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**Low-Cost Solar
Array Project**

DOE/JPL-1012-18

Distribution Category UC-63b

**Purification of Silicon
by the Silicon Fluoride
Transport Process**

A Thermochemical Study

MASTER

Robert A. Rhein

April 15, 1979

Prepared for

U.S. Department of Energy

Through an agreement with

National Aeronautics and Space Administration

by

Jet Propulsion Laboratory

California Institute of Technology

Pasadena, California

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The JPL Low-Cost Solar Array Project is sponsored by the Department of Energy
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major effort toward the development of low-cost solar arrays.

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ABSTRACT

A computer-assisted thermochemical equilibrium analysis was conducted for the silicon transport reaction:

The calculations indicated that a substantial transport rate should be possible at temperatures of 1700 K and one atmosphere pressure.

Computations were made to determine whether the elemental impurities present in metallurgical-grade silicon would transfer in this process. It was concluded that aluminum, chromium, copper, iron, manganese, molybdenum, nickel, vanadium, and zirconium would not transfer, but that boron, magnesium, phosphorus, and titanium would transfer.

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SECTION I

INTRODUCTION

One of the objectives of the Silicon Material Task of the Low-Cost Solar Array Project (JPL/DOE) is the development of a process for producing Si at a price of less than \$10/kg (1975 \$). Included among the various endeavors to accomplish this objective was the purification of commercial metallurgical-grade Si by the use of a transport process using silicon difluoride as an intermediate compound. A simplified description of the reactions comprising this process (Reference 1) is:

Reaction 1 has generally been observed at elevated temperatures and reduced pressures: 1623 K and 0.5 torr (Reference 1); 1473 K and 0.05 torr (Reference 2); 1423 K and 0.1-0.2 torr (References 3, 4); 1473 K and less than 1 torr (Reference 5); and 1523 K, 0.1-0.2 torr (Reference 6).

SiF₂ is reportedly stable only at low pressures: 5 torr (Reference 2); 0.2 torr (Reference 3); 1-2 torr (Reference 5); and 0.25 torr (Reference 1).

For Reaction 2, the polymerization took place in a cold trap, producing a polymer resembling Teflon, except that the polymer spontaneously ignited in air (Reference 3). The cold trap was generally held at the temperature of liquid nitrogen or liquid air; the polymer was observed after the cold trap was warmed to ambient temperature (References 2-6), although infrared spectroscopy studies indicate that polymerization may take place at temperatures as low as 50 K (Reference 7).

The thermal decomposition of (SiF₂)_x produces polyperfluorosilylene oligomers, including Si₂F₆, that upon heating to above 673 K further decompose to yield elemental Si (References 1, 3-5, 8).

The purpose of this report is to examine the feasibility of this Si transport process as a means of purification of metallurgical-grade Si. Two aspects are dealt with here: determination of Si subfluoride yields vs temperature and pressure, and determination of which of the impurity elements present in metallurgical-grade Si might be expected to transfer (as fluorides) in Reaction 1.

The method used here is a computer-assisted thermodynamic equilibrium analysis of the reaction of Si with SiF_4 , assuming the presence of small concentrations of the impurity elements. The computer program is from NASA-Lewis and is described by Gordon and McBride (Reference 9). The following impurity elements, and their concentrations (ppm wt) in metallurgical-grade Si, are (Reference 10): Al, 1570; B, 44; Cr, 137; Cu, 50; Fe, 2070; Mg, 50; Mn, 70; Mo, 50; Ni, 47; P, 28; Ti, 163; V, 100; and Zr, 100.

The thermodynamic data for these elements, their fluorides, and, where available, their silicides, were obtained primarily from JANAF tables. Some of the data were obtained courtesy of Dr. Sanford Gordon at NASA-LEWIS and Dr. C. A. Alexander at Battelle Institute, and the remainder were obtained from the collections of Barin and Knacke (References 11, 12) and from a paper by Brewer et al (Reference 13).

The concern with impurities arises from the fact that very small concentrations of impurities (in some cases as low as 1 ppba) can seriously degrade the efficiency of solar cells fabricated from this Si (References 14, 15).

SECTION II

RESULTS AND DISCUSSION

A. COMPUTED SILICON SUBFLUORIDE PRODUCTION FROM THE REACTION OF Si WITH SiF_4

The computed concentrations of Si fluorides resulting from the reaction of Si and SiF_4 are shown in Figure 1. It is seen that there is very little reaction anticipated at temperatures less than 1100 K, but there is substantial reaction at the Si melting point, 1695 K. Likewise, the computed concentrations of Si subfluorides increase with decreasing pressure, as might be expected. However, at one atm pressure, there is still appreciable Si subfluoride concentration predicted.

There are published accounts of the reaction between Si and SiF_4 at pressures in the order of one atm. Ingle (Reference 16) reported that at 1745 K and 0.67 atm SiF_4 , a weight loss of 7.5 mg/min was observed for Si of surface area 1.3 cm^2 . Kanaan and Margrave (Reference 17) reacted Si with SiF_4 at one atm, 878-1003 K, measured the Si weight loss, and concluded that a reaction took place that formed Si_2F_6 and possible higher homologues. Wolf (Reference 18) reported that the reaction between Si and SiF_4 at one atm pressure and 1423 K produced Si_2F_6 at an efficiency of approximately 7% and that the SiF_2 production rate should increase with the square root of the SiF_4 pressure (production rate is the product of concentration and total pressure).

It is conceivable that the step involving $(\text{SiF}_2)_x$ polymer formation and decomposition may not be necessary for Si transport. Wolf (Reference 18) reported Si_2F_6 decomposed to Si at 823 K. Si_2F_6 and the higher homologues are stable below 673 K, but disproportionate to Si and SiF_4 upon passage through a tube heated to 1123 K (Reference 8).

B. COMPUTED DETERMINATION OF IMPURITY TRANSPORT

Figure 2 shows that for temperatures to 1700 K and pressures 0.001-1.0 atm, there is very little interaction between SiO_2 and SiF_4 ; hence SiO_2 can be used as a material of construction up to its softening point, 1773 K (Reference 19). Figure 3 shows that aluminum would be expected to transfer as the fluoride; however, in the presence of SiO_2 , Figure 4, Al would not transfer but instead would form the silicate. Ingle (Reference 1) was unable to record the mass spectrum of AlF_3 in a heated quartz tube, presumably also because of aluminum silicate formation.

Figures 5 and 6 show that boron is expected to transfer primarily as BF_3 in the absence or presence of SiO_2 . BF_3 reacts with SiF_2 at low temperatures (Reference 5) forming Si_2BF_7 and possible other Si-B-F compounds. Such compounds may well incorporate into the $(\text{SiF}_2)_x$ polymer.

Figure 7 shows that the chromium impurity reacts to form the silicide and is not expected to transfer.

Copper was found to be unchanged in the Si/SiF₄ reaction, and is not expected to transfer.

Iron forms the silicide during the reaction, and is not expected to transfer. Figures 8 and 9 show that magnesium is expected to transfer as the fluoride above 1300 K in the absence or presence of SiO₂.

Molybdenum forms the silicide and is not expected to transfer. Manganese remains as either the element or silicide, Figure 10, and is not expected to transfer. Figure 11 shows that nickel reacts to form the silicide, and is not expected to transfer.

Figure 12 shows that at temperatures above 1100 K, phosphorus (boiling point 704 K, Reference 20) is expected to transfer as the element. Figure 13 shows that for temperatures above 1100 K, titanium is expected to transfer as the fluoride.

Vanadium forms the silicide, and is not expected to transfer. Zirconium is expected to transfer, Figure 14, at temperatures above 1200-1300 K; however, in the presence of SiO₂, Zr forms the silicate, and would not transfer.

SECTION III

CONCLUSIONS

Thermochemical computations indicate that a substantial transport rate of Si should be feasible at pressures in the order of one atm. This process should be capable of removing the following impurities from metallurgical-grade Si in the presence of SiO_2 : Al, Cr, Cu, Fe, Mn, Mo, Ni, V, and Zr. However, the following impurities may transfer: B, Mg, P, and Ti.

For this Si transport process to be effective in converting metallurgical-grade Si to solar-cell-grade Si, other means must be devised to eliminate the B, Mg, P, and Ti impurities. One possibility is the use of Si_2F_6 as the intermediate transport species, along with distillation to remove elemental P and the transported fluorides of B, Mg, and Ti.

Figure 1. The Reaction Between Si and SiF₄ Equilibrium Composition of Products. Initial Mole Fraction of Reactants: SiF₄, 0.5; Si, 0.5

Figure 2. Computed Reaction Products from the Interaction of SiF_4 and SiO_2 at Weight Ratio 1.0. SiF_4 , SiO_2 Not Shown, as Mole Fractions Essentially Unaffected

Figure 3. Computed Al Reaction Products Resulting from 1570 ppm Al in Equimolar Si and SiF_4

Figure 4. Computed Al Reaction Products Resulting from 1570 ppm Al in Si Reacting with SiF_4 in the Presence of SiO_2

Figure 5. Computed B Reaction Products Resulting from 44 ppm B in Si with Equimolar SiF₄

Figure 6. Computed B Reaction Products Resulting from 44 ppm B in Si, Reacting with Equimolar SiF₄ in the Presence of SiO₂

Figure 7. Computed Reaction Products from 137 ppm Cr in Si, Reacting with Equimolar SiF_4

Figure 8. Computed Reaction Products from 50 ppm Mg in Si, Reacting with Equimolar SiF_4

Figure 9. Computed Reaction Products from 64.06 ppm MgF_2 in SiF_4 with SiO_2

Figure 10. Computed Reaction Products from 70 ppm Mn in Si, Reacting with Equimolar SiF_4

Figure 11. Computed Reaction Products from 47 ppm Ni in Si, Reacting with Equimolar SiF_4

Figure 12. Computed Reaction Products from 28 ppm P in Si, Reacting with Equimolar SiF_4

Figure 13. Computed Reaction Products from 163 ppm Ti in Si, Reacting with Equimolar SiF_4

Figure 14. Computed Reaction Products from 100 ppm Zr in Si, Reacting with Equimolar SiF₄

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