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

Third Quarterly Progress Report, March 25 to June 24, 1978

By
L. Woerner

June 1978

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

J. C. Schumacher Co.
Oceanside, California

U.S. Department of Energy

MASTER

Solar Energy

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

THIRD QUARTERLY REPORT
L. WOERNER
JUNE, 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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FORWARD AND ACKNOWLEDGEMENTS

This is the third Quarterly Progress Report for a Program which began on October 24, 1977. It covers the period March 25, 1978 to June 24, 1978.

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

Mr. Edward Moore,
Chemical Engineer

and

Dr. John C. Schumacher,
Project Manager

ABSTRACT

During this quarter effort have been directed towards maximizing particle growth in the horizontal tubular or cocurrent reactor. These efforts have not been totally successful due to hardware limitations. A new reactor which allows passage of the substrate particles in a countercurrent direction to the gas flow was designed. Particle growth data obtained for particles after one pass in the reactor were not conclusive.

Tribromosilane decomposition studies were initiated during the quarter. Preliminary results indicate that the decomposition proceeds quite smoothly at approximately 975 °C and at a hydrogen to tribromosilane ratio of 22. The decomposition reaction appears to attain equilibrium quite rapidly. Silicon deposited under these conditions has a very nodular appearance. HBr has been isolated as one of the reaction products.

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I. INTRODUCTION

This is the third quarterly progress report for a program being carried out by the J. C. Schumacher Company for the purpose of determining the feasibility of a continuous high volume - high velocity reduction process as a means for producing low cost solar grade silicon. The concept underlying the approach being studied was described in the first quarterly report (1)

Briefly the process under consideration is the gas phase reduction of bromosilanes with hydrogen. It can be described by the following generalized reaction:

where x equals 0 or 1.

Both gaseous reactants are separately preheated to above the reaction temperature and 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 preheated silicon particles also provide a means of delivering more thermal energy to the reaction zone. Reaction products are then collected by standard techniques.

During the past two quarters chemistry studies have been carried out using tetrabromosilane, (x equal 0, in reaction 1)

as the silicon compound in reaction (1). These studies were carried out in the horizontal tubular or cocurrent reactor. Data presented in the second quarterly report and obtained this past quarter indicate that it is possible to produce silicon in the reactor and to attain what appears to be growth on the substrate particles. The deposition of silicon from tetrabromosilane was found to take place in the reactor when ratios of $H_2:SiBr_4$ of 17 to 20 were used at temperatures in the range of 1290 - 1340°K.

Deposition rate data has been difficult to obtain in this reactor as it is limited by particle residence time in the reactor and by the thermal energy carried by the particle and reactant input streams. Increasing the wall temperature of the reactor to alleviate the energy loss problem resulted in extensive wall deposition. To maximize particle growth rather than on the wall, it was felt expedient to heat the particles substantially above that of the gas phase. This would also serve as a means of increasing the total thermal energy available and reaction lifetime. The physical design of the countercurrent reactor precluded its use as a tool to study these ideas.

To implement this concept, a second reactor, which has the particle flow countercurrent to gas flow was designed. The reactor also has the capability of testing a theoretical deposition. The reactor model design was developed by Professor W. A. Tillier of Stanford University.

Particle growth data generated from this reactor were not conclusive as available measurement techniques were not able to discern if growth or etching occurred. The studies were carried out with particles containing a normal oxide film. Gas etching to remove the oxide film caused the particles to sinter together in the reservoir necessitating redesign of this part of the reactor. During the reactor modification period a fluid bed reactor was used to obtain particle growth data. The fluid bed reactor approximates to some degree particle recycling which is currently not possible in the countercurrent reactor. Data obtained from this system has given some insight as to conditions, yield, and other factors associated with tetrabromosilane.

As the contract specifications call for evaluation of tribromosilane, (x equal 1 in reaction (1)), studies were initiated this past quarter on the chemistry of the decomposition of this substance. In order to have a valid comparison of tribromosilane with tetrabromosilane and to normalize as many factors as possible the studies were initiated in the fluid bed reactor.

Section II of this report describes the events and results obtained from the various reactor systems and presents some of the initial results obtained for tribromosilane.

II. TECHNICAL DISCUSSION

II.0 Introduction

During the past quarter efforts have been devoted towards maximizing growth on the substrate particles and in understanding the chemistry occurring in the reactors. Several different approaches have been studied with respect to maximization of growth. These approaches have led to the design and use of two additional reactor systems. These are discussed individually.

II.1 Cocurrent or Horizontal Tubular Reactor

The design and operation of this reactor has been described in detail in the second quarterly report. In this reactor the heated silicon substrate particles travel in the same direction as the heated and mixed reactant stream. It has produced heavy wall deposition and some weight gain in the particles when operated at $H_2:SiBr_4$ ratio of about 18 and at a temperature of about 1,300°K.

Particle size analysis performed on the product of one of the runs indicated a shift in the mean particle diameter from 66 microns for an untreated sample to 70 microns for the particles after one pass through the reactor. Additionally, the particle mean mass diameter was shifted from 279 microns to 370 microns. (The particle mean mass diameter is defined as the diameter above which 50% of the total mass occurs.)

Several interpretations can be given for the results.

First the change in the mean diameter and the mean mass diameter can be viewed as the result of deposition on the particle. Another interpretation is based on the addition of particles to the initial charge. The added particles can originate by a scouring action of the initial particles on the silicon wall deposits. Addition of larger particle originating from this action would skew the distribution to larger sizes. This would increase both the mean and mean mass diameters.

Attempts were made to reduce the amount of silicon being deposited on the tube walls by reducing the ratio of wall area to total particle surface area for particles present in the reactor at any given time. Since the reactor tube diameter is fixed, this may only be achieved by increasing the particle flux. These attempts were not totally successful as several problems due to hardware and heat transfer limitations were encountered. Foremost among the problems was the inability of the hydrogen stream to efficiently transport large particle fluxes through the preheater. This problem caused the preheater to eventually plug and could not be rectified by increasing the hydrogen flow rate. A maximum particle feed rate of about 5 grams per minute was achieved under normal operating conditions; however, no appreciable diminution in the silicon deposited on the reactor walls was noted. Although, these attempts were not successful, this does not preclude achieving this in a larger scale reactor.

II.2 Countercurrent Reactor

The countercurrent reactor allows for the passage of heated silicon particles in a direction opposite to that of the preheated and mixed reactant streams. Basically the reactor consists of segments of 30 x 33 mm quartz tubing which may be fitted together to give various reactor lengths. Ports in the quartz tubing provide for the introduction of reactant streams, the exit of exhaust gases, and for the insertion of thermocouples for temperature measurements. Heat to the reactor is supplied by a resistance heater which is wound on the external surface of the reactor. The heater is used only for the purpose of maintaining the mixed gas streams at some desired temperature. Initially the two reactant streams are separately heated in a tube furnace to the desired temperature. The streams are conducted individually to the base of the reactor in insulated and heated transfer lines where they are mixed. Heat for the transfer lines is supplied by resistance heaters which are wound around the transfer tubes. The silicon particles used in the reactions are held in a reservoir which is mounted on the top of the reactor. A small clam shell type heater surrounds the reservoir and is used to heat the particles. Particle flow into the reactor is controlled by a quartz plunger which functions as a valve. Figure 1 is a diagram of the countercurrent reactor.

The basic reason for the use of the countercurrent reactor is

to determine the deposition rate of silicon on the particles on a per pass basis and to verify a theoretical model which was developed to predict the growth rate. The logic underlying the model is as follows.. If the preheated reactant streams are mixed and held at a temperature slightly below that temperature where wall deposition and homogeneous nucleation begin to take place, then if a substrate particle, which has been heated to some temperature substantially above that of the gas phase, is injected into the reactor, maximum deposition should occur on the particle. To insure that the particle will always pass through a constant gas composition, the gas phase velocity is adjusted so that the reactor volume is changed during the growth lifetime of the particle. The maximum growth lifetime is a function of the cooling rate of the particle. Deposition on the particle can only occur during that period when the temperature of the particle is greater than that of the gas phase. The actual deposition rate is however more complex and may depend on such factors as removal of any reaction product boundry layer which may form on the surface of the particle.

The initial experiments in the countercurrent reactor were carried out to determine the maximum temperature and conditions for the mixed reactant streams. Table 1 summerizes the results of these experiments. The results shown in Table 1 indicate that the particles should be heated to a temperature region of 1,523 to 1,573 °K. This would allow a growth lifetime equivalent to the time required for the particle to cool 250 °K to that of the gas phase.

FIGURE 1. COUNTERCURRENT REACTOR

TABLE 1. Countercurrent Reactor Gas Phase Temperatures.

Temperature °K	H ₂ :SiBr ₄ ratio ⁴	Observations
1280	18	No wall deposition
1285	5	No wall deposition
1300	3	No wall deposition
1307	12	Slight wall deposition

TABLE 2. Tribromosilane Decomposition Temperatures.

Temperature °K	H ₂ :SiHBr ₃ ratio	Observations
823	22	No deposit noted
1023	22	No deposit noted
1223-1248	22	Very heavy deposit of Si
1293	22	No deposit noted

Several experiments were undertaken to test the design of the valving mechanism of the silicon reservoir and to determine any other problems which might be encountered with the particle heating. When the particles were heated to 1548°K with the surface oxide film intact; that is, the particles were not etched, the particles remained free flowing and sintering was not encountered. However, when the particles were gas etched with HBr at about 1,273°K and then heated to 1,548°K, the complete bed of particles sintered together into a porous solid. This fact required the design of a new particle heating system which would alleviate the sintering problem. The oxide surface must be removed from the particle surface or else the resultant product will be composed of silicon and silicon dioxide.

Several experiments were carried out to determine if any growth could be detected after one pass through the reactor. In this case the particles were used with the oxide surface intact and were heated to 1,548°K. After one pass through the $H_2:SiBr_4$ gas phase, the results were not conclusive. Efforts are continuing in this area using the new particle heating system.

Particle growth rate studies were also carried out in a fluid bed environment. In this case the countercurrent reactor was converted into a fluid bed reactor by inserting a bed support. The two preheated gas streams were introduced at the bottom of the bed. Heat to the bed was supplied by the external resistance heater described earlier. A second objective of this study was to determine if low hydrogen to $SiBr_4$ ratios could be used.

The initial run was carried out with a bed temperature which ranged from 1,263 to 1,288 °K and at a hydrogen to SiBr_4 ratio of about 5.5. Under these conditions, it was found that about 25% of the initial bed weight was lost. Some wall deposition was noted; however, it was very small when compared to the loss in bed weight. A large amount of tribromosilane was isolated from the collection system. Other runs indicated that if the ratio of $\text{H}_2:\text{SiBr}_4$ was less than 7 in the temperature range cited, etching rather than deposition would occur. Tribromosilane was isolated as the major product whenever etching occurred. Further studies are planned in this area.

II.3 Tribromosilane Studies

The initial studies of the reaction of hydrogen with tribromosilane are being carried out in quartz tubes. Their purpose is to determine the optimum temperature and mole ratio of hydrogen to tribromosilane. Table 2 summarizes the best conditions obtained to date in the quartz tube reactor.

It is interesting to note that it appears that a rapid equilibrium is established for the reaction. Evidence of this fact is that the deposition of silicon occurs over a very short distance of the heated tube and a large amount of unreacted tribromosilane is recovered from the cold traps. HBr is also obtained as a reaction product. The silicon deposits obtained displayed a very nodular character.

The information obtained from the decomposition studies will be used in the tribromosilane preheating studies. It is expected that some redistribution might occur on heating the tribromosilane (2,3); however, it is felt that this will not be overly detrimental. Future efforts will be devoted to studying the decomposition reaction and obtaining particle growth data.

III. CONCLUSION

The conclusions which can be drawn from the experimental work to date are:

1. Tribromosilane is preferable to tetrabromosilane as feedstock for any reactor. It is preferred because it requires lower temperatures for decomposition, the decomposition reaction proceeds in a much smoother manner, and it produces more silicon on a per pound basis of material handled.
2. High mole ratios of $H_2:SiHBr_3$ decompose to silicon at approximately 1223 °K with the rapid establishment of equilibrium.
3. Although tribromosilane spontaneously ignites in air, it presents no great problems in handling. Fires can be readily extinguished with water or by blanketing the area with dry inert gas such as nitrogen.
4. Polymer formation from $SiHBr_3$ has not been detected in any of the reaction systems investigated.

IV. PLANS

The remaining 2.5 months of the contract will be devoted to increasing the yield of silicon obtained from the thermal decomposition of tribromosilane in both countercurrent and fluid bed reactors. Studies will also be carried out, with a newly purchased gas phase chromatograph, that will allow a more precise determination of the reaction product distribution.

V. NEW TECHNOLOGY

No reportable items have been identified during the past quarter.

VI. REFERENCES

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