the Tee and reactor area in this set of experiments was the same as that described in Part B-1. Silicon particles were introduced into the system at point (a), shown in Figure 1. Runs W-1 through W-3, shown in Table 1, give the experimental conditions for temperature, composition, and particle feed rate used in the experiments. No pretreatments, such as etching, etc., were carried out on the 50 mesh silicon particles.

The results obtained in this series of runs were similar to those reported in Part B-1. A finely divided white substance tentatively identified as hexabromodisilane was noted throughout the runs. Minute amounts of amorphous silicon were detected as a film in the reactor. HBr was collected in the liquid nitrogen cold traps and unreacted tetrabromosilane was collected in the other cold traps of the collection system. No particle growth was noted on the particles and the mass of particles collected in the cyclones at the end of each run nearly equalled the starting amount.

The similarity of results tend to indicate that the reasons given in Part B-1 are also probably correct for this series of runs and can be used to account for the observed products. The added energy brought into the system by the

heated silicon particles does not increase the total energy content of the system sufficiently to achieve complete reduction of tetrabromosilane to silicon. In this case, as in Part B-1, nearly all the tetrabromosilane was recovered. Only a small amount was converted to hexabromodisilane and silicon.

3. Energy From Preheated Gas Streams and Heated Reactor Walls

The experimental results described in Parts B-1 and B-2 suggested that a completed reaction, that is, complete reduction of tetrabromosilane to silicon, might be achieved by increasing the amount of thermal energy available for reaction and by increasing the residence time of the reactants in the reactor. Moving the Tee to point (c), shown in Figure 1, achieved both of the factors. This position increased the reactor length to 1 meter and allowed for input of energy over the total reactor length. Residence time in the reactor was increased by a factor of 7 over that used in the previous experiments. Runs W-4 through W-6, given in Table 1, summarize the experimental conditions.

The first significant factor observed in this series of runs was the reduction in the amount of the finely divided white material described earlier. Throughout the reactions, it was reduced to nearly zero. A light brown-to-cream colored, finely divided material which was identified as amorphous

silicon, was found in the collection system directly adjacent to the exit from the furnace hot zone. Polycrystalline silicon was uniformly deposited along the complete length of the heated reactor tube.

Liquids recovered from the various cold traps of the collection system proved to be quite interesting. The material recovered from the traps maintained at 0°C and those maintained at -78°C was not pure tetrabromosilane but, rather, a solution. Density measurements indicated that its density was considerably lower than that of the starting material. (The density of the tetrabromosilane being used is 2.815 grams/cc. Liquids collected in the cold traps had densities of 2.6 to 2.7 grams/cc.)

HBr was collected in the liquid nitrogen traps; however, when the HBr was allowed to boil off, a higher boiling fraction remained in the trap. Exposure of the residual fraction to air caused it to ignite spontaneously. This latter fraction is thought to be tribromosilane or a mixture of the homologs of the HySiBr_{4-y} series. (Tribromosilane, B.P. 111°C, has been reported to spontaneously ignite on exposure to air.

It is assumed that the same characteristic would be displayed by dibromosilane, B.P. ~ 66°C, and monobromosilane, B.P. ~ 1.9°C.)⁽⁴⁾

This series of experiments showed that a complete reduction of tetrabromosilane to silicon could be achieved by increasing the residence time and the total energy available for reaction.

Lower homologs, which were detected, can be accounted for by a number of different mechanisms. The simplest mechanisms are partial reaction of the tetrabromosilane with hydrogen to form the lower homologs, or by reaction of the silicon produced in the reaction, with HBr in the cooler areas of the reactor.⁽⁴⁾ The exact mechanism has not been ascertained at this time.

4. Energy From Preheated Gas Streams, Heated Reactor Walls, and Heated Silicon Particles

The same series of experiments described in Part B-3 were carried out with heated silicon particles being added to the reaction system. The particles were again introduced at point (a) in Figure 1. Runs W-7 through W-10, cited in Table 1, give the experimental conditions.

Results obtained from this series of runs were quite similar to those described in Part B-3. Extremely heavy wall deposits of silicon were obtained throughout the length of the reactor tube. Some weight gain in the particles was also noted; however, it is not possible to speculate at this time whether the gain is due to particle growth or due to a scrubbing of silicon from the walls of the reactor tube. Analysis of the particles for growth has not been completed.

It is interesting to note that the presence of the heated silicon particles appeared to promote the formation of

lower homologs. Volumes of lower homologs collected in this series of experiments were substantially larger than those collected in the runs described in Part B-3. Numerous mechanisms involving the silicon particles could be offered at this time to account for the observations; however, any mechanism offered at this time would be based on pure conjecture. This problem is being studied in more detail.

III. CONCLUSIONS

The most significant points which can be drawn from the experimental work to date are:

1. Tetrabromosilane can be reduced to elemental silicon in the high velocity continuous reduction reactor.
2. Homogeneous nucleation of amorphous silicon does occur in the same reactor.
3. The reduction reaction does not produce a reasonable yield in the experimental reactor being used if the only source of energy is the preheated gas streams and heated silicon particles. Heat must be added to the reactor from an external source.
4. Other products isolated from the reaction are: hydrogen bromide, hexabromodisilane, and lower homologs of the H_xSiBr_{4-x} series.
5. Polymer formation has not been detected in this work.

TABLE 1. RUN CONDITIONS

Run No.	Reactor Temp °K	Pressure Torr	Moles H ₂ / Moles SiBr ₄	Particle Rate g/min.	Notes
Nozzle/Mixer					Fog formed in reactor tube. Liquid condensed in cyclones. Small amount of unidentified solid in the reactor. Almost total recovery of starting volume of SiBr ₄ .
L-1	1012	200	38	-	
L-2	1022	200	33	-	Same as L-1, above
L-3	1030	200	28	-	Same as L-1, above
L-4	1025	760	34	-	Same as L-1, above
L-5	1030	Run aborted, Failure of hydrogen preheater.			
Tee configuration for mixing.					
L-6	1354	760	9.4	-	White, finely divided coating in collection system. Some finely divided light brown material in reactor. HBr isolated in cold trap.
L-7	1331	760	8.7	-	Same as L-6, above

TABLE 1. RUN CONDITIONS (cont'd.)

Run No.	Reactor Temp °K	Pressure Torr	Moles H ₂ / Moles SiBr ₄	Particle Rate g/min.	Notes
L-8	1344	760	6.7	-	White, finely divided coating in collection system. Some finely divided light brown material in reactor. HBr isolated in cold trap.
L-9	1300	760	15	-	Same as L-8, above
L-10	1330	760	12	-	Same as L-8, above
W-1	1341	760	15.5	0.86	Fog or finely divided white solid formed. Recovery of silicon introduced was nearly complete. Some finely divided brown-to-cream colored material recovered.
W-2	1373	760	8.0	1.5	Same as W-1, above
W-3	1353	760	12	2.7	Same as W-1, above
W-4	1319	760	17	-	Wall deposition in reactor. Some lower homologs captured. Reduction in volume of finely divided white solid.
W-5	1325	760	17	-	Same as W-4, above
W-6	1320	760	17	-	Same as W-4, above

TABLE 1. RUN CONDITIONS (cont'd.)

Run No.	Reactor Temp °K	Pressure Torr	Moles H ₂ / Moles SiBr ₄	Particle Rate g/min.	Notes
W-7	1333	760	18	2.2	Heavy wall deposition noted in reactor tube. Liquids in traps had densities which differed from starting material. HBr and lower homologs collected in traps.
W-8	1325	760	16	2.1	Same as W-7, above
W-9	1330	760	17	2.0	Same as W-7, above
W-10	1290	760	17	3.5	Same as W-7, above

IV. PLANS

The remaining two months of the contract will be devoted to increasing both the particle flux and residence time for growth in the reactor. These studies will utilize both tetra and tribromosilane. Efforts will also be directed towards the achievement of a better material balance and optimizing the yield of the reaction.

V. NEW TECHNOLOGY

No reportable items have been identified as new technology.

VI. REFERENCES

1. Woerner, L., "High Velocity Continuous-Flow Reactor for the Production of Solar Grade Silicon," First Quarterly Report, SE-655, ERDA/JPL 954914 - 77/1, December, 1977.
2. Chilton, T.H., and Genereaux, R.P., Trans. Am. Inst. Chem. Engrs., 25, 102 (1930).
3. "Handbook of Chemistry and Physics" 589, 39th Edition, Chemical Rubber Publishing Co., Cleveland, 1958.
4. Schumb, W.C. and Young, R.C., J. Am. Chem. Soc. 52, 1464 (1930).

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Figure 1. Mixing Area Locations