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PRODUCTION OF SILICON FOR SOLAR CELLS: PRESSURE EFFECTS ON THE SiF4-Na REACTION AND ITS PRODUCTS

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ABSTRACT

The effects of the SiF₄ pressure on the SiF₄-Na reaction and its products have been studied. Constant volume batch experiments were carried out in which Na, preheated to 250° C, was exposed to SiF₄ at different pressures. Because of the exothermic character of the reaction, the temperature at the reaction zone peaks to a maximum that depends on the pressure of SiF₄. At SiF₄ pressure around 1 atm, the temperature maximum reaches the highest values, near the melting point of silicon (1412°C). Depending on the SiF₄ pressure, three distinct reaction behaviors and corresponding reaction products can be identified. The pressure range of more interest for practical application of the SiF₄-Na reaction lies between 350 torr and 760 torr. At these pressures, clear segregation between the Si and NaF phases is observed and the average Si particle size is 0.2 mm.

Introduction

Photovoltaic conversion of sunlight is a very attractive, clean technology that can provide part of the energy needed by our society. The core of this new technology is the solar cell, and silicon is the chief material used currently. The production of high purity Si is a major factor (20-30%) of the total Si solar cell cost.

A process developed for the production of high purity Si involves the Na reduction of gaseous $SiF_4^{(1)}$ according to the reaction:

$$SiF_4(g) + 4Na(1) \rightarrow Si(s) + 4NaF(s)$$
(1)

Although this reaction is thermodynamically favored at room temperature, ΔG^{O} (298 K) = -145/kcal/mol Si⁽²⁾, it has been found experimentally that Na has to be heated to about 150°C before any appreciable reaction can be observed. Reaction efficiency may be decreased by the side reaction of NaF (formed by Equation 1) with SiF4 to produce Na₂SiF₆ according to

$$SiF_4(g) + 2NaF(s) \stackrel{?}{\rightarrow} Na_2SiF_6$$
 (2)

....

However, temperatures about 600° C in the product mass (Equation 1) are unfavor able for the formation of Na₂SiF₆ (Equation 2). Thus, the unwanted by-product Na₂SiF₆ may be easily avoided.

Reaction 1 products (r.p.) consist of a mixture of silicon particles intimately mixed with NaF particles. Silicon can be separated from the NaF by either acid leaching (1) or melting (3) the r.p. mixture.

It is expected that the rate of the reaction will depend on the conditions under which the SiF₄-Na reaction takes place and, for batch process in which Na is preheated above 150° C, the pressure of SiF₄ should be the main reaction variable. It is also expected that reactions performed at different SiF₄ pressures will yield r.p. with different characteristics. Porosity, degree of segregation between the Si and NaF phases, silicon particle size and microstructure, and weight percentages of unreacted Na and by-product Na₂SiF₆ formed are some of the most important r.p. characteristics. These characteristics will, in turn, be the major factors in determining the rate and extent of the silicon separation from the r.p.

In the current work, the SiF_4 -Na reaction product characteristics, such as size, morphology, composition, and phase segregation, have been studied as a function of the reaction pressure of SiF_4 .

Experimental Procedures

Pieces of sodium metal (Baker reagent grade) of approximately 5 grams each were cut from 2-inch diameter rods and stored under mineral oil. Prior to use, they were dipped successively in hexane to dissolve the mineral oil, in CH₃OH to etch the Na surface, and in tetrahydrofuran (THF) to stop the etching reaction and to remove the alcoholate formed.

In each experiment, a clear Na piece was introduced into a Ni cup and placed inside a 1-liter glass reactor (3 in i.d., Figure 1). Connection with the SiF4 source was provided by valve V1 and with the vacuum through valve V2. The temperature in the reaction zone was monitored by an Inconel-sheathed Chromel-Alumel thermocouple for temperatures below 1000°C and by molybdenum protected W-Re and graphite protected Pt-Pt Rh 10% thermocouples for temperatures above 1000°C. Reaction products were kept separate from the reactor wall by doublenickel crucibles. The pressure was controlled by a high capacity flow, constant pressure regulator.

Results

Effects of SiF₄ Pressure on the Temperature of the SiF₄-Na Reaction.--When SiF₄ gas was brought into contact with liquid Na at 250°C, the reduction reaction (Equation 1) started immediately. The temperature rose rapidly for a few seconds, reached a maximum T(max), then decreased slowly, as shown typically in Figure 2. The temperature was not constant throughout the reaction zone. Because of the heterogeneous character of the reaction, the temperature varied across the reaction products by as much as 200° C. The curve shown in Figure 2 corresponds to the temperature measured at the center of the reaction products.

Experimental curves were obtained for values of P (SiF₄) ranging from 0.1-10 atm. The maximum temperature for each reaction pressure of SiF₄ is plotted in Figure 3. The range of P (SiF₄) indicated in Figure 3 represents the observed pressure fluctuations as shown in Figure 2.





Schematic of the SiF4-Na Reaction System

<u>Effects of the SiF₄ Pressure on Reaction Rates.</u>—The characteristics of the reaction depended on the pressure of SiF₄. Three types of reaction conditions were identified, namely:

(A) At low pressures of SiF_4 (P [SiF₄] < 150 torr), the reaction occurred slowly. The liquid Na surface slowly became coated with a brown tarnish film. The temperature increase and decrease occurred over a period of several minutes, as shown in Figure 2.

(B) At pressures in the range of 200-300 mm Hg, the reaction went faster, with the temperature rising in a few seconds. A red glow was observed on the reaction surface, estimated to be about 850° C.

(C) At pressures higher than 350 mm Hg, the reaction became vigorous. The temperature rose almost instantaneously, and a flame several centimeters long formed above the reaction zone. In this case, the reaction took place not only in the liquid and solid phases, but also in the vapor phase. A column of brown dust formed and deposited on the reactor upper walls.



FIG. 3 Tmax Dependence with $P(SiF_4)$

Effects of SiF₄ Pressure on the Reaction Products.--At low magnification (100 X), the reaction product had a characteristic appearance for each of the above-mentioned conditions (A, B, and C).

Type A r.p. consisted of a very soft, brown and blue mass (Figure 4) that, when exposed to air, burst into flames producing white fumes of Na20 as a result of the oxidation of unreacted Na. The reaction products formed a layer a few millimeters thick under which large areas of Na were left completely unreacted. The upper part of the reaction product layer had a bubbly blue growth consisting of agglomerations of small spheres (diameter 1 mm to 0.1 mm) with a very smooth surface spreading for a few millimeters. When these spheres were broken, they showed a hollow interior and brown porous inner walls. The thickness of the walls was around one-tenth of the diameter of the sphere.

The brown formation had a smooth surface, and in some cases a bluish color could be seen through and underneath the brown layer. Qualitatively, the mechanical strength seemed to be higher than that of the blue formation.

Type B r.p. were usually dark brown and bubbly (Figure 4). Some of the surfaces were very smooth, suggesting a molten-like layer. Other surfaces were rougher, and their color had some yellow or brown tones. When broken, the r.p. mass showed a porous structure with pore sizes ranging from a few millimeters to a few micrometers, as observed by optical microscopy and SEM. A small amount of unreacted Na (less than 5% by weight) remained dispersed through the matrix. Many of the walls of the r.p. mass seemed to be formed by porous layers within which unreacted Na was trapped. White Na₂O growths, as well as NaOH formed by the absorption of H_20 from the atmosphere, were observed in these regions when the r.p. were exposed to air.

Type C r.p. consisted of a very hard grey crust that had partially wetted up the walls of the Ni crucible. A small fraction of a brown powder formed in the vapor phase and deposited on the reactor walls (Figure 4). The porosity of the grey layer depended on pressure-temperature conditions. At the lower end of the pressure range (350-600 mm Hg), the grey sponge presented a porosity of 20%, and the total mass of r.p. occupied practically all of the volume initially filled by the Na. At the higher end of the pressure range (600 torr), the grey crust became very compact and much harder, and the r.p. mass occupied only a thin horizontal zone at the original level of the Na.

X-Ray Analysis.--Typically, X-ray analysis indicated that the r.p. consisted mostly of Si and NaF. Occasionally, the presence of Na2SiF6 was also detected. Peak intensities were different for samples taken from different regions of the same reaction product. Thus, for r.p. Type C (P [SiF4] > 350 mm Hg), X-ray analysis showed a clear difference between the grey upper crust containing both Si and NaF and the brown lower mass containing almost exclusively NaF. When the reaction was carried out at pressures of 1 atm and above, the X-ray patterns of the fine powder deposited from the vapor phase on the reaction walls showed the presence of some Na2SiF6 in addition to Si and NaF.

Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis (EDAX) of r.p.--A wide variety of types and sizes of the silicon particles were formed in Reaction 1. Figure 5a shows a top view of the crusts of the r.p. magnified 200 times. Pressure of SiF4 does not seem to greatly affect the general appearance of the exterior surface of these crusts. EDAX analysis of the white and dark





Type A P_{SiF4} < 150 torr





Type B P_{SiF4} 200 - 300 torr





Type C $P_{SiF_4} > 350$ torr

MAGNIFIED 2.5 TIMES

ACTUAL SIZE

FIG. 4 Types of r.p. of the SiF_4 -Na Reaction areas detects both Si and Na in all cases. At 2000X (Figure 5b) the exterior surface of the top crust shows two types of formation: a flat formation with a very smooth surface (smooth even at 20,000X), crisscrossed with occasional cracks, and a multispherical formation that seems to grow out of the flat background. EDAX analysis shows Si and Na peaks for both types of formation. For r.p. obtained at low pressures of SiF4 (200 torr), there are no clear and consistent indications of composition discontinuities. For r.p. obtained at higher pressures of SiF₄ (300 torr), some segregation can be observed. Figure 5c shows the inside of a spherical formation where some NaF had completely segregated.

Observation of cross section of the r.p. reveals no evident discontinuties in composition for r.p. obtained at low pressures. However, at higher pressures, the segregation is evident. Figure 6 shows how the composition changes drastically for pure Si (A) on the upper part of the crust, which was in direct contact with the SiF4, to almost pure NaF in parts of r.p. bulk (D). A Si rich zone (B) and a NaF rich zone (C) complete the segregation sequence.

Another feature of interest in the Si rich zone is shown in Figure 7a. In the band and nodule formation, EDAX of the dark nodules shows only a Si peak. At higher magnification (5,000X), the microstructure of the Si nodule can be seen (Figure 7b). The light areas seem to be mostly NaF. EDAX detects high peaks of Na and very small peaks of Si. In some areas, complete segregation can be observed (Figure 7c), with Na and F being the only peaks detected.

Si Particles: Microstructure and Particle Size Distribution .-- The distribution and microstructure of the silicon particles in the r.p. can be revealed by leaching the NaF from the surface of the r.p. with a 1-NHCl solution. Figure 8a is a SEM of the leached surface showing two distinct types of silicon particles: compact silicon masses with crystalline facets and loosely bound smaller silicon particles with rounded surfaces. EDAX analysis of the same region detects only Si. If the silicon phase is then completely separated from the NaF matrix by leaching and filtration, a silicon brown powder is obtained that is formed by particles of irregular shape (Figure 8b). These particles are aggregates of smaller faceted and rounded silicon particles (Figure 8c).

Both types of particles are produced at pressures of SiF4 ranging from 0.1 atm to 10 atm, although the relative number of faceted particles increases qualitatively with pressure.

A qualitative idea of leached Si particle size was obtained by SEM. Particles ranging from millimeter to micrometer sizes were observed. The smallest particle observed was 0.3 µm long, near the limit of detection of the system. For a semiquantitative determination of the particle size distribution, the leached silicon powders were sieved through a set of five standard sieves: 3.5inch-diameter sieves ASTM No. 20, 40, 60, 100, and 230 mesh, corresponding to sieve openings of 0.841, 0.420, 0.250, 0.149, and 0.063 mm, respectively. For every sample, 0.2 g of dried silicon powder was sieved through this set, and the various fractions were collected and weighed to the nearest mg. The percentage of the total weight retained on each sieve was calculated from these weights. The cumulative weight percentage of five different experiments in the pressure range 55 mm Hg to 700 mm Hg is plotted in Figure 9.



(a) Upper view of the SiF₄-Na r.p. obtained at 300 torr of SiF₄. Mag. x 200



(b) Higher magnification of the white formations shown in (a). Mag. x 2000



(c)

Internal view of a spherical growth similar to that shown in (b). r.p. obtained at 620 torr of SiF₄. Mag. x 500





FIG. 6

Reaction Products of the SiF₄-Na Reaction with P (SiF₄) = 1.0 atm EDAX: A(Si), B(Si, some NaF), C(NaF, some Si), D(Na)

Discussion

Sodium reacts with SiF₄ only when the metal has been preheated to the temperature range $150^{\circ}-200^{\circ}$ C. The exact temperature at which the reaction starts depends on the state of oxidation of the Na surface; thus, Na that has been exposed to air needs to be preheated to nearly 200° C before any appreciable reaction is observed. The starting temperature is apparently independent of the pressure of SiF₄. The SiF₄-Na reaction takes place in three stages visible in Figure 2: an initiation step, an exothermic fast stage, and a final cooling stage.

The first stage of the SiF_4 reaction can be detected by a small drop in the pressure of the gas and by the simultaneous appearance of a brown layer on the Na surface. This initial reaction stage can last several minutes, but can be speeded up by preheating the Na to $250^{\circ}C$ before it is put in contact with the SiF₄. At this temperature, the reaction starts immediately after contact between reactants, reaches a maximum rate (second stage) and then decreases slowly (third stage). The duration of the second stage, the time interval between the moment at which the reaction ignites and the moment at which the reaction zone reaches its maximum temperature is dependent on the SiF₄ pressure. At 1 atm, a



(a) General view of r.p.crust.
A: Silicon nodules
B: NaF rich zones



(b) Silicon nodules shown in (A).



(c) NaF rich area shown in (B).

FIG. 7 Scanning Electron Micrographs of Reaction Products Obtained by the SiF_4 -Na Reaction $P_{SiF_4} = 1$ atm



(a) SEM photomicrograph of surface leached r.p. obtained at 1 atm of SiF₄. EDAX Si.



(b) SEM photomicrograph of a typical silicon powder particle after total leaching and filtration.



(c) SEM photomicrograph showing microstructure of silicon particle in (b).

FIG. 8 Microstructure of Leached Si



Cumulative Weight Percentage Versus the Particle Size of Silicon Powder for Different Pressures of SiF_4 Gas in the SiF_4 -Na Reaction

sharp temperature maximum is reached in a few seconds, whereas at 0.1 atm, a weak maximum is reached after several minutes. In addition, it can be observed that T(max) corresponds with the practical completion of the reaction as determined by the drop of the SiF₄ flow and the SiF₄ pressure drop during experiments carried out in a closed, constant volume reactor. It can be concluded from this evidence that the average rate of reaction of this second stage of the SiF₄-Na reaction depends on the SiF₄ pressure.

For a cylindrical (7 cm diam x 0.7 cm deep) Na pool, the Na consumption rate varies from 3.10^{-2} g cm⁻² min⁻¹ at 0.1 atm of SiF₄ to 2 g cm⁻² min⁻¹ at 1 atm. Unfortunately, after the reaction starts, the surface area of Na is no longer known, and reference to rates obtained with other geometries is difficult.

The increase of T(max) with the pressure of SiF₄ is another indication of the pressure dependence of the reaction rates. Because the geometry, and material amounts were repeated for each experiment, higher temperatures should mean higher rates of heat production, which in this case indicates higher reaction rates. The plateau for T(max) shown in Figure 3 between approximately 300 torr and 600 torr may be due to the NaF heat of transition from solid to liquid.

Based on the rate of reaction, T(max) dependence on the SiF₄ pressure, the visual observation of the reaction zone, and the microscopic examination of the products, a model can be constructed to explain the different types of reactions observed. At low SiF₄ pressures (below 300 torr), the reaction takes place on the Na surface. The reaction products NaF and Si form a barrier through which SiF₄ or Na or both have to diffuse. Two main driving forces cause the reaction to continue. First, the increase in temperature of the Na, as a result of the reaction, produces an expansion of the metal and aids in breaking the product crust and in transporting Na to meet SiF₄. The increase in temperature also increases the specific rate of reaction. The second driving force is probably the crystallization of NaF that produces porosity through which the metal is thermally pushed out. As the Na is pushed through the product crust, it adopts a frontal, spherical surface shape that immediately reacts, freezing this shape (Figure 4). The heat locally liberated by the reaction drives the inner, unreacted Na through the spherical products' walls at weaker points, creating several new spheres growing out of the original one. This process continues until the barrier created by the reaction products' crust is large enough to slow down the transport of reactants to the reaction zone. At this point, the reaction rate decreases, the heat dissipation rate becomes greater than the heat production rate, and the Na cools until the reaction finally stops. Evidence of this multispherical formation can be seen in Figure 5a, and, during chemical analysis, unreacted Na was indeed observed under the reaction products' crust.

At pressures of SiF_4 between 300 torr and 600 torr, the reaction rate accelerates; the reaction products reach temperatures near the boiling point of Na (892°C) so that in this pressure range, not only the liquid Na thermal expansion, but also the Na vaporization become the driving forces for the transport of Na through the already formed r.p. to meet fresh SiF4. The appearance of a glow, or even a flame, on top of the reaction is an indication of the vaporization of Na. Again, the morphology of the reaction products suggests a mechanism in which Na is thermally pushed out through the crust to meet the SiF4. In addition, the products expand to occupy a volume that is approximately double the original volume occupied by the Na. A preferential growth along the walls of the Ni reactor is probably a consequence of the Ni providing a heat sink for the products that enhances the solidification of the NaF. In contrast, in the middle of the product mass, a smooth, molten-like NaF layer can be seen. Thus, while at the Ni walls, Na probably oozes out through the pores created by the solidification of NaF; in the middle of the products, Na probably has to mechanically break through a layer of molten NaF or dissolve in the NaF and diffuse through it to meet the SiF4. Corresponding to each type of reaction condition, a type of reaction product can be identified. Thus, phase segregation, Si particle size, and crystallinity of the Si particles are observed to depend on the SiF4 reaction pressure.

The segregation of the Si and NaF phases increases with the reacting pressure of SiF4. For Type A reaction products, X-ray analysis of samples taken from different zones of the r.p. mass systematically shows the presence of both phases, indicating that appreciable segregation has not taken place. Concurrently, at high SEM magnification (10,000X), this type of r.p. does not show clear phase discontinuities or separations, and EDAX systematically detects both Si and Na peaks.

Type B reaction products also do not show clear segregation by X-ray analysis. SEM-EDAX analysis shows only occasional grains, layers, or nodules of one of the phases. Most of the r.p. seem to consist of a homogeneous mixture of both phases without clear discontinuities.

For Type C reaction products, the segregation becomes obvious because of formation of a visible upper grey crust on top of the brown porous mass. the X-ray analysis indicates that the grey crust consists of Si and NaF, and the brown mass consists mostly of NaF and some Na₂SiF₆ with a very low content of Si. Observation at high magnifications by SEM-EDAX clearly shows an overall enrichment of the upper crust in Si and of the lower brown mass in NaF (Figure 6). Figure 7a shows the banded structure, with areas rich in Si and areas rich in NaF alternating. In some zones, the Si-rich areas agglomerate in nodules of pure Si (Figure 7b), whereas other zones consist of pure NaF (Figure 7c).

The complete segregation of phases Si and NaF can be achieved by heating the mixture to 1450° C for 5 minutes. In this condition, Si collects at the bottom in a pool and NaF floats on top. At temperatures below the melting point of Si, NaF with melt (998°C) and flow, producing partial segregation; however, no Si coalescence can be observed⁽⁴⁾. In light of this evidence, the role of the SiF₄ in the segregation appears to be only indirect. It is the temperature reached by the r.p. during the reaction that is the main cause of the segregation. Thus, for reaction Type A with temperatures well below the melting point of NaF, no segregation can be observed. In contrast, for reaction Type C, the high temperatures reached produce partial coalescence that could be the result of the localization of high temperatures. This localization is the result of the heterogeneity of the reaction and/or of the short period of time during which the high temperatures are maintained.

Silicon particle size also increases with the pressure of SiF₄. A semiquantitative idea of this dependence can be obtained by sieve analysis. For clarity of presentation, the particle size distribution of only five experiments is shown in Figure 9. These five experiments were selected to give an idea of the general dependence of particle size on the SiF₄ pressure, as well as the typical experimental variations among experiments run in similar conditions (750 torr versus 760 torr). In general, the average particle size increases with the SiF₄ pressure from sizes smaller than 50 μ m for Si obtained at 0.1 atm, to nearly 300 μ m for Si obtained at 1 atm.

Observation of the leached Si particles at high SEM magnifications shows this dependence qualitatively. Silicon obtained at low pressures consists of small particles ranging in size from thousands of angstroms (detection limit of SEM) to several micrometers. As the pressure increases, larger particles can be detected, and at 1 atm Si particles in the millimeter range can be observed (Figure 8b). Two possible growth mechanisms can be invoked: partial melt coalescence and vapor transport.

The formation of agglomerates (Figures 8b) of small particles is the result of partial melt coalescence of silicon. The tremendous energy liberated by the SiF₄-Na reaction and its heterogeneous character produces local hot spots with temperatures as high as 2200 K, the adiabatic temperature. As the temperature of the reaction increases with SiF₄ pressure, the Si particle size increases because the number, size, and duration of the hot spots also increases. This mechanism has a tendency to form rounded masses because the interfacial energy between Si and NaF is very large, $320 \pm 20 \text{ ergs/cm}^2$ ⁽³⁾.

The second mechanism, vapor transport, is probably the main path for forming the crystalline faceted microstructure shown in Figure 8b. In addition to partial melt coalescence, at high temperature, Si will react with SiF_4 to form gaseous subfluorides according to

$$\operatorname{Si} + \frac{x}{4 - x} \operatorname{SiF}_{4} \stackrel{\rightarrow}{=} \frac{4}{4 - x} \operatorname{SiF}_{x}$$
(3)

where $1 \le x \le 3$. Assuming a pressure of SiF₄ of 1 atm and unit activity for Si, the estimated equilibrium pressures for the three subfluorides at 1700 K will be $5.1.10^{-7}$ atm for SiF, 1.0×10^{-3} atm of SiF₂, and 0.4 atm of SiF₃ ⁽²⁾. This temperature is just above the melting point of Si (1412°C) but well below the adiabatic temperature; therefore, pockets with this condition will exist through the r.p. mass. As the silicon subfluorides reach cooler regions within the r.p. mass, they disproportionate producing Si according to Equation 3. It is well known that this process produces well crystallized deposits of Si ⁽⁵⁾. Finally,

it is important to note that at high temperatures Equation 1 may reverse and NaF can react with Si to regenerate SiF₄ and Na. This silicon "etching" reaction has a free energy of -8.7 kcal/mol Si at 2200 K, but it is thought to play a minor role on the formation of the microstructure.

Conclusion

It has been observed that the temperature reached by the reaction products of the SiF₄-Na reaction varied with the reacting pressure of SiF₄ for batch experiments. The temperature of the reaction products reached a maximum for SiF₄ pressures around 1 atm. In addition, the rate and extent of the SiF₄-Na reaction, the degree of segregation between the Si and NaF phases, and the silicon particle size were also dependent on the SiF₄ pressure. Finally, the mechanism for silicon growth seems to be melt coalescence and vapor transport through silicon subfluorides

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