THE REDUCTION OF TETRACHLOROSILANE BY SODIUM AT HIGH TEMPERATURES IN A LABORATORY SCALE EXPERIMENT*

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ABSTRACT

In support of a project to develop a low cost solar grade silicon production process, tetrachlorosilane was reduced by sodium at plasma temperatures (3000°K) in a laboratory scale experiment. The reaction product silicon was separated and collected on the reaction tube wall through condensation. The experimental results show a basic agreement with results obtained from a heat and mass transfer model, and the observed differences can be qualitatively attributed to the model characterization of the experiment.

1. INTRODUCTION

The economic production of electric power using solar photovoltaic arrays depends upon the availability of sufficiently pure, inexpensive silicon. The Jet Propulsion Laboratory has undertaken the development of low cost silicon photovoltaic arrays as part of the National Photovoltaic Program.[1] In order to achieve the overall cost objectives, it is necessary to reduce the cost of polycrystalline silicon by nearly an order of magnitude. In a large scale process currently under development,[2] silicon will be produced by means of the high temperature reduction of tetrachlorosilane ($SiCl_4$) by metallic sodium (Na) in an arc heated hydrogen-argon gas mixture. As part of this development program, a more flexible, laboratory scale system was designed and operated to study reaction rates, product yield and product separation techniques. Results of this experiment and a model are presented.

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2. DESCRIPTION OF EXPERIMENT

The experimental system (see Figure 1) consisted of a commercial DC plasma torch to provide the arc heated stream of hydrogen and argon, a special nozzle for injecting the sodium and tetrachlorosilane into the gas stream, a test chamber with viewing ports for optical diagnostics and having a means for product collection by condensation or by filtration, a scrubber for removal of HCl and NaCl from the gas stream, and a hydrogen burn-off stack.

The liquid sodium was forced by argon pressure from a heated tank through heated lines to the injection nozzle. A manual valve controlled the flow which was monitored by an electromagnetic flowmeter. The tetrachlorosilane supply system consisted of a reservoir and an evaporator. Argon gas pressure forced tetrachlorosilane out of the reservoir into the evaporator. Flow was controlled by manual valves and measured with a glass tube rotameter. Both sodium and tetrachlorosilane reactants were delivered through separate heated manifolds to the heated injection nozzle, the temperature of which was maintained above the melting point of sodium (above 100°C) by a high pressure, hot water cooling system. The plasma flow channel through the injection nozzle was lined with a graphite sleeve, and the sodium was injected through radial holes in this sleeve, whereas the tetrachlorosilane injection holes were oriented towards the downstream direction.

The mixture of hydrogen-argon gas, reactants and products entered a flow channel consisting of several sections of silicon carbide tube, each 25 mm diameter by 15 cm long (see Figure 2). The tube sections were contained in four water-cooled stainless steel reaction chamber sections. Thus the heat transferred to each section was determined by normal calorimetric measurements. Following the last section, the gas entered a duct to the conventional water-spray scrubber.

The nominal gas and reactant input composition[3] on a molar basis (6.62 H_2: 1.66 Ar: 1.0 $SiCl_4$: 4.0 Na) was determined by the process energy requirements, the arc heater operating characteristics and the silicon product purity requirements. The total mass flow rate was scaled according to the power capability of the torch to provide the desired operating temperatures.

3. THEORY OF PRODUCT SEPARATION

Early in the process development it became evident[4] that the reaction rates are mixing limited. Thus, the major analytical consideration was given to the means of silicon product separation. A model was developed[3] to predict the transfer of silicon from the product gas stream to the reactor wall by condensation to a molten state. The model was developed for a turbulent stream (Re $\sim$50,000) representative of the large scale reactor.[3] In addition, the model included the effects of condensation in the boundary layer upon the transfer process. Due to size and power limitations, the laboratory scale experiment operated in the laminar mode (Re $\sim$2000). The model was applied to these laminar flow conditions by substituting those relations defining the heat and mass

transport, and by involving the analogy between heat and mass transfer.[5] The effect of condensation in the boundary layer was neglected. Since the axial pressure drop is negligible (<0.1 atm), the pressure was taken to be 1 atm throughout the tube. The conservation equations representing the stream temperature and silicon content were integrated numerically along the axis, using the calculated equilibrium composition and associated transport properties at the specific temperature. Two cases were calculated, one using Nusselt numbers for thermally and hydrodynamically developing flow,[6] the other with a constant Nusselt number representing developed flow. A constant wall temperature above the melting point of silicon (1683°K) was assumed. At this wall temperature, only silicon is condensing and collected at the wall, with all other species remaining gaseous.

Figure 3 shows the fraction of silicon remaining in the gas stream as a function of axial location and the axial temperature distribution for the two cases (developed and developing flow, respectively). The results for the developing flow indicate a rapid removal of silicon at the entrance, coinciding with a comparable change in the stream temperature. The experimental arrangement of a high velocity jet from a small diameter nozzle entering a tube of significantly larger diameter, is expected to produce results between these limiting cases.

4. RESULTS

Based upon the values for the power input and the calorimetric measurements of the heat losses, the bulk gas temperatures at the torch and injection nozzle exits and at the end of the first test section were determined from thermodynamic equilibrium properties. Table 1 lists bulk temperature values. Pyrometrically measured tube wall temperatures are also shown in this table. Weighing of the different silicon carbide tube sections before and after each run indicated the amount of material deposited. This product was then separated into water soluble and insoluble substances, and analyzed by Electron Dispersive Analysis of X-rays (EDAX), which gives the elemental composition, and by X-ray diffraction, to find the crystalline components.

The products were collected in the following forms:

(a) In the regions where the silicon carbide tube wall temperature was above the melting point of silicon and the dew point of sodium chloride, the wall was covered with silicon. During cooling after the experiment, this silicon solidified into small mounds around the circumference and frozen pools at the bottom of the silicon carbide tube.

(b) In the regions where the tube wall temperature was slightly below the melting point of silicon, the inside wall was covered with a gray scale which could be easily scraped off in the form of large flakes. These flakes consisted of crystalline silicon and varying amounts of sodium chloride ranging from trace values (1 to 2% of sodium chloride) in the flakes from tube sections with a wall temperature only slightly below the dew point of NaCl to more than 50% farther downstream.

(c) The end sections of the silicon carbide tube were covered with a glassy layer of sodium chloride, containing some silicon.

(d) The rest of the product in the gas stream formed brown particles upon mixing with cold gas. These particles ranged in size from 3 μm to 70 μm and consisted of a mixture of amorphous silicon and NaCl.

Figure 3 contains also the experimental silicon condensation results obtained by weighing the tube sections after one representative experiment. The shape of the experimental distribution is similar to the theoretical distribution for developing flow, but displaced in the downstream direction. There are two explanations for this downstream shift: (a) the flow condition of a small diameter jet entering a tube of larger diameter would mean that the vapor stream would not contact the tube wall until it had travelled a certain distance; (b) evaporation of the sodium droplets and the subsequent gas phase reaction process may not have been completed and equilibrium may not have been reached until the stream was well into the first tube section. The evidence of reduced flowrates leading to an increased initial condensation rate supports either explanation.

The calorimetrically determined bulk gas temperature value at the end of the first test section seems to indicate the applicability of the developing flow analysis for the heat transfer.

5. DISCUSSION

Since this experiment was conducted as part of a larger development program, we would like to consider the implications of the results on that program:

(a) We would like to point out that the model was developed for the flow geometry of the large scale reactor in which the effects to which we attribute the differences between theoretical prediction and experimental results would not be present. Therefore, the basic agreement between model predictions and experiment support the model used to predict the silicon collection rate.

(b) The much higher Reynolds number characterizing the flow in the large scale reactor will lead to increased heat and mass transfer to the reactor wall, and, therefore, to larger collection rates.

(c) The low power levels used in the laboratory scale experiment had the consequence that the collector tube wall temperature dropped below the dew point of sodium chloride after relatively short distance, leading to collection of sodium chloride together with the silicon. The design and operating power levels of the large scale reactor avoid this problem.

6. CONCLUSIONS

We can draw the following conclusions from our results:

- The controlled reduction of tetrachlorosilane by sodium at plasma temperatures proceeds as predicted from thermodynamic considerations.
- The reaction product silicon can be separated and collected on a wall

at a temperature above the dew point of sodium chloride.
- The experimentally determined condensation rate essentially follows the predictions from model calculations, and the observed differences can be explained by the simplifying assumptions made in the model characterizing the experiment.

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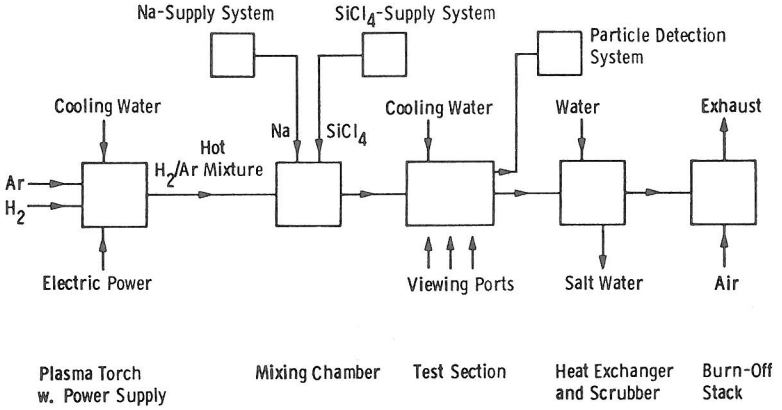

Fig. 1 — System lay-out schematic of kinetics experiment

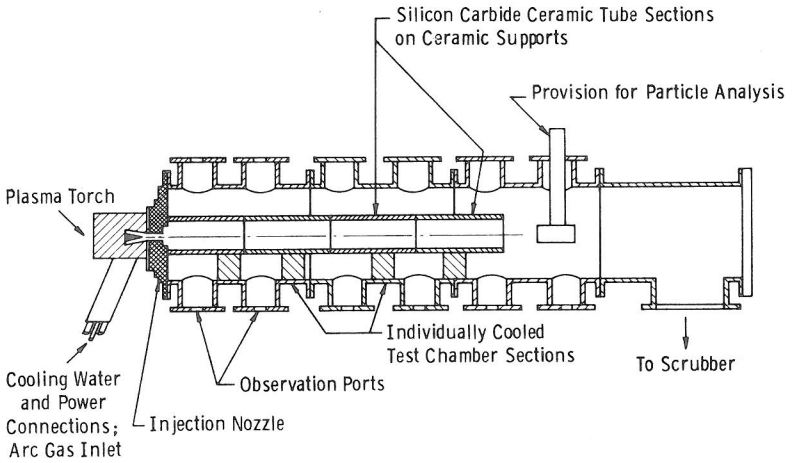

Fig. 2 — Assembly drawing of test apparatus

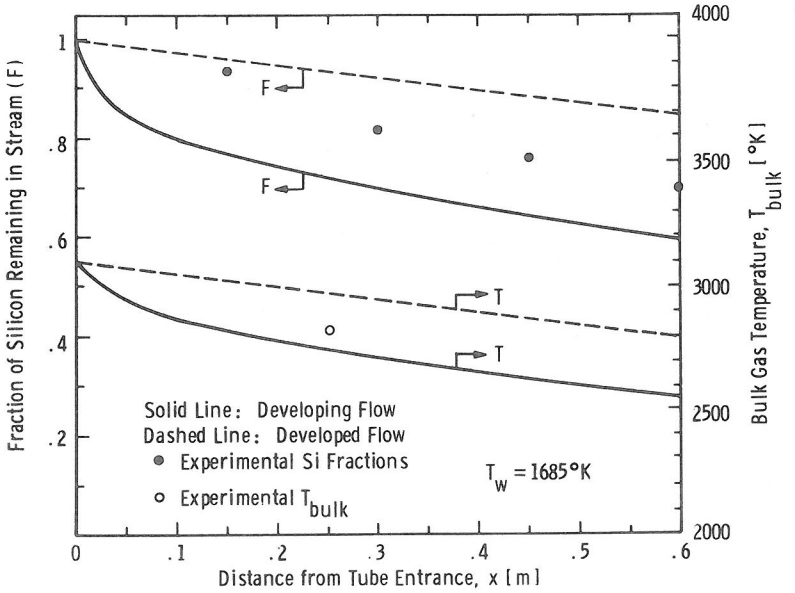

Fig. 3 — Theoretical and experimental axial distribution of the fraction of silicon remaining in the gas stream, and axial bulk temperature distribution

TABLE 1

TUBE WALL TEMPERATURES AND BULK GAS TEMPERATURES AT A TORCH POWER OF 26 kW

Axial Location (see Figure 2)	Distance from Injection Nozzle	T_{bulk} °K	T_{wall} °K
Torch exit		3670	
Injection Nozzle	0	3100	
1st Window	5 cm		1900
2nd Window	16 cm		1650
End of Test Section I	25 cm	2820	