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

Fourth Quarterly Report, June 25—September 24, 1978

By
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September 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

FOURTH QUARTERLY REPORT
L. WOERNER
SEPTEMBER, 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 ACKNOWLEDGEMENTS

This is the fourth Quarterly Progress Report on a program which began on October 24, 1977. It covers the period of June 25, 1978, to September 24, 1978.

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

Mr. Edward B. Moore,
Chemical Engineer

and

Dr. John C. Schumacher,
Project Manager

ABSTRACT

During the past quarter our main effort has been concentrated on investigating the pyrolysis of tribromosilane in a fluid bed reactor. Excellent results have been achieved in this area with the yields running in excess of 90% of the theoretical possible for the reaction given below.

An average growth rate of 0.5 microns per minute, based on starting and ending sieve analysis data for the bed, has been noted. This coating on the particles is a very fine nodular coherent coating.

Since the reaction cited above generates 3 moles of SiBr_4 for each mole of Si, an investigation was begun to determine if SiBr_4 could be converted to SiHBr_3 by reaction with a heated bed of silicon and hydrogen. Preliminary experiments have shown that this is readily feasible. This factor allows the description of closed loop process in which only silicon is consumed and produced. The cycle is given below.

Decomposition

Conversion

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I. INTRODUCTION

This is the Fourth Quarterly progress report for a program being carried out by the J. C. Schumacher Company for the purpose of evaluating a continuous high volume-high velocity hydrogen reduction process for bromosilanes as a means for producing low cost solar grade silicon. The concept underlying the approach was described in detail in the first quarterly report⁽¹⁾; however, to refresh the reader's mind a brief discussion will be given.

The concept involves the thermal reduction of bromosilanes with hydrogen in an environment containing heated silicon particles. These particles serve as both nucleation and deposition sites. The following idealized reaction best describes the systems being investigated:

where $x = 0$ or 1 .

Each reactant is separately preheated to a temperature where ΔF for the reaction is less than zero. They are then mixed in the presence of heated silicon particles, allowing the reaction to proceed and deposition to occur on the substrate particles.

During the first three quarters the bulk of our efforts were concentrated on studying the reduction of tetrabromosilane. This work was carried out in basically two different types of reactors. These were:

1) A cocurrent or horizontal tubular reactor. 2) A countercurrent vertical reactor, (cocurrent and countercurrent refer to the direction of the heated silicon particles with respect to that of the mixed gas stream). The operation and design of these reactors was discussed in detail in the First⁽¹⁾ and Third⁽³⁾ Quarterly Reports.

Data presented in earlier reports^(2,3) indicate that it is possible to deposit silicon from tetrabromosilane in both of the reactors; however, conclusive particle growth data was not obtained in either of the reactors. In part, this was due to the extremely short resident time of the particles in the reactor. In order to increase the particle residence time and to obtain particle growth data, fluid bed reactor studies were initiated. Minimal success was obtained with tetrabromosilane in this reactor. When low hydrogen to tetrabromosilane ratios were used, etching rather than deposition was noted.

During this past quarter, studies on the use of tribromosilane in a fluid bed reactor were carried out. These studies were initiated during the third quarter and some preliminary results were reported in the Third Quarterly Report. (3)

Section II of this report describes the results of preheating and fluid bed reactor studies utilizing tribromosilane as the reactant. It also presents some initial results on the conversion of tetrabromosilane to tribromosilane to effect a closed-loop process.

II. TECHNICAL DISCUSSION

II.0 Introduction

Throughout the past quarter our efforts have been devoted to studying the decomposition of tribromosilane to silicon. These studies were initially carried out in a heated quartz tube and later extended to a fluid bed reactor. The results obtained from these studies also initiated some preliminary studies on converting tetrabromosilane to tribromosilane. Each of these areas are discussed individually.

II.1 Tribromosilane Properties

Tribromosilane is a colorless liquid which spontaneously ignites on contact with air. It has a boiling point of 109°C - 111°C and a freezing point of -73°C. Its density is 2.7 grams/ml. It is normally synthesized by the method of Schumb⁽⁴⁾ which uses the reaction of hydrogen bromide with powdered silicon at a temperature of about 350°C. A SiHBr_3 yield of about 50% is obtained at this temperature; however, at higher temperatures the yield of tribromosilane decreases.

Ignition of tribromosilane in air produces an orange-white flame similar to silane. Fires can readily be extinguished with water or by blanketing the area with a dry inert gas such as argon or nitrogen.

II.2 Preheating Studies with Tribromosilane

The first series of experiments to determine the thermal stability of tribromosilane were carried out in a 10mm O.D. quartz tube, resistance heated with Kanthal type A-1 wire. Several different temperature zones were fabricated along the length of the tube. Tribromosilane was metered as a liquid and flash vaporized into the reactor tube. The effluents from the reactor were collected in cold traps maintained at liquid nitrogen temperature.

In the initial experiment the various zones were held at temperatures ranging from 500°C to about 975°C. Inspection of the tube after the run showed a very light deposit of silicon starting in the temperature region of 550°C and becoming heavier in the 700°C to 900°C region. Above about 900°C no silicon deposits were noted.

The experiment was repeated with the reactor tube being maintained at a temperature of 700°C to 875°C.

In this case silicon was deposited over the total length of the tube. Some homogeneously nucleated silicon was obtained in the first trap. Subsequent analysis of this material showed it to be particles slightly less than one micron in size and of crystalline rather than amorphous nature. Hydrogen was isolated as one of the reaction products as well as tetrabromosilane. The silicon deposited on the tube wall appeared to be very finely grained and the deposit did not display a nodular type deposition.

Another experiment was carried out with the tube being held at a temperature in excess of 900°C. Inspection of the tube showed that a slight deposit of silicon was noted at the inlet where the temperature of the gas was known to be below 900°C, no silicon was noted in the 900°C or greater region and a deposit of silicon was noted at the exit where the temperature was again known to be below 900°C. Analysis of the effluent products captured in the cold traps indicated the presence of a large amount of hydrogen bromide.

The fact that the effluent reaction products differ with temperature and the absence of any silicon deposition above 900°C suggests that possibility of two different reaction paths as a function of temperature. For example,

the silicon deposited in the region below 900°C could be explained by the following sequence of reactions:

That the above sequence is possible can be inferred from the fact that trichlorosilane is known to redistribute at about 350°C ⁽⁵⁾ and redistribution of trichlorosilane to silane in good yield using an amine ion exchange resin has been reported by Union Carbide ⁽⁶⁾. It is also well known that organobromosilanes as well as organochlorosilanes redistribute readily ^(7,8). Addition of reaction (2) through (5) yields the following:

Free energy calculations based on the data presented by Sirtl and Hunt ⁽⁹⁾ indicate that reaction (6) is favorable in the 700°C to 900°C range.

The absence of silicon deposition above 900°C could possibly be explained by the following set of reactions. When the temperature is above 900°C the following could take place:

Hydrogen bromide as noted earlier has been isolated in large amounts when tribromosilane is subjected to temperatures in excess of 900°C. An analogous reaction has been reported for trichlorosilane.⁽¹⁰⁾ To account for the silicon deposit noted at the exit end of the reactor the disproportionation reaction given below might be used.

This is somewhat confirmed by the volume of tetrabromosilane that was isolated from the cold traps.

Similar experimental results were noted when tribromosilane was replaced with trichlorosilane. Decomposition of trichlorosilane to silicon according to reaction (9) was noted to occur at 800°C - 825°C.

However, a large amount of homogeneously nucleated silicon bearing reaction product, either amorphous silicon or a silicon-hydrogen-chlorine type polymer (known to form readily in the chlorosilane-hydrogen system) was obtained in this case. No polymer formation of any type was noted while working with tribromosilane.

Several additional experiments were carried out to determine the effect of the addition of hydrogen to the system. In this case a horizontal reactor similar to that described

earlier was used. Hydrogen was bubbled through a thermostated flask containing tribromosilane. A molar ratio of hydrogen to tribromosilane of 22 was used. Cold traps maintained at liquid nitrogen temperature were used to collect the reaction products.

These experiments showed that the addition of hydrogen to the system increased the decomposition temperature; that is, reaction (6), which is a thermal decomposition was inhibited as would be expected by Le Chatelier's principle. Silicon deposition began when the temperature was approximately 975°C. The products isolated from the reaction were hydrogen bromide, unreacted tribromosilane, and tetrabromosilane. No evidence of polymer formation was noted during the course of the reaction. Silicon deposited from the reduction displayed a very heavy nodular type growth pattern.

The results of the preheating experiments as well as those using hydrogen are tabulated in Table 1.

II.3 Fluid Bed Studies

The fluid bed reactor studies utilizing tribromosilane as the silicon source compound were carried out in a 30 x 33mm diameter quartz tube about 2 meters in length.

TABLE 1. Tribromosilane Decomposition Temperatures.

Temperature °K	H ₂ :SiHBr ₃ ratio	Observations
823	-	Slight deposit
943-996	-	Deposit of Si noted
1073-1123	-	Deposit of Si noted
1173	-	No deposit noted
823	22	No deposit noted
1223-1248	22	Very heavy deposit of Si
1293	22	No deposit noted

A clam shell heater was used to supply heat to the particle bed. Thermocouple ports for measuring the bed temperature were provided. The remainder of the tube, which served as a disengaging space, was heated with Kanthal type A-1 wire. This area was maintained at a temperature of 175°C to about 200°C to prevent the condensation of the effluent products from the bed. The effluent gaseous stream was subsequently condensed in several traps. Figure 1 is a diagram of the experimental system.

The gaseous reactant stream was introduced into the reactor in a direction either perpendicular or parallel to the longitudinal direction of the reactor tube. Introduction of the reactant stream was generally at a point below where the particle bed began. In one case the stream was introduced in a perpendicular manner into the lower part of the particle bed. This resulted in the particles becoming cemented together into a solid mass which eventually caused the reactor to plug.

Various bed supports have been used in the experiments. These include: 1) quartz wool which was packed in the base of the reactor, 2) a porous refractory wool packed in the same manner as described above, and 3) a bed of large silicon particles or nuggets. The various supports also served as gas distributors. Because of the small

FIGURE 1

size of the fluid bed as well as the materials of construction, and design, use of more elaborate distributors such as those described in Perry ⁽¹¹⁾ or Kunii and Levenspiel ⁽¹²⁾ were not considered.

In order to introduce the tribromosilane into the reactor at a smooth rate, a metered stream of argon was bubbled through the vessel containing the tribromosilane, which was mounted in a heating mantle. By controlling the temperature of the tribromosilane vessel and the flow of argon through the vessel, it is possible to achieve numerous input rates of tribromosilane to the reactor. All lines from the vessel to the reactor were heated so as to prevent condensation of the tribromosilane. The various rates that have been used have provided good bed fluidization. In some cases at very high flow rates, slugging of the bed was noted.

Generally, the following procedure was used during an experimental run. A weighed amount of -50 mesh silicon particles was placed in the reactor on top of the bed support. The amount of silicon used was determined by the depth desired for the static bed. Argon was then allowed to flow through a by-pass to fluidize the bed while it was being heated. When the bed had reached the desired temperature, the argon stream was then allowed to flow through the thermostated tribromosilane vessel.

Both the argon flow rate and vessel temperature were adjusted so as to give the desired input rate of tribromosilane as well as the desired fluidized bed. During the course of a run both the bed temperature and input rate were held constant.

Reaction yields were initially calculated on the amount of tribromosilane fed into the reactor during the course of a run. This was determined by weighing the tribromosilane storage vessel before and after a run. Initially the assumption was made that the tribromosilane being used was 100% tribromosilane; however, later work, using the gas phase chromatograph showed this to be incorrect and that the material contains a large fraction of tetrabromosilane. The amount of silicon deposited during the run was measured by determining the weight increase in the bed. Table 2 summarizes the results of a number of runs carried out during the reporting period. It should be noted that the yield figures cited in Table 2 for runs 1 through 9 were computed on the basis of the input material being pure tribromosilane. Investigations currently being carried out with the chromatograph have shown these yields to be lower than actual.

Current reaction yields are being determined with the chromatograph. The procedure being employed is as follows:

FLUID BED REACTOR SUMMARY
Test Run Data

Run I.D.	Date	Aug. Rx Temp.	SILICON			SiHBr ₃ Charge	Carrier Gas Rate	Run Time	Notes
			Bed Depth (in hot zone)	Initial Mass	Final Mass				
001	19 July	750°C	35cm	249.29	250.29	406g	1 l/min	325 min	Run upset due to break in carrier gas delivery system.
002	20 July	825°C	35cm	248.64g	262.53	450g	1 l/min	255 min	
003	24 July	775°C	26cm*	260.37	266.82	347g	1 l/min	400 min	Rx. modified to get inlet below hot zone to pre- vent plugging.
004	26 July	725°C	26cm	258.69	266.34	421g	1 l/min	240 min	
005	27 July	800°C	26cm	255.17	268.44	815g	1.5 l/min	240 min	10ml liquid thought to be SiBr ₄ remains in bubbler after run.
006	31 July	850°C	25cm	253.91	263.11	491g	1.0 l/min	405 min	Fresh bubbler.
007	02 Aug.	900°C	21cm	242.14	244.30	234g	1.0 l/min	240 min	
008	03 Aug.	750°C	13cm	176.16	181.07	510g	1.5 l/min	120 min	
009	04 Aug.	750°C	13cm	178.67	200.63	2202g	.75 l/min	220 min	

TABLE II

CALCULATED REACTOR OPERATING & PERFORMANCE DATA

Run I.D.	Date	SILICON YIELD % Theoretical	SiHBr ₃ Aug. Charge Rate	Residence Time	Temp. Reactor	NOTES
001	19 July	5.3 %	1.25 g/min*	3.8 sec	750	Low yield apparently due to carrier gas flow upset which lead to slugs of liquid SiHBr ₃ going to reactor.
002	20 July	118.8 %	1.76 g/min	3.2 sec	825	Apparent yield thought to be skewed upward because of incomplete removal of silicon after run 001.
003	24 July	72.0 %	0.87 g/min	2.75 sec	775	
004	26 July	76.5 %	1.76 g/min	2.70 sec	725	
005	27 July	62.7 %	3.39 g/min	1.57 sec	800	
006	31 July	84.0 %	1.21 g/min	2.56 sec	850	
007	02 Aug.	26.0 %	0.97 g/min	1.92 sec	900	
008	03 Aug.	36.5 %	4.25 g/min	0.98 sec	750	
009	04 Aug.	38.4 %	10.0 g/min	1.15 sec	750	
010	28 Aug.	20-30 %	8 g/min	2.7 sec	750	

TABLE II (continued)

Samples are collected simultaneously from both the input and effluent streams. These samples are then chromatographed and the decrease in the tribromosilane peak area between the input and output used to arrive at yield. Likewise the increase in the peak area associated with tetrabromosilane is used to confirm the data.

Using this technique, we have found yield to be in excess of 90% and also to not vary greatly within the 700°C to 900°C region.

The product obtained from the reaction displays a typical vapor deposition coating. Figures 3 and 4 represent the material obtained from run 009. An initial bed having a size of >60 <80 mesh was used. Figure 2 is a photo of the starting bed. At the end of the run approximately 70% of the recovered product had a size greater than 50 mesh.

It should be noted that no wall deposition is noted in the reactor, nor have any polymers been detected in the reactor and collection system. Homogeneous nucleation, if it occurs in the bed, has not been detected; that is, no deposits of fine dust have been found in any area of the reactor or collection system.

FIGURE 4

II.4 Tetrabromosilane Conversion Studies

Since the results obtained from the fluid bed decomposition studies have been quite favorable as far as theoretical yield is concerned, it seemed logical to investigate the conversion of the tetrabromosilane to tribromosilane according to reaction (6). This would allow the establishment of a closed-loop system as given below:

A. Synthesis

B. Intermediate clean-up

C. Decompositon

In this closed-loop system the only material theoretically consumed is metalurgical grade silicon with the only product being solar grade silicon.

Our experiments were carried out in a 25mm O.D. quartz tube which was packed with lump metalurgical grade silicon of an unknown composition. Tetrabromosilane was carried from a thermostated flask with a stream of hydrogen and was introduced at the bottom of the bed. The reaction products were allowed to pass out of the reactor and subsequently condensed in a

receiver flask. Heat to the bed of lump silicon was supplied by a small clam shell type heater.

In the initial experiments with the lump silicon, a copper catalyst (small pieces of copper wire) was added to the bed. Copper was selected as the catalyst as it is normally used in the Rochow process ^(7,8) and good success has been reported by Union Carbide in their conversion of tetrachlorosilane to trichlorosilane. These experiments were refined by replacing the lump silicon with silicon powder of -50 mesh size and replacing the copper wire with -100 mesh copper powder. The experimental results are summarized in Table 3. (It should be noted that the conversion percentage cited in Table 3 is based on the amount of tetrabromosilane introduced into the system and the amount of tribromosilane collected after one distillation carried out at atmospheric pressure).

From Table 3, it can be inferred that the optimum temperature for the reverse of reaction (6) is between 650°C - 680°C. It is also quite obvious that residence time within the bed is a critical factor. It appears that longer residence times are favorable; however, this may not truly be the case.

TABULATION OF DATA
SILICON CONVERSION REACTION

RUN I.D. NO.	DATE	REACTOR DATA			TEMPS		AVG. FEED RA1.			RESIDENCE TIME SEC.	YIELD %	REMARKS
		A, cm ²	L, cm ³	Vol. cm ³	T c°	T b°	H ²	SiBr ₄	RATIO			
001	June 1-6	4.54	40	190	620	112	.5 l/min	3.9g/min	1.75	4.6	21	Yield suspect due to different placement of thermocouple.
002	June 13	"	"	"	650	125	.5 l/min	3.2g/min	2.23	5.1	36	
003	June 15-16	"	"	"	698	104	.5 l/min	8.8g/min	0.80	3.14	37	
004	June 28	4.9	20	98	560	120	1.0 l/min	2.2g/min	5.3	2.12	NIL	
005	July 5	"	"	"	600	130	.5 l/min	8.8g/min	0.81	1.78	8	
006	July 7	"	"	"	675	120	.8 l/min	4.8g/min	2.35	1.64	13	
007	July 11	4.52	10	45	650	130	.26 l/min	9.3g/min	.43	.93	12	
008	July 12	"	"	"	690	125	.15 l/min	3.9g/min	.55	1.98	15	
009	July 12	"	"	"	550	82	1.0 l/min	4.6g/min	8.5	.88	NIL	

NOTE: 1. Residence time based on reaction gas @ Tc and volume of bed.

2. Yield is defined as $\frac{\text{moles of SiHBr}_3}{\text{moles SiBr}_4} \times 100\%$.

TABLE 3

It is the author's opinion that the yield or conversion rate of this reaction can be readily improved by using a fluidized bed of silicon particles and copper particles. An alternative to this type of bed is to use a bed of particles composed of a silicon-copper alloy, such as normally used in the Rochow process. Variations in the molar ratio of hydrogen to tetrabromosilane could also prove to be beneficial as well as running the reaction at increased pressure.

To date, studies of the reverse reaction have only directed towards establishing the cyclical nature of the process. This has been demonstrated and needs additional study to both improve the yield and learn more of the chemistry of the reverse reaction.

III. CONCLUSION

The following points can be drawn from the experimental work carried out to date on tribromosilane.

1. Yields of silicon in 90% of theoretical yield, based on the reaction below, have been noted.

2. The yield versus temperature curve appears to be flat in the 700°C to 900°C range; that is, within this region the yield is in excess of 90% and changes very little with temperature.
3. Excellent deposition on the bed particles is obtained in this region.
4. No wall deposition has been noted in the fluid bed reactor.
5. Formation of polymers has not been detected during any of the runs.

6. Tetrabromosilane can be converted to tribromosilane by reaction of it with a heated silicon bed.
7. The cyclical nature of the process described earlier has been established.

IV. FUTURE PLANS

A two month contract extension has been granted. During this period we plan to continue the studies of tribromosilane deposition in the fluid bed reactor and to duplicate these studies for the hydrogen-tribromosilane system. An economic comparison between the two systems will be carried out.

V. NEW TECHNOLOGY

No reportable items have been identified as new technology.

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