Synthesis of silicon nanoparticles with a narrow size distribution: a theoretical study

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Abstract

This work presents a fully-coupled gas-phase and particle model for the synthesis of narrowly-distributed silicon nanoparticles from the thermal decomposition of silane, which simultaneously solves the kinetic mechanism of Swihart & Girshick (1999, *J. Phys. Chem. B* **103** 64–76) with a detailed particle model. The model was applied to simulate the hot-wall reactor and process conditions of Körmer *et al.* (2010, *J. Aerosol Sci.* **41** 998–1007). It was found that after a short burst of inception and condensation, growth occurred through coagulation and sintering of small particles into larger primaries. The sintering parameters were estimated by fitting the mode and variance of the experimental primary particle PSD to experimental data. Excellent agreement was obtained for four cases at a range of temperatures and residence times. The model is additionally in qualitative correspondence with homogeneous nucleation theory and comparison of TEM-style images is encouraging.

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1 Introduction

When synthesised to a controlled diameter, silicon nanoparticles can be used as photoluminescent standards or as 'building blocks' for use in hierarchically ordered systems [22, 27]. Understanding the mechanism by which they are formed is therefore important in developing improved techniques of manufacture. The mechanism is thought to consist of complex interconnected processes including gas phase reactions, nucleation, coagulation, condensation and surface reaction [9, 22, 31, 42].

The gas-phase mechanism for the thermal decomposition of silane has attracted considerable attention over the past eighty years. The mechanism was first studied by Hogness, Wilson & Johnson in 1936 who reported that silane decomposed by a simple single-step reaction into only pure silicon and hydrogen [19]. This view was subsequently modified by Purnell and Walsh, who proposed it was a multi-body reaction which could also form di- and tri-silanes [38]. Since then, the mechanism has been continuously expanded with larger and more complex processes involving the formation of silenes (doubly-bound silane species, e.g. SiH₂SiH₂, suffixed 'A'), silylenes (radical species, e.g. SiH₃SiH, suffixed 'B'), silyl anions and three-dimensional polycyclic silicon hydride species [3, 12, 43, 47].

Ho *et al.* used laser-induced fluorescence measurements of silicon atoms during the chemical vapour deposition (CVD) of silicon from silane to determine kinetic parameters for the formation of silicon hydride species with up to Si_3H_8 [18]. This work formed the basis for the mechanism of Swihart & Girshick, who used the parameters of Ho *et al.* and reaction rules to generate reactions for silane, silene and silylene species up to twenty silicon atoms. The result was a total of 2615 reactions with 221 silicon hydride species [42]. This mechanism will be discussed in more detail in §4. More recently, automatic mechanism generation was used to generate a mechanism with 8076 reactions among 1398 species for clusters up to eight silicon atoms [49] and quantum chemical calculations were undertaken to investigate the molecular transition steps involved in the decomposition of silane [1, 2].

Modelling the formation of silicon nanoparticles also requires treatment of the particle growth processes as well as the gas-phase chemistry. Swihart *et al.* used their chemical mechanism [42] as the basis for aerosol dynamics models including particle growth by surface reactions, coagulation and diffusion [31, 44]. These models used the method of moments and the sectional method to provide solutions to the aerosol general dynamic equation (GDE) [10, 11]. Dang & Swihart expanded upon these by preparing a two-dimensional model for the decomposition of silane driven by laser heating in a tubular reactor [9]. This model included the chemical kinetics and particle processes of the previous model as well as terms for laser heating, fluid dynamics and thermophoresis.

There is limited work available on numerical modelling of the synthesis of nanoparticles with a narrow particle size distribution (PSD). Tsantilis & Pratsinis used a moving sectional model to solve the aerosol GDE for the formation of titania, reporting that accounting for surface reaction leads to narrower PSDs [45]. Körmer *et al.* presented experimental [22] and theoretical [23] studies on the synthesis of silicon nanoparticles with a narrow size distribution: this is discussed in more detail in §2 as it is central to the model

development and analysis of results presented in this paper.

The present work aims to build on the experimental and theoretical results of the studies by Körmer *et al.* [22, 23] by combining the detailed chemical mechanism of Swihart & Girshick [42] with a particle model which incorporates inception, surface growth, coagulation and sintering processes. The model will then be used to gain insights into the important chemical and particle processes which manifest themselves in the synthesis of silicon nanoparticles.

The structure of the paper is as follows: $\S2$ outlines the previous model of Körmer *et al.* for silicon nanoparticle synthesis. $\S3$ describes the philosophy behind the development of a multi-scale numerical model as well as the input parameters required. $\S4$ discusses the kinetic mechanism of Swihart & Girshick [42] which is implemented in the gas-phase chemistry solver. $\S5$ explains the salient features of the particle model. The choice of inception process is outlined in $\S5.1$ and the analysis of particle formations in $\S5.2$. The estimation of sintering parameters is provided in $\S5.3$, followed by the comparison of a computer-generated TEM image to experimental data in $\S5.4$. The paper is concluded by assessing the significance of the model as well as future avenues in which work could be pursued.

2 Previous work

In the experimental work of Körmer *et al.* [22] silicon nanoparticles were produced in the range of 20-40 nm and with a geometric standard deviation (GSD) of 1.06-1.08. It was found that these narrow distributions could only be obtained at high temperatures (900-1100 $^{\circ}$ C) and low pressures (1 mbar silane with 25 mbar total pressure).

The theoretical paper [23] used a population balance model to study the particle processes leading to the narrowly-distributed particles obtained experimentally. The model treated the gas-phase with a single-step homogeneous reaction according to Equation 1, where a modified form of the kinetic parameters of Petersen *et al.* [36] were applied.

$$SiH_4 \rightarrow Si + 2H_2$$
 (1)

Nucleation of particles from the homogeneous vapour was assumed to occur through a homogeneous nucleation process. This assumed that particles were formed through the collision of monomers or subcritical clusters forming clusters with size larger than a critical cluster diameter d_{crit} . Particles could subsequently grow through surface reaction (heterogeneous reaction of the precursor monomer with particle surface) or condensation (collision and coalescence of subcritical clusters with a particle). The collision, adhesion and subsequent coalescence of particles is labelled as coagulation.

With appropriate scaling of the gas-phase decomposition and surface growth rates, the model showed excellent agreement with experimental data. It was reported that after a short burst of particle nucleation, growth occurs primarily through surface reaction and condensation processes. A key role was attributed to condensation, as numerical calculations could only match experimental observations if condensation was included in the model.



Figure 1: Schematic of the model used in the present work.

However, the model's type space described all particles as spheres, an assumption valid at low pressures but possibly incorrect at elevated pressures [22]. The use of a spherical particle model also assumes that a collision of two particles creates a new spherical particle with volume equal to the sum of the previous particles. This effectively asserts that sintering occurs instantaneously; an assumption which again may be invalid for nonspherical particles. It additionally prevents the model from considering the formation of aggregates, while these are clearly formed in the SEM images of [22].

Finally, the model only included a single-step gas-phase reaction, despite evidence of a much more complicated gas-phase decomposition process [18, 20, 31, 36, 42]. The model developed in the present work applies an alternative modelling methodology to address these issues and assess their significance. It is hoped that extending the type space will provide additional insight into the system.

3 Model description

A multi-scale model is characterised by three main components: an application model (AM), an instrumental model (IM) and a data model (DM) [24]. The DM describes the experimental apparatus and settings as well as the raw data obtained. The raw data is then processed into useful information - this comprises the IM. The AM is typically formulated from mathematical equations and aims to reproduce the underlying phenomenon measured by the DM and interpreted by the IM. The inter-relationship of the present work's AM and the IM of [22] is displayed in Figure 1. Each of the sub-processes and key parameters are outlined in more detail in the following sections.

3.1 Overview of model processes

This paper is primarily concerned with the development of an AM to accurately predict PSDs for the synthesis of silicon nanoparticles with a narrow size distribution. This is achieved through the use of an operator-splitting code (*MOPS*) which solves the gas-phase chemistry and particle population balance while periodically exchanging information between them. *MOPS* has already been applied to model the synthesis of silica [16, 40] and titania [26, 48] nanoparticles.

The kinetic mechanism is solved by use of an in-house-developed open-source software *Sprog* to solve the system of ordinary differential equations (ODEs) describing the gasphase chemistry [6]. It calculates the chemical reaction rates and the composition of the gas-phase mixture, modelling the rates as Arrhenius processes. The gas-phase chemical reactions and chemistry behind them used in the present work are discussed in §4.

The particle model (*Sweep*) includes terms for inception, surface-growth, coagulation and sintering; describing primary particles by their volume. These processes are outlined in more detail in §5. *Sweep* is capable of calculating the rates at which these processes occur and tracking the evolution of primary and aggregate particles.

3.2 Numerical processes

In order to accurately model a physical system, an AM typically requires a mathematical description of key processes and input parameters to generate results. The numerical processes and key parameters used in the present work are described in this section, where the latter are tabulated in Table 1. The operator-splitting code which couples the gas-phase chemistry and population balance is described in detail by Celnik *et al.* [6–8]. Strang splitting is applied to reduce the splitting error, where the stochastic population balance equations are solved for one step followed by the deterministic gas-phase for one more step [7].

The timesteps Δt and number of splits N_{splits} must be defined for *MOPS*, the latter describing the number of times which information is exchanged between gas- and particle-phase. *MOPS* also takes input of the basic process conditions such as temperature (*T*), component partial pressure (p_{SiH4} , p_{Ar}) and residence time (τ). The conditions used here are those of Körmer *et al.* A temperature gradient is also applied across the reactor, displayed in Figure 2. The profile is 'stretched' at longer residence times, maintaining the same initial and final temperatures and lineshape. This profile is identical to that used in [23].

Sprog requires input of the chemical mechanism and thermodynamic polynomials describing the silicon hydride species' thermodynamic properties as a function of temperature. For this work, the thermodynamic polynomials and Arrhenius kinetic parameters were primarily sourced from the work of Swihart & Girshick [42]. Absolute and relative error tolerances (ε_a and ε_r respectively) were chosen to ensure the ODE system was converged.

The particle population balance is solved by a stochastic particle algorithm first used in the modelling of formation of soot nanoparticles [13]. It has since been further refined by Patterson *et al.* to incorporate a wider variety of processes and more efficient numerical

Parameter	Symbol	Value	Ref.				
Numerical parameters							
Number of splits	$N_{\rm splits}$	30	-				
Timestep	Δt	$1.0 imes 10^{-6} ext{ s}$	-				
Absolute error tolerance (<i>Sweep</i>)	ε_{a}	1×10^{-18}	-				
Relative error tolerance (<i>Sweep</i>)	$\varepsilon_{ m r}$	1×10^{-4}	-				
Number of stochastic particles	$N_{\rm SP}$	16,384	-				
Number of runs	L	1	-				
Maximum zeroth moment	$M0_{max}$	1×10^{10}	-				
Proc	ess settings	5					
Initial temperature	T	750 °C	[22]				
Residence time	au	0.08–0.42 s	[22]				
SiH ₄ partial pressure	p_{SiH4}	1.0 mbar	[22]				
Ar partial pressure	p_{Ar}	24 mbar	[22]				
Model parameters							
Kinetic Arrhenius parameters	A, n, E_A	various	[42]				
Diameter of species Si_iH_j	$d_{\mathrm{Si}_i\mathrm{H}_i}$	various	-				
Mass of species Si_iH_j	$m_{\mathrm{Si}_i\mathrm{H}_i}$	various	-				
Molecular weight	$M_{\mathbf{w}}$	28.1 g/mol	[35]				
Bulk density of silicon	$ ho_{ m Si}$	2.33 g/cm^{3}	[35]				
Sintering pre-exponential	$A_{\rm s}$	2.02×10^{-13} s/m	this work				
Sintering characteristic temp.	$E_{\rm s}$	81,200 K	this work				
Sintering minimum diameter	$d_{p,\min}$	6.28 nm	this work				

Table 1: Summary of base-case parameters input to MOPS.

methodology [32–34]. Two numerical parameters must be defined for proper operation of the stochastic algorithm: the number of runs L and stochastic particles N_{SP} , which were chosen sufficiently high such that doubling them does not alter the ultimate PSD.

Sweep additionally requires input of the molecular weight (M_w) and bulk density of silicon $(\rho_{\rm Si})$ to calculate the volume added into the particle-phase with each inception or surface growth step. The mass and diameter of each silicon hydride species is required for evaluation of the coagulation kernel - these were obtained from the quantum mechanical calculations of Swihart & Girshick [43] and estimated from the structures reported in [42]. The AM was fitted to the IM of [22] by adjusting the sintering parameters A_s , E_s and $d_{p,min}$ using a two-step methodology, discussed in more detail in §5.3.

4 Kinetic model

The group of Swihart has devoted considerable attention to developing detailed kinetic mechanisms to describe the gas-phase thermal decomposition of silane. This work uses a partially simplified version of the mechanism reported in their 1999 paper [42], which contains 131 silicon hydride species (up to Si_{13}) and 1098 chemical reactions. The mech-



Figure 2: *Temperature profile applied across the reactor for 0.08 s residence time. The temperatures describing each series refer to the maximum reactor temperature.*

Table 2: Reaction rules used in generation of Swihart & Girshick's mechanism [42].

Reaction type	General form
H ₂ elimination from a silane	$\mathrm{Si}_{n}\mathrm{H}_{2m} ightarrow\mathrm{Si}_{n}\mathrm{H}_{2(m-1)}$ + H_{2}
Silylene elimination from a silane	$\mathrm{Si}_{n}\mathrm{H}_{2m} \rightleftharpoons \mathrm{Si}_{l}\mathrm{H}_{2k}\mathrm{B} + \mathrm{Si}_{n-l}\mathrm{H}_{2(m-k)}$
Silylene elimination from a silene	$\mathrm{Si}_{n}\mathrm{H}_{2m}\mathrm{A} \rightleftharpoons \mathrm{Si}_{l}\mathrm{H}_{2k}\mathrm{B} + \mathrm{Si}_{n-l}\mathrm{H}_{2(m-k)}\mathrm{A}$
Silylene to silene isomerisation	$\mathrm{Si}_{n}\mathrm{H}_{2m}\mathrm{B} ightarrow\mathrm{Si}_{n}\mathrm{H}_{2m}\mathrm{A}$
Ring opening	$\mathrm{Si}_{n}\mathrm{H}_{2m} ightarrow\mathrm{Si}_{n}\mathrm{H}_{2m}\mathrm{B}$

anism was generated using five reactivity rules which are presented in Table 2 and are briefly discussed in the following paragraphs.

Hydrogen elimination from a silane has been shown to occur through a 1,1 elimination process [14], typically causing an unstable silylene (Si_{*i*}H_{*j*}B) to be formed. This molecule will subsequently undergo a 1,2 rearrangement to form a silene species: a rapid threecentred migration process [14]. All silene species included in the model are considerably more stable than their silylene counterparts [14, 42]. The other intramolecular process (ring opening/closing) is additionally included as it was assumed that the reactivity of the divalent silicon atom was the same internally as it is with other molecules [42].

The silvlene elimination reactions and their reverse (silvlene insertion) are the characteristic reactions of the thermal decomposition of silane [42]. The reverse reactions act as the key chemical growth processes for the silicon 'clusters', where silvlene species such as SiH_2 insert themselves into silanes or silenes, forming larger clusters. These processes have been experimentally and theoretically shown to occur with no activation energy bar-



Figure 3: Temporal evolution of the concentration of silicon hydride species according to the mechanism of Swihart & Girshick [42].

rier [42].

To verify the integrity of *Sprog* in solving this expansive gas-phase mechanism, the kinetic model was first solved at the process conditions of Swihart & Girshick [42]. The evolution of the concentration profiles was identical, so the system was subsequently solved at the baseline conditions of Körmer *et al.* [22]. The results of this calculation are presented in Figure 3.

It is evident here that with only the gas-phase mechanism considered, one-silicon species $(SiH_4 \text{ and } SiH_2)$ are still present in large concentrations, even as the residence time is reached: this suggests that the reaction does not go to completion in this model. The concentration of 'nuclei' (arbitrarily labelled as species with eleven silicon atoms or more in [42]) gradually increases as the higher species are irreversibly formed. In a fully coupled model, these nuclei would subsequently react to form particles.

However, the distinction of particle nuclei being only those greater than ten silicon atoms is fairly arbitrary. For dilute H_2/SiH_4 systems, detailed kinetic modelling has suggested a critical particle size of five to seven silicon atoms [49]. As dilute He/SiH_4 systems typically proceed faster than H_2/SiH_4 systems [42], it is possible that the critical nucleus could consist of even fewer atoms. The following section couples a particle model to Swihart & Girshick's mechanism with inception occurring at different thresholds of silicon hydride species in an attempt to resolve this issue.

5 Particle model

The particle model considers the formation of silicon nanoparticles from the gas-phase. It is described by a population balance which is solved with the stochastic algorithm employed by Patterson & Kraft [33]. The properties of a particle P_i may be completely described by the variables of its *type space*. This model's type space is represented by a finite dimensional vector, given by:

$$P_i = P_i(p_1, \dots, p_n, \mathbf{C}, \mathbf{I}, \mathbf{S})$$
⁽²⁾

where $i \in \{1, ..., N\}$ and N is the total number of particles in the system. Each particle P_i consists of n primary particles p_j ($j \in \{1, ..., n\}$), where N and n vary with time. C, I and S are matrices which describe the sintering between primaries [39]. The primaries are described by their volume v_j :

$$p_j = p_j(v_j) \tag{3}$$

and the sum of all primary volumes is equal to the total volume V of the particle:

$$V = \sum_{j=1}^{n} v_j. \tag{4}$$

Thus, particles are modelled by tracking the volume of every primary particle and the common surface between any two. A variety of submodels are also included in the particle model which describe particle formation, growth and sintering. These are briefly outlined in the following paragraphs, however a detailed description is provided by Celnik [6] and Sander *et al.* [39].

Inception: An inception event is modelled as a collision of two silicon hydrides and is dependent on their gas-phase concentration and the transition regime coagulation kernel [26, 37]. The inception model is the primary focus of $\S5.1$. Inception events increase the number of particles N in the type space by 1:

molecule + molecule
$$\rightarrow P_{N+1}(p_1, \mathbf{C}, \mathbf{I}, \mathbf{S}).$$
 (5)

Surface growth: Sweep can consider surface growth as a condensation process (requiring the gas-phase species' diameter) or a surface reaction process (requiring modified Arrhenius parameters). Surface growth alters the type space by increasing the volume of a selected primary p_j of particle P_i by increment δv :

$$p_j(v) \to p_j(v + \delta v)$$
 (6)

For reasons discussed in $\S5.1$, surface growth was modelled as condensation, where all species were permitted to condense. This is implemented with the transition regime coagulation kernel [26]. The evolution of hydrogen at the particle surface [18] was not modelled.

Coagulation: Coagulation is modelled as the collision and subsequent adhesion of two primary particles. Storing the common surface information in the C, I and S matrices allows for the connectivity of primaries to be tracked, and thus the collision diameter of the aggregate particle d_{col} to be calculated [40]. A coagulation event may be represented by the following change in the type space:

$$P_i + P_j \to P_k(p_1, \dots, p_{n(P_i)}, p_{n(P_i)+1}, \dots, p_{n(P_k)}, \mathbf{C}, \mathbf{I}, \mathbf{S})$$
(7)

Sintering: The process of sintering is incorporated in this model by calculating the level of sintering between two neighbouring primary particles in a single particle. The sintering model and its effect on the type space are described in detail by Sander *et al.* [39], who use the formula of Tsantilis *et al.* [46] to calculate the characteristic sintering time τ_s . This is given by:

$$\tau_{\rm s} = A_{\rm s} \times d_{i,j} \times \exp\left[\frac{E_{\rm s}}{T}\left(1 - \frac{d_{\rm p,min}}{d_{i,j}}\right)\right] \tag{8}$$

where $d_{i,j}$ is the minimum diameter of two adjacent primary particles. $d_{p,\min}$ is the diameter below which the particles are assumed to behave liquid-like and sinter instantaneously [39, 40]. The parameters A_s , E_s and $d_{p,\min}$ are free parameters, the estimation of which is described in §5.3.

It is also important to highlight the difference in nomenclature between the present model and the model of Körmer *et al.* [23]. Here, condensation is assumed to be the collision and coalescence of gas-phase species with a particle. In [23], a distinction is made between collisions of gas-phase species and subcritical clusters with a particle: the former is labelled 'surface growth', while the latter 'condensation'. This distinction can not be made for the present model as the type space does not consider the formation of subcritical silicon clusters.

The interaction of these processes with the ensemble of stochastic particles is implemented with a Linear Process Deferment Algorithm [33]. This particle solver is coupled with the kinetic mechanism described in $\S4$ through the operator-splitting method described by Celnik *et al.* [6–8].

5.1 Analysis of inception nucleus size

The gas-phase mechanism used in the present work contains approximately 131 silicon hydride species from Si_1 to Si_{13} . This provides tremendous scope for elucidation of the most important species in the nucleation process. It also creates a large number of combinations of potential collisions which could act as inception reactions into the particle model. Furthermore, it raises the question of which gas-phase species will interact with the particle surface. To determine an appropriate inception model, a general inception reaction of the following form was considered:

$$\operatorname{Si}_{i}\operatorname{H}_{j} + \operatorname{Si}_{k}\operatorname{H}_{l} \to [\operatorname{Si}_{i+k}] + \frac{j+l}{2}\operatorname{H}_{2}$$
 (9)



Figure 4: Comparison of the mean and variance primary diameter and the mean collision diameter at baseline process conditions. The experimental data of [22] is given by the horizontal line.

where the left-hand species Si_iH_j and Si_kH_l are in the gas-phase and the right hand species is a newly-incepted particle (square brackets denoting a particle). Then, a critical nucleus number $N_{Si,min}$ was chosen; the minimum number of silicon atoms present in the smallest particle incepted. $N_{Si,min}$ falls in the range of 2 to 26 due to the number of silicon atoms present in the smallest and largest species of the gas-phase mechanism. All combinations of *i* and *k* whose sum was greater than or equal to $N_{Si,min}$ were subsequently assumed to form particles in a collision event.

The model also requires treatment of surface growth. While experimental parameters exist for surface reaction [18], these only extend as far as Si₃ species. Thus, surface growth was for consistency modelled as a condensation process where two extreme cases were considered: all species condensing, or no condensation. The results of the former model are displayed in Figure 4 for baseline process conditions (1100 °C maximum temperature, 0.08 s residence time, 1 mbar SiH₄ & 24 mbar Ar).

Where condensation was not permitted to occur, the primary particles did not grow above the diameter at which the particles are initially incepted, also observed by Körmer *et al.* [23] in their theoretical model. Experimentally, the silicon particles grow to significantly larger sizes than their incepting diameter, suggesting that the no-condensation case is unrepresentative of the physical system: it will therefore not be further discussed.

With all species condensing, the primary particle size range from 26–40 nm for the set of sintering parameters found in §5.3. The particles obtained for different values of $N_{\text{Si,min}}$ varied in characteristics; from highly spherical, narrowly distributed particles similar to those observed experimentally ($N_{\text{Si,min}}$ of 2–5) to broadly distributed and sintered agglom-

erates ($N_{\text{Si,min}}$ of 6–16). The latter phenomena are represented by the increase in primary diameter and variance, coupled with a decrease in collision diameter.

Figure 4 clearly demonstrates that the choice of critical nucleus number can strongly affect the PSD obtained. Despite this, there are multiple values of $N_{\text{Si,min}}$ which match the experimentally obtained [22] primary diameter and variance. This raises the issue of model discrimination: given that several acceptable models have been found, how should an appropriate inception mechanism be chosen?

The models with broad distributions ($N_{\text{Si,min}}$ of 6–16) can be immediately discounted as this is not observed experimentally. The broadening of the distribution can be attributed to inception occurring over a longer period of time. The duration of inception is linked to the specific gas-phase species which collide to form particles, a result of some gas-phase species in the mechanism of Swihart & Girshick [42] lasting longer than others.

As discussed previously, other studies [25, 49] have suggested critical nucleus numbers between 5 and 7 for nucleation of silicon in hydrogen. Thus, the higher values of $N_{\text{Si,min}}$ which appear to satisfy experimental conditions (values 17–24) can be excluded. This leaves values of $N_{\text{Si,min}}$ between 2 and 5 satisfying the experimental primary diameter and variance. Homogeneous nucleation theory is applied in the following section to ascertain which of these values (if any) would be an appropriate threshold for the mechanism of particle inception.

5.2 Critical cluster size & formation mechanism

Homogeneous nucleation theory (HNT) uses information about the surface activity of particles (or surface tension of liquids) to provide insight into the nucleation process involved in formation of those particles. Like the critical cluster number $N_{\text{Si,min}}$, the critical cluster diameter d_{crit} is the smallest diameter above which stable particle nuclei can be formed. It is related to the surface energy γ by the the Kelvin equation [21]:

$$d_{\rm crit} = \frac{4\gamma v_1}{k_{\rm B}T\ln(S)} \tag{10}$$

where v_1 is the volume of a silicon atom, k_B is Boltzmann's constant and S is the supersaturation, given by:

$$S = \frac{p_{\rm Si}}{p_{\rm Si,sat}} \tag{11}$$

where p_{Si} is the 'silicon' partial pressure and $p_{Si,sat}$ is the saturation vapour pressure of silicon, dependent on temperature. The latter may be determined through the following correlation from the data of Gray [15] which gives $p_{Si,sat}$ in atm:

$$\log_{10} p_{\rm Si,sat} = 7.5341 - \frac{23399}{T(\rm K)}$$
(12)

The surface energy can be estimated directly by linear interpolation from the data of Mezey & Giber [29], who quote values over the temperature range of 25–1410 °C. Assuming that the partial pressure of silicon may be estimated as that of silane (as nucleation

Table 3: Comparison of critical diameters and surface energies. Arrows indicate the directon of calculation.

Reference	$N_{\mathrm{Si,min}}$		$d_{\rm crit}~({\rm nm})$		γ (N/m)
Interpolation from Mezey & Giber [29]	-		0.20	$\stackrel{\rm HNT}{\longleftarrow}$	0.99
This work (Si_2H_4A)	2	\xrightarrow{QM}	0.59		-

Table 4: Simplified gas-phase and particle model used in the present work.

Process	Reaction
SiH ₄ dimer inception	$SiH_4 + SiH_4 \rightarrow [Si_2] + 4H_2$
SiH ₂ dimer inception	$SiH_2 + SiH_2 \rightarrow [Si_2] + 2H_2$
SiH ₄ & SiH ₂ inception	$SiH_4 + SiH_2 \rightarrow [Si_2] + 3H_2$
SiH ₄ condensation	$\operatorname{SiH}_4 + [\operatorname{Si}_i] \to [\operatorname{Si}_{i+1}] + 2\operatorname{H}_2$
SiH ₂ condensation	SiH_2 + $[\mathrm{Si}_i] \rightarrow [\mathrm{Si}_{i+1}]$ + H_2
SiH ₄ decomposition	$\mathrm{SiH}_4 ightarrow \mathrm{SiH}_2$ + H_2

proceeds almost instantaneously), γ be substituted into Equation 10 to 'back-calculate' the critical diameter at the initial temperature 750 °C, given in Table 3.

The smallest particle nucleus considered in §5.1 is a Si₂ nucleus, for $N_{\text{Si,min}} = 2$. The corresponding gas-phase species to this is silene (Si₂H₄A). A quantum mechanical calculation at the B971/3-21G level in *Gaussian 03* was carried-out on silene to estimate its molecular volume, from which the isotropic collision diameter [17] was determined. This is also given in Table 3.

Under the assumptions made here, the critical diameter is less than the diameter of the smallest precursor nucleus. This corresponds to the collision-limited regime of homogeneous nucleation [21], where growth of clusters is not inhibited by a thermodynamic barrier. It is therefore reasonable to choose $N_{\text{Si,min}} = 2$ for the critical nucleus number, as the smallest nucleus number must be at least two for homogeneous nucleation [25]. A simplified model was formulated (described in Table 4) in order to conserve computational resources. The gas-phase mechanism was also truncated so that only the decomposition of silane remained: there was negligible effect on the PSD or particle rates from this modification.

While no information about the chemical nucleation pathway could be gained from the analysis presented in $\S5.1$, it allows for insight into the particle processes to be gained. This is illustrated in Figure 5, where the evolution of the particle rates and primary diameter (at baseline conditions) is presented. The rapid particle inception observed in this figure is in agreement with the results of Kruis *et al.* [25], who report short time-lags before nucleation for the decomposition of silane at high temperatures.

The right panel indicates that a short burst of nucleation and condensation occurs, causing the precursor to be quickly consumed. This is qualitatively consistent with the phenomena reported by Körmer *et al.* [23] and Tsantilis *et al.* [46]. The left panel illustrates the evolution of the mean primary particle and collision diameters. It is shown here that the collision diameter is approximately equal to the primary diameter until 2×10^{-3} s, after

which particles begin to aggregate and the collision diameter 'separates' from the primary diameter.

The temporal evolution of particles in the reactor may also be analysed by examination of the primary particles PSD, displayed in Figure 6. Here, it is evident that primaries are rapidly incepted and grown to several nanometers through condensation. Coagulation of primaries subsequently begins to broaden the distribution, after which the smaller primaries rapidly sinter to form large primaries, as shown by the shoulder in the 8×10^{-3} s curve. Continuous coagulation and sintering narrows the PSD and causes aggregation of the primaries. This is typical of a collision-limited nucleation process, which exhibit a rapid sintering rate relative to the collision rate, causing a high degree of sphericity in primary particles [21].

It is important here to compare this analysis with the results reported by Körmer *et al.* [23]. Here, particle growth occurs initially by condensation of the gas-phase species, followed by collision-limited coagulation and sintering of small primaries into larger particles. Körmer's work attributes growth of particles to the collision of precursor species and subcritical clusters with the surface: named 'surface growth' and 'condensation' processes respectively.

While the two models describe particle nucleation and growth in different frameworks, they both agree on the importance of condensation in the growth of particles with a narrow size distribution. The coagulation-sintering growth mechanism illustrated in the present work has been reported previously by Nguyen & Flagan [30] for silicon nanoparticle synthesis. This highlights that there are at least two potential mechanisms for growth of narrowly-distributed particles, and that it is difficult to ascertain which is responsible without experimental data between the initial and final process times.

5.3 Estimation of sintering parameters

Choice of appropriate model parameters is of key importance in obtaining theoretical results comparable to the experimental results which they seek to reproduce. In the model proposed here, the sintering parameters A_s , E_s and $d_{p,min}$ are the only adjustable inputs (excluding the gas-phase mechanism) and therefore can be optimised to fit the model to experimental data.

The initial sintering parameters were taken from the work of Sander *et al.* [39] and adjusted manually until primary PSDs comparable to those reported in [22] were obtained. A two-step parameter optimisation process was then implemented which is explained by Smallbone *et al.* [41]. The uncertainty in the model parameters could be calculated through the method of Braumann *et al.* [4, 5, 28] if the uncertainties in experimental data were available. This system's three-dimensional parameter space is given by:

$$\mathbf{x} = (A_{\rm s}, E_{\rm s}, d_{\rm p,min}) \tag{13}$$

The objective function for optimisation is given by:

$$\Phi(\mathbf{x}) = \sum_{i=1}^{N_{\text{exp}}} \left(\left[M(d_{\text{pri}})_i^{\text{exp}} - M(d_{\text{pri}})_i^{\text{sim}}(\mathbf{x}) \right]^2 + \left[\text{Var}(d_{\text{pri}})_i^{\text{exp}} - \text{Var}(d_{\text{pri}})_i^{\text{sim}}(\mathbf{x}) \right]^2 \right) \quad (14)$$



Figure 5: *Temporal evolution of the primary and collision diameters compared with the simulated particle rates (right panel).*



Figure 6: Evolution of the primary particle PSD.



Figure 7: *PSDs for variation of process conditions. The experimental data of Körmer et al. [22] is given by crosses, and the theoretical PSD by the solid line.*

where N_{exp} is the number of experimental cases from Körmer *et al.* [22], $M(d_{pri})_i^{exp}$, $Var(d_{pri})_i^{exp}$, $M(d_{pri})_i^{sim}$ and $Var(d_{pri})_i^{sim}$ are the experimental and simulated mode primary diameter and variance of the primary diameter respectively. First, the low-discrepancy Sobol sequences were used to locate a point near a possible global minimum in the three-dimensional parameter space. The simultaneous perturbation stochastic approximation (SPSA) algorithm was subsequently applied, leading to the set of optimal sintering parameters \mathbf{x}^* which minimise the objective function $\Phi(\mathbf{x})$:

$$\mathbf{x}^* = \arg\min_{\mathbf{x}} \left\{ \Phi(\mathbf{x}) \right\} \tag{15}$$

These are given in Table 1. The resulting primary PSDs are displayed in Figure 7 with the process conditions for each case given above the corresponding PSD. The optimised model response is directly compared to experimental values in Table 5

The primary PSDs show excellent agreement with the experimental data of Körmer *et al.* [22]. The PSD for baseline process conditions is almost exactly coincident with the

		Experimental		Simula	tion
au (ms)	<i>T</i> (°C)	$\langle d_{\rm pri} \rangle$ (nm)	GSD (-)	$\langle d_{\rm pri} \rangle$ (nm)	GSD (-)
80	1100	27	1.07	26.9	1.06
420	1100	32	1.07	31.8	1.05
420	1000	29	1.08	25.5	1.02
420	900	22	1.08	21.1	1.01

Table 5: Optimised model response compared with experimental data of Körmer et al. [22]. All runs at 1.0 mbar SiH₄ in 25 mbar total pressure.

experimental points. However, the cases at longer residence time predict a considerably narrower PSD than that measured. This could potentially be attributed to the larger particles 'mopping-up' the smaller particles through coagulation and sintering, causing the primary distributions to narrow with residence time. Despite this, all three long residence time cases correspond closely to the peak frequency of the experimental data.

No set of parameters could be found which could simultaneously fit the model to lowand high-pressure process conditions (0.5 mbar and 3.2 mbar SiH₄ respectively) with the cases at different temperatures and residence time. This could potentially be attributed to a fundamental change in the sintering mechanism. It could also be associated with the breakdown of the applicability of the simplified model proposed in Table 4. This remains to be further investigated.

5.4 Computer-generated TEM image

TEM-style images may be generated by assuming that primary particles randomly adhere to each other to form the secondary particle. These are projected onto a plane to model the particle ensemble at the final residence time. A TEM-style image was generated for the ensemble at baseline process conditions using POV-Ray and is compared to its corresponding experimental SEM image in Figure 8. It is qualitatively apparent that the theoretically-predicted primary particles share a similar size and sphericity to their experimental counterparts.

6 Conclusions

This paper has presented the development of a robust fully-coupled gas-phase and particle model for the synthesis of narrowly-distributed silicon nanoparticles under the process conditions of Körmer *et al.* [22]. The chemical mechanism of Swihart & Girshick [42] was initially coupled to a particle model with coagulation, sintering and surface growth processes. It was observed that the particles did not grow above their incepting diameter without condensation, thus surface growth was assumed to occur by condensation, with all species permitted to condense.

This analysis also demonstrated that the ultimate PSD was dependent on the number of silicon atoms in the critical nucleus. Application of homogeneous nucleation theory sug-



Figure 8: An experimental SEM image of Körmer et al. [22] (left panel) compared with a computer-generated TEM-style image (right panel) from the present work at baseline process conditions.

gested that at these conditions, the critical nucleus size is smaller than the diameter of the precursor, corresponding to collision-controlled nucleation. Thus, a simplified model was developed, considering only two silicon atoms in the initial nucleus. The phenomena typically observed in homogeneous nucleation under such conditions were consistent with the predictions of the simplified model.

The model was then optimised through low-discrepancy series and a perturbation algorithm by fitting the sintering parameters from the formula of Tsantilis *et al.* [46] to the experimental data of Körmer *et al.* [22]. There was excellent agreement of the model's prediction with the experimental results for results at different temperature and residence time conditions. A computer-generated TEM image also gave qualitative agreement with the appearance of particles.

At this stage, the model does not track the hydrogen chemistry in the particle-phase. Including this would allow for accurate description of the 1,1 elimination of hydrogen from the surface of silicon clusters. This could potentially expand the space of process conditions (such as increased pressures) for which it is valid. Finally, the model's ability to predict collision PSDs is currently under-exploited: if experimental data were available for comparison, the validity of the model could be further assessed.

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