5101-105
Low-Cost
Solar Array Project

DOE/JPL-1012-20
Distribution Category UC-63b

Modeling of Silicon Particle Growth

A Progress Report

Ananda K. Praturi
George C. Hsu
Ralph Lutwack

MASTER

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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Prepared by the Jet Propulsion Laboratory, California Institute of Technology,
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ABSTRACT

Efforts at the Jet Propulsion Laboratory toward the production of pure polycrystalline silicon are centered on the concept of silicon particle growth in a fluidized bed reactor (FBR) and a continuous flow pyrolyzer (CFP). The CFP possibly can provide the seed particles which will be grown to larger sizes in the FBR. In both the reactors polycrystalline silicon is obtained from the pyrolysis of silane. A part of the JPL effort is to develop a model of silicon particle growth for the purpose of predicting particle growth rates and product particle size distributions in the FBR and the CFP. This report describes the mathematical models of silicon particle growth in the FBR and the CFP.

NOMENCLATURE

a	jump distance on silicon surface, lattice constant
a'	inverse of the specific surface area of particles in fluidized beds, cm
C	concentration of total gas phase, g-mole/cm ³
C_h	concentration of molecular hydrogen, g-mole/cm ³
C_{si}	concentration of silane in bulk vapor phase, g-mole/cm ³
C_m	concentration of total active sites, site/cm ²
d_p	particle diameter, cm
D	diffusion coefficient, cm ² /sec
k	Boltzmann constant, erg/molecule °K
k_1	mass transfer coefficient, cm/sec
k_2	specific reaction rate constant for homogeneous pyrolysis
k_5	specific reaction rate constant for adsorption of silane
k'_6	specific reaction rate constant for desorption of hydrogen
k_7	specific reaction rate constant for surface reaction of silane
K_h	equilibrium adsorption coefficient for molecular hydrogen
K_{si}	equilibrium adsorption coefficient for silane
l	mean free path, cm
m	molecular mass, g/molc
M	molecular weight, g/g-mole
p	partial pressure of gas, atm
p'	equilibrium vapor pressure of gas, atm
p_{si}	partial pressure of silane, atm
r^*	radius of the critical nucleus, cm
r	rate of silane pyrolysis, g-mole/sec cm ³
r_1	rate of silane pyrolysis by homogeneous mechanism, g-mole/sec cm ³
r_2	rate of silane pyrolysis by heterogeneous mechanism, g-mole/sec cm ³

R	gas constant
S	supersaturation ratio, p/p'
t	time, sec
T	temperature, $^{\circ}\text{K}$
U	gas velocity, cm/sec
V_m	molecular volume, cm^3
X	extent of silane conversion, dimensionless
Z	axial coordinate, cm
α_c	condensation coefficient
ΔF^*	critical free energy change for nucleation, cal/nucleus
ΔF_{sd}	Gibbs free energy change of activation for surface diffusion, cal/g-mole
θ	contact angle, deg
μ	viscosity coefficient, g/cm sec
ρ	density, g/cm
σ	specific surface free energy, erg/cm
χ	functional relationship for contact angle
$\bar{\omega}$	frequency factor for activated species.

Subscripts:

f	final value
h	hydrogen
i	initial value
s	silicon
si	silane

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SECTION I

INTRODUCTION

One of the most attractive technologies for environmentally compatible uses of solar energy is photovoltaic conversion. Significant commitments have been made by the U.S. Department of Energy to bring this technology to commercial application, and toward this end efforts to develop technology for the production of pure polycrystalline silicon are in process. The Jet Propulsion Laboratory is investigating several chemical processes for the production of polycrystalline silicon, with a cost goal of \$10.00 per kilogram (1975 dollars) for solar grade polycrystalline silicon. In one of these studies* the decomposition of silane (SiH_4) in a fluidized bed reactor (FBR) and a continuous flow pyrolyzer (CFP) is being investigated.

The JPL in-house program supporting the technology development for silicon production includes efforts to develop a model of silicon particle growth from silane pyrolysis. The objectives of this modeling effort are to identify the problem areas, to guide and coordinate the experimental research and development, to analyze and correlate the experimental results and to develop a computer model for purposes of process design, optimization and scale-up. This report describes the mathematical models of silicon particle growth in the FBR and the CFP that have been developed in an effort to meet the objectives stated above.

*Under contract with Union Carbide

SECTION II

PROCESS DESCRIPTION - SILICON PARTICLE GROWTH (SPG)

A. FLUIDIZED BED REACTOR (FBR)

In the fluidized bed reactor process, silicon produced from the pyrolysis of silane is deposited on the bed particles. A gas mixture of silane and hydrogen and feed silicon particles are admitted to the FBR. The product particles are withdrawn from the lower section of the FBR. The product gases (hydrogen and unconverted silane) are withdrawn from the upper section of the FBR and the entrained particles are separated from this gas flow by a cyclone separator. The entrained particles may be recycled to the FBR as feed particles. Thus the polycrystalline silicon particles in the bed grow to larger sizes from the decomposition of silane to silicon. The FBR is operated at atmospheric pressure and in the temperature range of 450° to 1200°C. The process is shown schematically in Figure 2-1.

B. CONTINUOUS FLOW PYROLYZER (CFP)

In the continuous flow pyrolyzer process a gas mixture containing silane and hydrogen and silicon seed particles are fed to the tubular reactor. The reactor contents are heated to temperatures of 450° to 1200°C, at which silane is decomposed to fine silicon particles. The silicon nuclei and seed particles grow in size due to chemical vapor deposition of silicon from silane. The resulting polycrystalline silicon particles may be used directly as feed particles to the FBR or may be compacted and agglomerated to larger sizes before being fed to the FBR. This reactor is shown schematically in Figure 2-2.

Figure 2-1. Silicon Particle Growth in a Fluidized Bed Reactor

Figure 2-2. Silicon Production in a Continuous Flow Pyrolyzer

SECTION III

PHILOSOPHY OF SILICON PARTICLE GROWTH MODELING

A. SILICON PARTICLE GROWTH MECHANISMS

Silicon particle growth in the FBR and the CFP is a very complex process involving many physical and chemical steps (Reference 1). These steps are:

- R1. Mass transport of silane to the particle surface and hydrogen away from the particle surface.
- R2. Homogeneous pyrolysis of silane to silicon vapor and hydrogen.
- R3. Homogeneous nucleation and growth of silicon nuclei from silicon vapor.
- R4. Adsorption of silicon vapor on particle surface.
- R5. Adsorption of silane on particle surface.
- R6. Desorption of hydrogen from particle surface.
- R7. Heterogeneous pyrolysis of adsorbed silane.
- R8. Heterogeneous nucleation of adsorbed silicon.
- R9. Mass transport of silicon vapor to particle surface.

The actual silicon particle growth may occur by many different mechanisms involving some of the steps mentioned above. A schematic of the various steps involved in these mechanisms is shown in Figure 3-1.

Figure 3-1. Schematic of Silane Pyrolysis

Praturi (Reference 1) has pointed out that data are nonexistent for many of the parameters involved in the rate equations of the steps described above. On the basis of available information, two SPG mechanisms (homogeneous and heterogeneous) have been selected for the purpose of developing a model.

1. Homogeneous Mechanism

This mechanism involves generation of new silicon particles by homogeneous pyrolysis, nucleation, and growth. The steps involved are R2 and R3. The particles generated are of extremely small size. The actual size of the particles depends on the gas phase temperature (T) and silane super saturation (S).

2. Heterogeneous Mechanism

This mechanism involves silicon particle growth by steps R1, R5, R6, R7, and R8.

One crucial assumption is implicit in the mechanisms postulated above: that the heat transfer process by which the gases and the particles are brought to the reaction temperatures is not the rate limiting step in the CVD mechanisms. In other words, the rate of heat transfer is assumed to be much faster than the rate of any of the steps R1 through R8.

B. FLUIDIZED BED MODELS

The bed characteristics and the rates of mass and heat transfer are to a large extent functions of particle diameter, superficial velocity of the gas stream, and gas distributor design. The results of our preliminary fluidization experiments with silicon particles showed that for particle sizes greater than 50μ the traditional fluidized bed models will hold. Bubbling or slugging modes of fluidization were observed, depending upon the superficial velocity. The data showing pressure versus superficial gas velocity and minimum fluidization velocities agreed very well with theoretical predictions. Thus, with particles having an average diameter greater than 50μ the traditional fluidized bed models can be used. The same fluidized bed models (bubbling bed model of Kunii and Levenspiel (Reference 2) and particulate bed model of Nelson and Galloway (Reference 3)) that are used by Kim et al (Reference 4) will be used in this model.

SECTION IV

SILANE CONVERSION

A. RATES OF SILANE CONVERSION

The rate expressions for various steps involved in the growth of silicon particles were developed by Praturi (Reference 1). The overall rate of silane conversion may be calculated by assuming a particular step in SPG to be the controlling step. As discussed in Section III, we selected two mechanisms (homogeneous and heterogeneous) as the pathways for producing solid silicon from silane gas. These two mechanisms consist of the steps: mass transport of silane to the particle surface (R1), homogeneous pyrolysis of silane (R2), homogeneous nucleation and growth of silicon nuclei (R3), adsorption of silane on the particle surface (R5), desorption of hydrogen from the particle surface (R6), heterogeneous pyrolysis of adsorbed silane (R7), and heterogeneous nucleation of adsorbed silicon (R8). Equations that determine the overall rates of silane conversion are described below. Refer to NOMENCLATURE (in front of report) for explanation of symbols and units of measure.

1. Mass Transport of Silane Controlling

If the mass transport of silane to the particle surface is the limiting step in the heterogeneous mechanism, the overall rate of silane conversion can be obtained from the equation

$$r_2(1) = k_1 C \ln(1 + C_{si}/C) \quad (1)$$

where the subscripts for rate constants, frequency factors and activation energies refer to the step numbers of the CVD mechanism shown on page 3-1.

2. Silane Adsorption Controlling

If the adsorption of silane is the controlling step in the heterogeneous mechanism, the overall rate of silane conversion can be obtained from the equation

$$r_2(2) = \frac{k_5 C_{si} C_m}{1 + K_h C_h} \quad (2)$$

3. Hydrogen Desorption Controlling

If the desorption of hydrogen molecules is the controlling step in the heterogeneous mechanism, the overall rate of silane conversion can be obtained from the equation

$$r_2(3) = \frac{k'_6 C_m}{K_h} \quad (3)$$

4. Heterogeneous Pyrolysis Controlling

If the surface reaction of adsorbed silane is the controlling step in the heterogeneous mechanism, the overall rate of silane conversion can be obtained from the equation

$$r_2(4) = \frac{k_7 K_{si} C_m C_{si}}{(1 + K_{si} C_{si} + K_h C_h)^3} \quad (4)$$

5. Heterogeneous Nucleation Controlling

If the heterogeneous nucleation of adsorbed silicon on the particle surface is the limiting step in the heterogeneous mechanism, the overall rate of silane conversion can be obtained from the equation

$$r_2(5) = A_8 \exp(-\Delta E_8/kT) C_{si}^2 \quad (5)$$

where

$$A_8 = \frac{m \bar{a} \sin \theta \bar{\omega} RT \ln S}{2 N_A^2 (\sigma k T / \chi(\theta))^{1/2}}$$

$$X(\theta) = (2 + \cos \theta) (1 - \cos \theta)^2 / 4$$

$$\Delta E_8 = \Delta F_{sd} - \Delta F^*$$

$$F^* = \frac{16\pi\sigma^3 M_s^2 \chi(\theta)}{3(\rho RT \ln S)^2}$$

6. Homogeneous Pyrolysis Controlling

If the homogeneous pyrolysis of silane in the bulk gas phase is the limiting step in the homogeneous mechanism, the overall rate of silane conversion can be obtained from the equation

$$r_1(1) = k_2 C_{si} \quad (6)$$

7. Homogeneous Nucleation Controlling

If the homogeneous nucleation of silicon vapor is the limiting step in the homogeneous mechanism, the overall rate of silane conversion can be obtained from the equation

$$r_1(2) = A_2 \exp(-\Delta E_2/kT) C_{si}^2 \quad (7)$$

where

$$A_2 = \frac{\alpha_c}{N_A^2 \rho_s} \frac{2 \sigma_m}{\pi}^{1/2}$$

$$\Delta E_2 = \Delta F^* = \frac{16 \pi M_s^2 \sigma^3}{(3 \rho_s RT \ln S)^2}$$

The seven rate expressions (equations 1-7) represent the steady state rates of silane conversion. To evaluate the rates, it is necessary to specify the values of various physical properties of silane, silicon and hydrogen; reaction rate constants ($k_1, k_2, k_3, k_4, k_5, k_6, k_7, k_8$); equilibrium adsorption constants (K_{si}, K_h); and the parameters involved in the nucleation rates. All these data need to be obtained from the literature, evaluated from extensive experimental data on silicon particle growth in the FBR and the CFP, or estimated from theory. Such data are particularly important in the case of homogeneous and heterogeneous nucleation steps. Research in the kinetics and mechanisms of SPG is needed for any precise modeling effort.

In summary, the rates of silane pyrolysis via the two parallel mechanisms can be estimated by the following relationships:

Homogeneous mechanism:

$$r_1 = r_1(I), I = 1 \text{ or } 2 \quad (8)$$

Heterogeneous mechanism:

$$r_2 = a' r_2(I), I = 1, 2, 3, 4, \text{ or } 5 \quad (9)$$

B. EXTENT OF SILANE CONVERSION

The extent of silane conversion in the FBR and the CFP can be estimated using a plug flow model for the gas phase in the reactors, allowing for axial variations in velocity, concentration, and density. The plug flow model for the FBR and the CFP is shown schematically in Figure 4-1. Making mass balances for silane and hydrogen in the differential volume, we arrive at the two differential equations

$$\frac{d(UC_{si})}{dz} - r = 0 \quad (10)$$

$$\frac{d(UC_h)}{dz} + 2r = 0 \quad (11)$$

Figure 4-1. Plug Flow Model

Making the overall mass balance for the gas stream from $Z = 0$ to $Z = Z$, we obtain

$$U = \frac{U_i (C_{h,i} + 2C_{si,i})}{(C_h + 2C_{si})} \quad (12)$$

The rate of silane pyrolysis (r) is a function of silane concentration and can be expressed as the sum of homogeneous and heterogeneous rates:

$$r = r_1(I) + a'r_2(I), \quad I = 1, 5$$

Notice that for the homogeneous mechanism, pyrolysis is assumed to be the controlling step. The assumption is justifiable, since the rate of homogeneous pyrolysis is not affected by the homogeneous nucleation rate; i.e., these two steps are not interconnected. This assumption, however, implies that silicon does not exist in the vapor state. The silicon vapor generated by homogeneous pyrolysis is either instantaneously nucleated or condensed on existing nuclei.

A simultaneous solution of equations 10, 11, and 12 yields the axial profiles of silane concentration, hydrogen concentration, and gas velocity. The initial conditions for solving these equations are:

$$\text{at } Z = 0 \quad C_{si} = C_{si,i}, \quad C_h = C_{h,i}, \quad \text{and } U = U_i$$

The molecular weight and density of the gas stream at any axial location can be calculated from the relationships:

$$M = \frac{C_{si}}{C_{si} + C_h} M_{si} + \frac{C_h}{C_{si} + C_h} M_h \quad (13)$$

$$\rho = \frac{MRT}{P} \quad (14)$$

Finally, the extent of silane conversion is obtained from the relationship:

$$X = \frac{U_i C_{si,i} - U_f C_{si,f}}{U_i C_{si,i}} \quad (15)$$

SECTION V

SILICON PARTICLE GROWTH

Silicon particle growth in the FBR and in the CFP are phenomena which differ significantly from each other in two aspects: 1) mechanism of particle growth and 2) particle dynamics. In the FBR, in general (Reference 5), particle growth by the heterogeneous mechanism is the predominant process, while in the CFP particle generation and growth by the homogeneous mechanism is normally the predominant process. In the FBR, bed particles of considerable size (e.g., 100-300 μ) grow to larger sizes, while in the CFP very fine silicon particles (1-5 μ) are produced. Particle dynamics in the FBR can be modeled by a continuous Stirred Tank Reactor (CSTR) model assumption; i.e., the particle size is the same everywhere in the reactor. In the CFP, silicon particles move with the gas flow and change in size continuously along the length of the reactor. Because of these fundamental differences, silicon particle growth is modeled separately for the FBR and the CFP.

A. SILICON PARTICLE GROWTH IN A FLUIDIZED BED

Studies of silane pyrolysis in a fluidized bed reactor carried out at JPL are conducted in a batch fashion. Particle growth in batch fluidized beds is an unsteady-state process and has to be modeled accordingly. The modeling of silicon particle growth in the FBR is based on the following assumptions:

- (1) SPG takes place by the heterogeneous mechanism only.
- (2) All the fines produced by the homogeneous mechanism are completely elutriated.
- (3) Silicon deposition on the reactor walls is insignificant.
- (4) There is no entrainment of bed particles.
- (5) The change in the bed particle size is small enough that the gross characteristics of the fluidized bed do not change significantly.
- (6) The temperatures of the gas stream and the bed particles are the same and are constant.
- (7) The bed particle size is the same everywhere in the reactor.

Under these assumptions, the growth rate of silicon particles in the FBR, can be calculated from the relationship below that follows directly from the amount of silane converted per unit time according to the heterogeneous mechanism:

$$\frac{d(d_p)}{dt} = \frac{2M_s r_2}{\rho_s} \quad (16)$$

where

d_p = particle diameter
 M_s = silicon molecular weight
 t = time
 ρ_s = silicon density
 r_2 = rate of silane conversion by the heterogeneous mechanism per unit of surface area

The constant, steady state value of r_2 is estimated from the plug flow model for silane pyrolysis.

B. SILICON PARTICLE GROWTH IN A CONTINUOUS FLOW PYROLYZER

The predominant process of silicon product formation in the CFP involves two steps: 1) formation of silicon nuclei, and 2) growth of the nuclei. It is assumed that all of the silicon involved in this process is generated by homogeneous pyrolysis of silane. The critical size and rate of formation of silicon nuclei can be estimated from the homogeneous nucleation theory (Reference 6). The critical size is the minimum size necessary for nucleation to occur and is given by the relationship

$$r^* = \frac{2\sigma}{\rho_s RT \ln S} \quad (17)$$

In the range of the operating parameters of practical interest for CFP operation (silane partial pressure = 0.05 to 0.5 atm, gas temperature = 500°-1200°C), the super saturation (S) varies in the range of 10^9 - 10^{19} . At these very high super saturations, the critical radius of silicon nuclei is approximately the same as that of the silicon atoms, as can be seen in Table 5-1. This indicates that nucleation is extremely rapid and that silicon atoms themselves act as nuclei. Therefore, the silicon particle size is determined by the growth of the nuclei.

Conceptually, the growth of the silicon atoms may be treated as either coagulation or condensation. The growth rate as given by coagulation or condensation is considered to be the same for nuclei as small as atoms, at least in the early stages of nuclei growth. From a physical viewpoint, it is more appealing to consider the growth process as condensation of silicon vapor on nuclei, as it is hard to imagine coagulation of silicon atoms as solid particles. Hence, the growth of silicon nuclei is modeled on the basis of vapor condensation.

Table 5-1. Critical Radius of Silicon Nuclei
(in angstroms)

<div style="display: inline-block; transform: rotate(-45deg);"> $S \rightarrow$ $T^{\circ}K \downarrow$ </div>	10	10^2	10^3	10^6	10^{12}
500	21.88	10.44	7.29	3.64	1.82
600	18.24	9.12	6.08	3.04	1.52
700	15.63	7.81	5.21	2.60	1.30
800	13.68	6.84	4.51	2.28	1.14
900	12.16	6.08	4.05	2.02	1.01
1000	10.94	5.47	3.64	1.82	0.91
1100	9.94	4.97	3.31	1.65	0.82
1200	9.12	4.56	3.04	1.52	0.76
1300	8.41	4.20	2.80	1.40	0.70
1400	7.81	3.90	2.60	1.30	0.65
1500	7.29	3.64	2.43	1.21	0.60
2000	5.47	2.73	1.82	0.91	0.45
2500	4.37	2.18	1.45	0.72	0.36
3000	3.64	1.82	1.21	0.60	0.30

The task of estimating the relative influences of various factors involved in silicon nuclei growth by mathematical computations must necessarily be left to future endeavors. The present modeling effort on silicon nuclei growth in the CFP will, be based on the following set of assumptions:

- (1) The process of silicon nucleation is instantaneous, and the size of the nuclei is of the order of the size of silicon atoms.
- (2) Silicon nuclei grow to larger sizes by the diffusion limited heterogeneous vapor condensation process.

- (3) The large seed particles in the CFP grow via the heterogeneous pyrolysis of silane only.
- (4) Growth of silicon nuclei is not limited by heat transfer from nuclei to the surrounding gas.
- (5) Silane flow in the CFP can be described by a plug flow model.

The growth rate of silicon nuclei can now be estimated from the following relationships given by Friedlander (Reference 7):

for $d_p \gg \ell$

$$d(d_p) = -\frac{4 D V_m p}{kT} dz \quad (18)$$

for $d_p \ll \ell$

$$d(d_p) = \frac{2 V_m p}{(2\pi mkT)^{1/2}} dz \quad (19)$$

Equation 18 applies in the continuum range, i.e., when the mean free path (ℓ) of silicon is much greater than the nuclei size (d_p). In the molecular regime ($d_p \ll \ell$) equation 19 holds. The mean free path of silicon at various pressures and temperatures is shown in Table 5-2. Since the CFP is intended to be operated at atmospheric pressure, equation 19 can be used until the nuclei have grown to a size of 0.1 μ , after which equation 18 can be used for calculating the growth rate of silicon particles.

The growth of seed particles in the CFP is calculated in a manner analogous to that used to calculate the rate of growth in the FBR.

$$d(d_p) = \frac{2M_s r_2}{\rho_s U} dz \quad (20)$$

Table 5-2. Mean Free Path for Silicon Vapor
(in angstroms)

T °K	PRESSURE →			
	10 ⁰ atm	10 ⁻¹ atm	10 ⁻² atm	10 ⁻³ atm
500	960	9600	96000	960000
600	1152	11520	115200	1152000
700	1344	13440	134400	1344000
800	1536	15360	153600	1536000
900	1728	17280	172800	1728000
1000	1920	19200	192000	1920000
1100	2112	21120	211200	2112000
1200	2304	23040	230400	2304000
1300	2496	24960	249600	2496000
1400	2688	26880	268800	2688000
1500	2880	28800	288000	2880000
1600	3072	30720	307200	3072000
1700	3264	32640	326400	3264000
1800	3456	34560	345600	3456000
1900	3648	36480	364800	3648000
2000	3820	38400	384000	3840000
2500	4800	48000	480000	4800000
3000	5760	57600	576000	5760000

SECTION VI

SUMMARY AND FUTURE PLANS

A. SUMMARY

Integrated mathematical models were developed to describe silicon particle growth from silane pyrolysis. Two specific reactors, viz., the fluidized bed reactor (FBR) and the continuous flow pyrolyzer (CFP) were considered for this model. The pyrolysis of silane was modeled on a rate limiting step approach. All the essential steps involved in the chemical vapor deposition of silicon were modeled. Pyrolysis of silane was modeled based on a plug flow model for the gas phase in both the FBR and the CFP systems. The growth of silicon particles in both reactors was modeled as a direct consequence of heterogeneous deposition of silicon. The growth of silicon nuclei and very small particles was modeled on the basis of a diffusional growth mechanism, as in the case of the growth of water nuclei in clouds. This modeling effort brought out the need for rigorous information on the mechanisms and kinetics of silicon particle growth.

B. FUTURE PLANS

Plans are underway for the development of two computer codes based on the models presented in this report to describe silicon particle growth in the FBR and the CFP. The computer models will be used to evaluate experimental data obtained in further experiments in silicon particle growth, to determine the mechanisms of silane pyrolysis and silicon particle growth, and to develop scaling laws for the design of large silicon production units.

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