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**DEVELOPMENT OF PROCESSES FOR THE PRODUCTION OF SOLAR
GRADE SILICON FROM HALIDES AND ALKALI METALS. PHASE II**

Fourth Quarterly Report for Period July 1—September 30, 1980

By
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**DEVELOPMENT OF PROCESSES FOR
THE PRODUCTION OF SOLAR GRADE
SILICON FROM HALIDES AND ALKALI
METALS
Phase II**

**FOURTH QUARTERLY REPORT
for the period 1 July to 30 September 1980**

C.R. DICKSON, W.FELDER, AND R.K. GOULD

OCTOBER 1980

**JPL Contract No. 955491
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Approved by:

**Hartwell F. Calcote
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AeroChem

Research Laboratories, Inc.

Princeton, New Jersey

ABSTRACT

The objective of this program is to characterize the kinetics and mechanism of the formation and growth of silicon particles from the decomposition of silane at high temperatures. The experiments are aimed at determining the rates at which gas-phase species form silicon particle precursors, the time required for silane decomposition to produce silicon particles, and the competing rate of growth of silicon seed particles injected into a decomposing silane environment.

In this reporting period an AeroChem high-temperature fast-flow reactor (HTFFR) was modified to study the decomposition of silane. The useful length (for kinetic measurements) of the reactor is the uniform temperature zone extending about 30 cm upstream from the optical observation plane. Experiments are being performed at pressures from 5-760 Torr, temperatures from 600-1300°C, and average gas velocities of 1-100 m s⁻¹ (i.e., reaction times from about 0 to 300 ms). A cooled inlet is used to inject room temperature silane into any part of the uniform temperature zone of the HTFFR and a fluidized bed feed system will be used to inject silicon seed particles.

The basic experiment consists of varying the position of the cooled inlet and measuring scattered light intensity in the observation plane to determine the particle size as a function of time available for silane decomposition. The techniques under consideration to measure average particle density and particle size distribution are turbidity, 90° scattering, polarization, forward scattering, and Mie resonances. The amount of silane entering the HTFFR is known from the flow rate through a precision orifice and the amount leaving the HTFFR is measured by the IR absorption cell. In addition, simultaneous probing for the Si atoms (not particles) and the SiH (and SiH₂) molecular species are made using spectroscopic diagnostics (resonance fluorescence or absorption) at the observation plane.

The apparatus has been assembled and tested. Preliminary observations of turbidity and 90° scattering on Si particles formed from SiH₄ decomposition have been made. These observations indicate that the apparatus and optical systems are capable of providing the detailed particle density and size measurements necessary to describe the SiH₄-to-particle kinetics.

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I. INTRODUCTION

The thermal decomposition of silane is one of the processes currently being considered by JPL as a source of cheap solar grade silicon. The objective of the work underway at AeroChem is to provide data to support production process development by characterizing the kinetics and mechanism of the formation and growth of silicon particles from the decomposition of silane at process temperatures. The experiments are aimed at determining the rates at which gas-phase species form silicon particle precursors, the time required for silane decomposition to produce silicon particles, and the competing rate of growth of silicon seed particles injected into a decomposing silane environment.

The kinetics of monosilane pyrolysis were first studied by Hogness et al¹ and later by Stokland,² using static methods and manometric rate measurements. Hogness et al report that the only products of the reaction were silicon and hydrogen, and that no disilane was formed. Consequently, they interpreted their kinetic measurements on the assumption of a constant stoichiometry of

Stokland, on the other hand, detected disilane as a reaction product. He suggested the occurrence of

A thorough investigation of monosilane decomposition was made by Purnell and Walsh.³ They were able to monitor the reaction products using gas chromatography. They suggest two possible mechanisms

or

The origin of the solid product of empirical formula $(\text{SiH}_2)_n$ which they found during their studies is

Such steps imply that the higher silanes are formed in the pyrolysis of mono-silane by successive insertion of SiH_2 or SiH_3 into lower silanes until eventually a sufficiently long one is formed. It diffuses to the wall and condenses.

A possible alternative is that the silene species continuously condense together in a reaction such as

The presence of $(\text{SiH}_2)_n$ as an intermediate shows that in the pyrolysis of mono-silanes there is a greater tendency for Si-Si bonds to be formed than to be broken. Finally, the decomposition of the solid silicon hydride is described by

Thus, the ability to monitor the growth of silicon particles formed either by homogeneous or heterogeneous nucleation and to observe the reaction products in situ could prove useful in understanding the growth mechanism of silicon particulates formed from silane decomposition.

II. TECHNICAL DISCUSSION

A. HTFFR APPARATUS FOR MONITORING PARTICLE GROWTH

In this reporting period, the high-temperature fast-flow reactor (HTFFR), Fig. 1, has been adapted so that heterogeneous chemical reactions, such as the thermal decomposition of silane to form particulates can be studied. With this apparatus, the rates at which gas-phase species form silicon particle precursors, the time required for silane decomposition to produce silicon particles, and the competing rate of growth of silicon seed particles injected into a decomposing silane environment are being studied. The modified apparatus allows several light scattering techniques to be used for determining the average size or the size distribution of particles formed during the course of silane decomposition.

Particle growth is monitored at the HTFFR observation plane as a function of the time the silane gas resides in the uniformly heated reaction zone. This time is varied by positioning a cooled inlet at differing distances upstream of the observation window. For example, at a gas velocity of 10^3 cm s^{-1} and at various positions ranging from 0 to 30 cm upstream of the observation plane, the silane resides in the reaction zone for between 0 and 30 ms. A wide range of contact times is accessible by changing the gas velocity as well as the inlet position.

The flow reactor portion of the HTFFR has been described previously.^{4,5} It consists of a 2.5 cm i.d. alumina reactor wound with 0.040 in. molybdenum resistance wire in three contiguous, independently-powered zones. Because the planned experiments involve a reducing atmosphere, and because rigorous leak prevention steps have been taken, it is possible to use molybdenum resistance heaters instead of the Pt/Rh normally used.⁵ The reactor tube is insulated with zirconia insulation and about 1 kW of power applied to each heater section enables the temperature inside the HTFFR to easily reach 1500°C. A movable Pt/10% Rh thermocouple allows the temperature throughout the reactor tube to be monitored.⁵

Silane gas enters the reactor tube through a movable water-cooled inlet shown in Fig. 2. The cooled inlet enters from the bottom and can be positioned at varying distances from the observation plane. The useful length of the reactor (for kinetic measurements) is the uniform temperature zone (controlled by adjusting the current flow to the resistance heaters) extending about

30 cm upstream of the observation ports. The cooled inlet has been tested and shown to deliver room-temperature silane gas to any point in the reaction zone when that zone is at $\approx 1100^\circ\text{C}$. Silane and argon buffer gas are metered into the reactor through calibrated orifices.

Four 1 cm diam holes at 90° to one another are located at the HTFFR observation plane. Through these ports various optical diagnostics can be applied as silane is decomposed in a controlled fashion. Figure 3 shows the details of the observation plane as set up for the turbidity/ 90° scattering measurements used for initial tests (see Section II.B.3). A 1 mW Spectra Physics model 133 He-Ne laser beam is chopped at 1000 Hz and passes through a beam splitter to provide a measurement of I_0 . The laser beam enters the HTFFR through a flat window (or a lens which focuses the beam to the center of the reactor tube). Light baffles, constructed from graphite discs with 0.6 cm diam holes and spaced 1 cm apart, define the optical paths and eliminate unwanted light scattering. The laser beam exits the HTFFR through a Brewster angle window mounted on a Wood's horn to prevent back reflections of the laser beam. Detector A (Fig. 3) is a trialkali (red-sensitive) phototube (RCA 5845) which measures the scattered He-Ne laser light at 90° to the direction of the laser beam. Detector B (for turbidity) and the detector for I_0 are both silicon photodiodes (Molelectron power meter T3-02-DW).

A fluidized bed feed system (Fig. 4) was built to inject Si seed particles into the reactor. Before entering the HTFFR, a portion of the diluent gas flow (Ar or N_2) can be diverted through the bed to fluidize it; some Si particles are suspended above the bed and entrained in this gas flow for transport to the HTFFR. The fraction of the total gas flow that passes through the bed will determine the particle concentration entering the HTFFR. A calibrated optical extinction monitor at the output of the bed will be used to measure the particle concentration in the flow stream. The fluidized bed has been tested successfully with $150\text{ }\mu\text{m}$ diam Si particles and will be used with $5\text{ }\mu\text{m}$ diam Si particles during seeding experiments.

To measure the amount of undecomposed silane gas, a long path (97 cm) absorption cell is connected near the exhaust of the HTFFR. The IR absorption optical system (see Fig. 5) consists of a Globar light source (a resistively heated SiC rod) using a pinhole collimator combined with two planoconvex CaF_2 lenses, a 1 m absorption cell with CaF_2 windows, and a PbSe detector with a 4.2 to $4.8\text{ }\mu\text{m}$ bandpass filter. The light source is chopped and the signal is detected with a lock-in amplifier.

The infrared absorption of silane is shown in Fig. 6. The 4-5 μ absorption band was chosen for the absorption measurements primarily because this region is easily accessible by common IR detectors and the optics could be made from BaF_2 or CaF_2 , relatively inexpensive and durable materials. The PbSe detector (No. 5055 IR Industries) has its peak sensitivity in the 4-5 μ region and the response is nearly flat as shown in Fig. 7. The optical bandpass filter spans several features of the absorption spectrum. It was anticipated that the effect of this structure would be somewhat averaged and the absorption would not deviate too severely from Beer's law. Three calibration runs were made by filling the IR absorption cell with silane gas at various pressures from 0.1 to 20 Torr and measuring the corresponding signal outputs from the PbSe detector. All pressures were measured with a Wallace and Tiernan pressure gauge so a true force per area reading was obtained. If lower silane concentrations need to be measured, a capacitance manometer pressure gauge will be used to calibrate the absorption in the 0.01 to 0.1 Torr range. The data shown in Fig. 8 were taken at a Globar source temperature of 1240°C.

B. LIGHT SCATTERING DIAGNOSTICS

1. Overview

Optical light scattering techniques are being used to determine the size and growth rate of silicon particles. In general, it will be necessary to determine both a particle number density, N , and a total extinction cross section, C , which is related to the particle size. The basic relationship for light extinction is given by

$$I/I_0 = \exp -[CN\ell] \quad (8)$$

where ℓ is the path length (2.54 cm in the HTFFR) and I/I_0 is the ratio of transmitted to incident light intensity. The product $C \cdot N = \tau$ is the turbidity and is measured directly from attenuation of the light beam. Thus, an additional measurement to determine C or N independently is needed, and many procedures exist for accomplishing this. For this project we will choose from among those which give the most easily and directly interpreted results. The list of candidate procedures which are compatible with the present apparatus configuration includes⁶ 90° scattering, forward (0° to $\sim 20^\circ$) scattering, Mie resonances, and diagnostic wavelength variations. Additional information on particle shapes can be obtained

using polarization measurements.⁶ Since it is anticipated that the size of the particle will be 0.1 to 10 μ , the well-known Mie theory⁷ applies and will be used for interpreting the measurements.

In the next quarter several or all of these techniques will be tested and those applicable for specific measurements on the SiH_4 -to-particle process will be described in forthcoming reports.

2. Refractive Index of Silicon

Errors are often introduced into the light scattering results because of uncertainties in the values of the refractive index of the material being studied. To obtain the complex index of refraction for silicon, we used the absorption spectrum for Si obtained by Dash and Newman⁸ to calculate the extinction index, k , from

$$k = \frac{\lambda \alpha}{4\pi} \quad (9)$$

where α is the absorption coefficient and λ is the wavelength of light. Figure 9 shows the results of this calculation at the lasing wavelengths for He-Ne and argon ion lasers, the two light sources to be used. It is clear that k is varying over this wavelength region and this variation may have to be accounted for in interpreting the scattering results. The k values presented here should be considered tentative and indicating only a trend. More refined calculations will be made.

Since there are ambiguities about the application of bulk properties to particulates, another alternative is possible. Silicon particles of a known size distribution (obtained by electron microscopy) will enter the HTFFR via a fluidized bed attachment (see Fig. 2). Each light scattering measurement can then be calibrated with the material, of a known size distribution, to be studied. This procedure would then eliminate any ambiguities from the calculations required in the data analysis using the Mie code available at AeroChem.

3. Observations of Silane Decomposition and Si Particle Formation

Silane gas was admitted to the HTFFR using the cooled inlet at a reaction zone temperature of about 1000°C. With contact times of less than 1 ms and silane flow rates of about 0.001 mol s⁻¹, complete extinction of the He-Ne laser beam due to particle formation was observed. Simultaneous 90°

scattering intensities were more than a factor of 10^4 above the detector limit. Decreasing the SiH_4 flow rate decreased both the turbidity and 90° scattered intensity. These simple "turn on" observations indicate that the system will allow the sensitive and detailed measurements of particle formation and growth necessary to provide information on both the silane-to-particle process and the competing growth of Si seed particles injected into a decomposing silane environment.

III. PLANS

During the next reporting period efforts will be directed toward determining the time required for the silane decomposition to produce silicon particles as a function of pressure and temperature. Optical diagnostic methods for particle size and concentration measurements will be selected.

IV. NEW TECHNOLOGY

No reportable items of new technology were identified in this quarter.

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FIGURE 1 HIGH-TEMPERATURE FAST-FLOW REACTOR FOR MEASUREMENTS OF Si PARTICLE FORMATION AND GROWTH KINETICS

80-138

FIGURE 2 SCHEMATIC DIAGRAM OF WATER-COOLED INLET
FOR INTRODUCING SILANE TO HTFFR

80-134

FIGURE 3 OBSERVATION PLANE OF HTFFR FOR MEASUREMENTS OF PARTICLE FORMATION AND GROWTH KINETICS

Detector A for 90° scattering; Detector B for turbidity/forward scattering.

FIGURE 4 FLUIDIZED BED FEED SYSTEM FOR ADDING PARTICULATES TO GAS FLOW

FIGURE 5 IR ABSORPTION SYSTEM FOR MEASUREMENTS OF RESIDUAL SILANE EXITING THE HTFFR

FIGURE 6 INFRARED ABSORPTION SPECTRUM OF SILANE

FIGURE 7 PbSe DETECTOR AND IR BANDPASS FILTER CHARACTERISTICS COMPARED TO SILANE ABSORPTION SPECTRUM IN THE 3.0-6.0 μm REGION

FIGURE 8. CALIBRATION CURVE FOR SILANE INFRARED ABSORPTION SYSTEM

Path length = 97 cm, 4.2-4.8 μm bandpass, PbSe detector.
Silane pressure measured at 293 K.

FIGURE 9 VARIATION OF EXTINCTION INDEX OF Si PARTICLES
WITH WAVELENGTH

Points are wavelengths of lines emitted by the diagnostic lasers.
See text, Section II.B.2.