Low-Pressure Chemical Vapor Deposition of Polycrystalline Silicon: Analysis of Nonuniform Growth in an Industrial-Scale Reactor

W. L. M. Weerts, a M. H. J. M. de Croon, and G. B. Marin b

Laboratorium voor Chemische Technologie, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

ABSTRACT

The performance of an industrial-scale low-pressure chemical vapor deposition reactor is simulated for the deposition of undoped polycrystalline silicon from silane at 25 Pa and 900 K using a one-dimensional, two-zone model with independently obtained rate equations. The radial growth rate nonuniformity across a wafer is completely determined by the radial variations in the growth rates from silylene and disilane. The shape of the concentration profiles of these species can be adequately described in terms of a (modified) Thiele modulus based on the kinetics of their most important formation and disappearance reactions. With increasing reactor tube radius the radial growth rate nonuniformity increases significantly due to higher concentration levels of silylene and disilane in the annular zone. A smaller reactor tube radius promotes radial uniformity across the wafers but is detrimental for the axial uniformity along the length of the wafer load. The effect of interwafer spacing on radial growth rate nonuniformity is less pronounced. Moreover, an improvement in radial uniformity by an increase in interwafer spacing is achieved at the cost of wafer packing density. A quantification of these opposing effects is possible with the model presented.

Introduction

In the microelectronics industry the most common reactor for the deposition of polycrystalline silicon is the hot-wall, multiwafer, low-pressure chemical vapor deposition (LPCVD) reactor (see Fig. 1). Despite its batchwise operation, it is able to realize a high throughput owing to the high packing density of silicon wafers perpendicular to the axis of the tube and the satisfactory layer thickness uniformity across each wafer as well as from wafer to wafer.

However, recent trends toward smaller feature sizes and larger silicon wafers cause the uniformity demands imposed on the deposited silicon films to become more and more stringent. Currently 150 mm diam wafers are used most frequently, but in the near future 200 mm wafers will become standard. Table 1 lists typical values for the geometrical features of an industrial-scale LPCVD reactor capable of processing 200 mm wafers and the process conditions at which it is operated.

Without sound knowledge of the underlying physical and chemical processes, it is difficult to predict the effect of scale-up on the growth uniformity inside a hotwall multiwafer LPCVD reactor. In the literature, several mathematical reactor models of very different degrees of sophistication have been proposed to gain quantitative insight into the relation between layer deposition rate and uniformity on one hand and reactor geometry and process conditions on the other. These reactor models generally range from simplified, one-dimensional models to more sophisticated, two-dimensional models treating the hydrodynamics and the mass transport with chemical reactions in a more detailed manner.

In a recent paper Weerts et al. 18 tested the validity of both a one-dimensional, two-zone model and a fully two-dimensional model by comparing calculated with experimental growth rate data for undoped polycrystalline silicon obtained in a commercial LPCVD reactor at operating conditions that are industrially relevant, i.e., total pressures around 25 Pa and temperatures around 900 K. The applied rate equations were obtained independently by regression of a set of kinetic rate data collected with a microbalance reactor at similar conditions. 19, 20 Four elementary gas-phase reactions between six gas-phase species and ten elementary surface reactions were considered. Simulations revealed that experimental layer thicknesses could be accurately described using the simplified, one-dimensional, two-zone reactor model without adjusting any model parameter. The much higher degree of sophistication applied in the fully two-dimensional model appeared to be redundant.

The present work reports on the application of the above-mentioned one-dimensional, two-zone model and the independently obtained rate equations to gain insight into the interplay between chemical reaction kinetics and mass-transport phenomena in relation to the growth uniformity inside an industrial-scale, hotwall, multiwafer LPCVD reactor for the deposition of undoped polycrystalline silicon. For all simulations a silane conversion of about 53.5% was chosen. This is a very high value compared to the industrially employed conversions of less than about 10%. However, at high conversions the coupled effects of chemical kinetics and multicomponent diffusion on deposition uniformity are more pronounced and can be studied more easily. Note that a radial growth nonuniformity

![Fig. 1. Schematic diagram of a conventional hotwall multiwafer LPCVD reactor.](image)

| Table I. Geometrical features and operating conditions of an industrial-scale reactor. |
|---------------------------------|------------------|
| Reactor length | L | 0.75 m |
| Reactor tube radius | R | 0.16 m |
| Wafer radius | R_w | 0.10 m |
| Interwafer spacing | Δ | 0.00503 m |
| Boat surface area/tube surface area | α | 0.1 |
| Surface-to-volume ratio | A/V | 168.8 m⁻¹ |
| Number of wafers | NRWF | 150 |
| Total pressure | P | 25 Pa |
| Temperature | T | 900 K |
| Silane inlet flow rate | Q_{in} | 400 sccm |

*The reactor length as specified here comprises the wafer section only. b The surface-to-volume ratio applies to the wafer section.
mity is more critical than an axial one. Silane conversion effects on the axial growth rate can generally be compensated for by imposing a small axial temperature profile and/or increase of the total flow rate. The simulations presented here do not account for this and are primarily aimed at an analysis of the effects of typical operating conditions, such as interwafer spacing and reactor tube radius, on the growth uniformity inside the reactor. Moreover, the simulations also demonstrate the advantages of a detailed elementary reaction mechanism above a very simplified one, e.g., of the Langmuir-Hinshelwood type and neglecting gas-phase reactions, for the unraveling of strongly coupled physical and chemical phenomena.

**One-Dimensional Two-Zone Reactor Model**

In the one-dimensional, two-zone reactor model, effects from the mixing, preheating, and downstream sections are neglected. The model development is therefore reduced to the description of the performance of the wafer section only, which is thought to consist of an annular zone between the wafer edges and the reactor wall and an inter-wafer zone (see Fig. 2). In reality the wafer section consisted of a quartz boat on which the wafers are mounted. This boat is not modeled explicitly; only its effect on surface reactions is taken into account. Thereto a boat surface of unimolecular reaction steps is introduced. The value of this ratio is based on similar values for industrial LPCVD reactors. The model corresponding to an annular zone and an inter-wafer zone is similar to that developed by Roenigk and Jensen and consists of two sets of one-dimensional continuity equations for all gas-phase components, as shown in Table II. One set allows calculation of the concentration profiles along the radial coordinate in the inter-wafer zone, while the other set allows the concentration profiles along the radial coordinate in the inter-wafer zone, to be calculated. Multicomponent diffusion effects are accounted for by the Stefan-Maxwell equations. Coupling between both sets is accomplished by the boundary conditions at the wafer edges. The binary diffusion coefficients are calculated from the Chapman-Enskog kinetic theory of gases.

To integrate the complete set of differential equations with corresponding boundary condition, 6th-order orthogonal collocation is applied in both the r-direction of the inter-wafer zone and the z-direction of the annular zone. The resulting set of algebraic equations is solved using a modified Newton-Raphson method in the standard NAG library routine C05NBF. A typical reactor simulation requires a CPU time of 30 min on a Silicon Graphics Power Challenge computer.

After solving the complete set of model equations, the radially averaged silicon growth rate is obtained from

\[
\frac{dN_1}{dz} = \frac{2}{R_1^2 - R_w^2} \left( R_1 \left( 1 + a \right) \sum_{m=1}^{N_G} v_n \int r N_n^m + R_w N_1^w \right) \sum_{k=1}^{N_G} v_k \int r N_k^w
\]

**Table II. One-dimensional, two-zone reactor model equations.**

<table>
<thead>
<tr>
<th>Zone</th>
<th>Equation</th>
</tr>
</thead>
</table>
| Interwafer zone | \[
\frac{1}{r} \frac{d}{dr} \left( r N_1^w \right) = 2 \sum_{m=1}^{N_G} v_n \int r N_n^m + \sum_{k=1}^{N_G} v_k \int r N_k^m
\] |
| Annular zone | \[
\frac{dN_1}{dz} = \frac{2}{R_1^2 - R_w^2} \left( R_1 \left( 1 + a \right) \sum_{m=1}^{N_G} v_n \int r N_n^m + R_w N_1^w \right) \sum_{k=1}^{N_G} v_k \int r N_k^w
\] |

where \( R_{10}(r) \) is the silicon growth rate at radial position \( r \) calculated according to

\[
R_{10}(r) = \frac{M_s}{\rho_{Si}} \sum_{m=1}^{N_G} v_{m,Si} \int r N_{m,Si}\text{,} \quad (r)
\]

**Kinetic Model**

The kinetic model used has been developed by modeling a large set of kinetic experiments performed in the range of industrially relevant operation conditions for the deposition of polycrystalline silicon. It consists of four elementary gas-phase reactions coupled to ten elementary surface reactions (see Table III). The description of the surface reaction of SiH\(_4\) reaction 7, which leads to gaseous SiH\(_3\) and an adsorbed SiH\(_3\) species, is chosen on the basis of temporal analysis of products (TAP) experiments, as described by Weerts et al. The dehydrogenation of surface species formed during adsorption reactions is assumed to proceed instantaneously toward solid silicon.

Hence, besides the gas-phase species hydrogen, silane, silylene (SiH\(_2\)), disilane (Si\(_2\)H\(_6\)), disilene (H\(_2\)SiSiH\(_2\)), and silylsilylene (H\(_4\)SiSiH\(_3\)), hydrogen adatoms form the only kinetically significant surface species. Higher silanes, such as Si\(_2\)H\(_8\) or Si\(_4\)H\(_m\), are not considered. They were not detected by means of mass spectrometry in a perfectly mixed LPCVD reactor setup under the same reactor operation conditions. The homogeneous net production rates of these gas-phase components, represented by the last terms on the right side of Eq. 1 and 6 in Table II, follow from the law of mass action for the rates of forward and reverse steps of the elementary gas-phase reactions. Rate coefficients of unimolecular steps are calculated using an empirical relation accounting for the pressure falloff behavior of these steps. The rate coefficients of the
Table III. Elementary reactions and corresponding kinetic parameter values considered in the gas phase (Reactions 1 to 4) and on the silicon surface (Reactions 5 to 14).

<table>
<thead>
<tr>
<th>Gas-phase reactions</th>
<th>A (s⁻¹ or m³ mol⁻¹ s⁻¹)</th>
<th>E_a (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ + H₂ -&gt; SiH₂ + H₂</td>
<td>1.28 x 10⁻³</td>
<td>215.8</td>
</tr>
<tr>
<td>SiH₂ + SiH₄ -&gt; Si₂H₆</td>
<td>3.52 x 10⁻³</td>
<td>163.3</td>
</tr>
<tr>
<td>SiH₂ + SiH₂ + H₂</td>
<td>9.68 x 10⁻³</td>
<td>180.9</td>
</tr>
<tr>
<td>H₂SiSiH₂ + H₂SiS</td>
<td>6.02 x 10⁻³</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table IV. Thermodynamic data for chemical species considered in the gas phase. Standard state 1 atm.

<table>
<thead>
<tr>
<th>Gas-phase species</th>
<th>H₂S (kJ mol⁻¹)</th>
<th>S (J mol⁻¹ K⁻¹)</th>
<th>C (J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.0</td>
<td>130.3</td>
<td>28.9</td>
</tr>
<tr>
<td>SiH₂</td>
<td>34.3</td>
<td>204.2</td>
<td>43.1</td>
</tr>
<tr>
<td>SiH₄</td>
<td>268.0</td>
<td>208.7</td>
<td>34.8</td>
</tr>
<tr>
<td>Si₂H₆</td>
<td>78.9</td>
<td>273.2</td>
<td>79.9</td>
</tr>
<tr>
<td>H₂SiSiH₂</td>
<td>312.1</td>
<td>282.4</td>
<td>69.0</td>
</tr>
<tr>
<td>H₂SiS</td>
<td>264.0</td>
<td>273.2</td>
<td>70.7</td>
</tr>
</tbody>
</table>

Origin of Nonuniform Growth

Model predictions.—Figure 3 shows the total silicon growth rate, the growth rate due to gas-phase intermediates, and individual silicon growth rates from the most abundant silicon-containing gas-phase species vs. the axial reactor coordinate. (+) SiH₂, (o) SiH₄, and (x) Si₂H₆, calculated with the one-dimensional two-zone model presented in Table II and the reaction network given in Table III. Conditions: Q_m = 400 sccm, 100% SiH₂, P = 25 Pa, and T = 900 K.

Figure 3 shows that the total growth rate is almost completely determined by heterogeneous decomposition of silane. Silane conversion increases from 47.8% at the entrance to 66.3% at the exit of the wafer section. The contribution from all gas-phase intermediates to the growth rate is approximately uniform over the complete length of the wafer section. It corresponds to the growth rate contributions from SiH₂ and Si₂H₆ and amounts to roughly 3%. The growth rate from silylene is more or less uniform over the length of the wafer section, reflecting the high reactivity of this intermediate. The fact that disilane is less reactive, both in the gas phase and on the surface, is consistent with the decrease in the corresponding growth rate along the axial coordinate in the wafer section. Note, however, that the actual concentration variations are partially leveled off by axial diffusion in the annular zone. The lumped contribution from H₂SiSiH₂ and H₂SiS, to the total growth rate due to gas-phase intermediates is typically less than 1%. Hence, these species are not considered in the following discussion concerning the radial growth rate uniformity. Figure 4 shows similar results vs. the radial coordinate in the interwafer space corresponding to a silane conversion of 53.5%. In order to mark the radial variations in silicon growth rate, especially those existing close to the edge of the wafer, a measure of nonuniformity is plotted as well, calculated relative to the growth rate in the center of the wafer according to

Local radial nonuniformity = \frac{R_s(r) - R_{s0}}{R_{s0}} \bigg|_{r=1} - \bigg|_{r=0} [4]
The growth rate nonuniformity sharply increases on the periphery of the wafer and shows a maximum of 6.3% at the edge of the wafer. Clearly, the wafer edge nonuniformity, which slightly decreases from 7.5 to 5.7% along the length of the wafer section, is caused by the radial variations in the growth rates from silylene and disilane. This is in contrast to the results of Badgwell et al.,22 who attributed similar radial growth rate nonuniformities to radial temperature variations across the wafers.

As mentioned earlier, growth nonuniformity in the radial direction is more critical than that in the axial direction. Based on the foregoing discussion, it is clear that the presence of homogeneous reactions is detrimental for radial growth uniformity, despite the minor role these reactions play with respect to the total silicon growth rate. It was shown that radial nonuniformity is completely determined by radial nonuniformities in the growth rates from silylene and disilane and, hence, by the shape of the radial concentration profiles of these species. It is therefore important to know in what way these concentration profiles are affected by mass transport and chemical reaction kinetics. In this context approximate analytical expressions are derived describing the radial concentration profiles of silylene and disilane at given silane conversion, i.e., in a single interwafer space. First, however, the most important formation and disappearance reactions of both species are identified by means of reaction path analysis.

The most important reaction paths.—In order to determine the most important reaction paths for silylene and disilane, a contribution analysis was carried out for the conditions prevailing in the interwafer space with a silane conversion of 53.5%. A contribution analysis in general determines the relative importance of an elementary step with respect to the total formation or disappearance rate of a species.

With reference to the equations of Table III, it was found that formation of silylene is determined for 99% by homogeneous decomposition of silane and for 1% by homogeneous decomposition of disilane according to reactions 1 and 2, respectively. Silylene consumption takes place for 10% via insertion into silane, reaction 2, and for 90% via heterogeneous decomposition according to reaction 6, followed by instantaneous decomposition of the so-formed surface dihydride species into solid silicon and hydrogen adatoms via reactions 11 and 12. Disappearance of silylene through insertion into molecular hydrogen, reaction 1, is not significant. Disilane consumption is for 2% accounted for by homogeneous decomposition into silane and silylene, reaction 2, and for 98% by heterogeneous decomposition, reaction 7, followed by the instantaneous reactions 11 and 12. Finally, insertion of silylene into silane accounts for 100% to production of disilane.

Figure 5 shows schematically the most important reaction paths to and from silylene and disilane. Silylene production is assumed to proceed at a uniform rate \( r_f \) (mol m\(^{-3}\) s\(^{-1}\)), equal to the product of the unimolecular reaction rate coefficient \( k_r \) (s\(^{-1}\)) of Table III and the silane concentration \( C_{SiH_4} \) (mol m\(^{-3}\)), the latter being uniform in each interwafer space. The insertion reaction of silylene into silane, which contributes to both the disappearance of silylene and the production of disilane, is characterized by a pseudo-first-order reaction rate coefficient \( k_i \) (mol m\(^{-3}\) s\(^{-1}\)) of Table III and again the uniform concentration of silane. Consumption of silylene and disilane at the surface is characterized by the surface reaction rate coefficients \( k_{sSiH_4} \) and \( k_{SiH_2} \) (mol m\(^{-3}\) s\(^{-1}\)) being the products of the rate coefficients \( k_L \) and \( k_i \) (mol m\(^{-1}\) mol\(^{-1}\) s\(^{-1}\)) of Table III and the concentration of vacant surface sites, \( L_v \) (mol m\(^{-3}\)).

\[
\begin{align*}
\text{SiH}_4 & \quad \text{SiH}_2 \\
& \quad \text{Si}_2\text{H}_6
\end{align*}
\]

Figure 5. Most important reaction paths to and from silylene and disilane.

\[
\begin{align*}
\text{SiH}_4 & \quad r_f \rightarrow \text{SiH}_2 \\
& \quad 2k_{sSiH_2}\text{H}_2 \\
& \quad 2k_{sSiH_2}\text{H}_6 \\
& \quad \text{Si}(s)
\end{align*}
\]

Table V. Values of the kinetic and transport parameters used in Eq. 9 to 14.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_f )</td>
<td>( 9.32 \times 10^{-1} ) mol m(^{-3}) s(^{-1})</td>
</tr>
<tr>
<td>( k_r )</td>
<td>( 1302 ) s(^{-1})</td>
</tr>
<tr>
<td>( k_{sSiH_4} )</td>
<td>( 29.175 ) m s(^{-1})</td>
</tr>
<tr>
<td>( k_{SiH_2} )</td>
<td>( 2.029 ) m s(^{-1})</td>
</tr>
<tr>
<td>( L_v )</td>
<td>( 1.65 \times 10^{-1} ) mol m(^{-2})</td>
</tr>
<tr>
<td>( D_{\text{SiH}_4} )</td>
<td>( 0.488 ) m(^{2}) s(^{-1})</td>
</tr>
<tr>
<td>( D_{\text{SiH}_2} )</td>
<td>( 0.431 ) m(^{2}) s(^{-1})</td>
</tr>
</tbody>
</table>

\* Conditions: \( Q_{\text{in}} = 400 \) sccm, 100% \( \text{SiH}_4 \), \( P = 25 \) Pa, \( T = 900 \) K, \( X_{\text{SiH}_4} = 53.5\% \), \( C_{\text{SiH}_4} = 3.406 \times 10^{-2} \) mol m\(^{-3}\) and \( C_{\text{SiH}_2} = 1.978 \times 10^{-7} \) mol m\(^{-3}\).
under deposition conditions. For values of \( L_s \) under other conditions see Weerts et al.\(^5\)

Interplay between chemical reaction kinetics and mass-transport phenomena.—On the basis of the foregoing considerations and neglecting possible axial concentration gradients, the continuity equations for silylene and disilane in an interwafer space become (see also Eq. 1, Table II)

\[
- \frac{D_{SiH_2,m}}{r} \frac{d}{dr} \left( r \frac{dC_{SiH_2}}{dr} \right) = r^2 - k_s C_{SiH_2} - \frac{2}{\Delta} k_{sSiH_2} C_{SiH_2} \tag{5}
\]

\[
- \frac{D_{SiH_2,m}}{r} \frac{d}{dr} \left( r \frac{dC_{SiH_2}}{dr} \right) = k_s C_{SiH_2} - \frac{2}{\Delta} k_{sSiH_2} C_{SiH_2} \tag{6}
\]

with \( D_{SiH_2,m} \) denoting the effective molecular diffusion coefficient of species 1 in a multicomponent mixture as postulated by Wilke.\(^30\) Note that the factor \( 2/\Delta \) represents the surface-to-volume ratio of each interwafer space. The appropriate boundary conditions are similar to those expressed by Eq. 4 and 5 of Table II

\[
r = 0 \quad \frac{dC}{dr} = 0 \tag{7}
\]

\[
r = R_w \quad C = C_i \tag{8}
\]

with the superscript \( i \) denoting the annular zone.

The second-order differential equation for silylene, Eq. 5, is linear in \( C_{SiH_2} \) and features constant coefficients at a given silane conversion, i.e., at a given axial position in the annular zone. Integration of this equation with the corresponding boundary conditions leads to the following expression for the silylene concentration as a function of the radial coordinate in an interwafer space\(^9,31\)

\[
C_{SiH_2} = r^2 \frac{r_1'}{k_s + \frac{2}{\Delta} k_{sSiH_2}} + \left( C_{SiH_2}^s \right) \frac{r_1'}{k_s + \frac{2}{\Delta} k_{sSiH_2}} I_0 \left( \phi_{SiH_2} \frac{r}{R_w} \right) \tag{9}
\]

with \( I_0 \) a modified Bessel function of the first kind and order zero and \( \phi_{SiH_2} \) a modified Thiele modulus defined as

\[
\phi_{SiH_2} = R_w \sqrt{1 - \frac{2 \Delta}{D_{SiH_2,m}}} \tag{10}
\]

and corresponding to the ratio of the time scale of diffusional mass transport to the time scale of disappearance via gas-phase as well as surface reactions. The first term on the right side of Eq. 9 denotes the concentration of silylene obtained by applying the steady-state approximation to this species

\[
C_{SiH_2}^{SSA} = \frac{r_1'}{k_s + \frac{2}{\Delta} k_{sSiH_2}} \tag{11}
\]

The first term inside the brackets of Eq. 9, \( C_{SiH_2}^s \), denotes the steady-state concentration of silylene in the annular zone, corresponding to the locally prevailing concentration of silane. Substitution of Eq. 9 into the second-order differential equation for disilane, Eq. 6, and integration of the latter with the corresponding boundary conditions leads to the following expression for the disilane concentration as a function of the radial coordinate in an interwafer space\(^9,31\)

\[
C_{SiH_2}^{SSA} = \frac{r_1'}{k_s + \frac{2}{\Delta} k_{sSiH_2}} \tag{11}
\]

The first term on the right side of Eq. 12 represents the disilane concentration obtained by applying the steady-state approximation to this species

\[
C_{SiH_2}^{SSA} = \frac{k_s C_{SiH_2}^{SSA} \Delta}{2 k_{SiH_2,m}} \left( \frac{C_{SiH_2}^s - C_{SiH_2}^{SSA}}{R_w} \right) I_0 \left( \phi_{SiH_2} \frac{r}{R_w} \right) \tag{12}
\]

\[
+ \frac{k_s C_{SiH_2}^{SSA} \Delta}{2 k_{SiH_2,m}} \left( \frac{C_{SiH_2}^{SSA} - C_{SiH_2}^s}{R_w} \right) I_0 \left( \phi_{SiH_2} \frac{r}{R_w} \right) \tag{13}
\]

with \( \phi_{SiH_2} \) the Thiele modulus defined as

\[
\phi_{SiH_2} = R_w \sqrt{1 - \Delta D_{SiH_2,m}} \tag{14}
\]

As shown in Fig. 6, the analytical expressions given by Eq. 9 and 12 adequately describe the numerically obtained concentration profiles of silylene and disilane. The full lines represent the concentration profiles as calculated with the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Dashed lines: calculated with Eq. 9 and 12 and the values given in Table V. The effective molecular diffusion coefficients are calculated based on radially averaged molar fractions.

The values for the kinetic and transport parameters listed in Table V lead to the following expressions for the silylene concentration obtained by applying the steady-state approximation to this species

\[
C_{SiH_2}^{SSA} = \frac{k_s C_{SiH_2}^{SSA} \Delta}{2 k_{SiH_2,m}} \tag{11}
\]

The first term on the right side of Eq. 12 represents the disilane concentration obtained by applying the steady-state approximation to this species
and $c_{SiH_2}^{0}$ and, hence, by the time scale of silylene consumption through surface as well as gas-phase reactions, provided the effective molecular diffusion coefficient, $D_{SiH_2}$, and the silylene production rate, $r_{SiH_2}$, remain the same. Two extreme situations can now be distinguished. In the absence of silylene consumption, i.e., $S_{SiH_2} = 0$, silylene is uniformly distributed throughout the interwafer space and a flat concentration profile results at the level prevailing in the annular zone, $C_{SiH_2}^{0}$. In case silylene consumption proceeds extremely fast, i.e., in the limit $S_{SiH_2} \rightarrow \infty$, diffusion cannot keep up with the reactions and a pronounced concentration gradient exists over an infinitesimally small distance from the wafer edge, while the concentration in the center of the interwafer space approaches zero. At intermediate values of $S_{SiH_2}$, a decrease in the time scale of silylene consumption is accompanied with a decrease in both the concentration in the center of the interwafer space and the thickness of the layer over which the concentration gradient can be localized. In case $S_{SiH_2}$ is not large enough to completely eliminate mass-transport effects in the center of the interwafer space, the concentration in that region does not equal the steady-state concentration as given by Eq. 11.

An analysis if the disilane concentration profile shown in Fig. 6 on the basis of Eq. 12 is less straightforward. The shape of the disilane concentration profile is affected by that of silylene as well, since formation of disilane is completely accounted for by insertion of silylene into silane. The disilane concentration in the center of the interwafer space is, contrary to the silylene case, not solely determined by chemical kinetics but is affected by mass transport as well. As a result of the relatively small value of $S_{SiH_2}$, the value of the third term on the right side of Eq. 12 is comparable to the value of the first term. Moreover, the third term can be equated with $C_{SiH_2}^{0}/k(S_{SiH_2})$, since the other terms inside the brackets are in an absolute sense much smaller than $C_{SiH_2}^{0}$. The expression for the disilane concentration at $r = 0$ thus becomes

$$C_{SiH_2}^{0} = C_{SiH_2}^{0} + \frac{C_{SiH_2}^{0}}{k(S_{SiH_2})} \left( \frac{S_{SiH_2}}{k(S_{SiH_2})} \right)$$

with the first term on the right side merely reflecting chemical kinetics and the second term accounting for diffusional mass transport.

A quantity that is frequently used in the following sections is the ratio between the concentrations of silylene and disilane prevailing in the center of an interwafer space, i.e., at $r = 0$. Based on the foregoing considerations, the following expression holds

$$\frac{C_{SiH_2}^{0}}{C_{SiH_2}^{0} + C_{SiH_2}^{0} + \frac{C_{SiH_2}^{0}}{k(S_{SiH_2})} \left( \frac{S_{SiH_2}}{k(S_{SiH_2})} \right)}$$

with the steady-state concentrations of silylene and disilane given by Eq. 11 and 14, and the Thiele modulus for disilane defined by Eq. 13.

**Effect of Interwafer Spacing**

Figure 7 shows the effect of interwafer spacing on the shape of the silicon growth rate profiles from silylene and disilane across the radius of the wafer for the conditions listed in Table I. The interwafer spacing has been altered by changing the total number of wafers positioned in the wafer load (NRWFP) while keeping the length of the wafer section fixed at 0.75 m. In order to investigate the effect of interwafer spacing without interference of gas-phase composition effects, all growth rate profiles apply to interwafer spaces at a similar silane flow condition, namely, 93%. In this way the effects of changing gas-phase composition on the effective molecular diffusion coefficients $D_{SiH_2}$ and $D_{SiH_2}$, and the rate coefficients $k_1$ and $k_2$ are eliminated. Furthermore, note that the shapes of the growth rate profiles of Fig. 7 fully reflect the shapes of the corresponding concentration profiles, since the adsorption rate coefficients $k_1$ and $k_2$ are constant and the concentration of vacant surface sites, $L_*$, is uniform in each interwafer space. As discussed before, $L_*$ is predominantly determined by heterogeneous decomposition of silane and desorption of hydrogen.

Clearly, with decreasing interwafer spacing, i.e., with increasing surface-to-volume ratio $2/A$ of the interwafer space, the growth rates from both silylene and disilane in the center of the interwafer space and, hence, the corresponding concentrations of silylene and disilane, $C_{SiH_2}^{0}$, decrease. For silylene this concentration equals the steady-state concentration, $C_{SiH_2}^{0}$, given by Eq. 11, which indeed decreases with decreasing interwafer spacing. Note that the corresponding silylene concentration in the annular space, $C_{SiH_2}^{0}$, has no effect on the steady-state value in the center. In the case of disilane, the above-mentioned concentration, expressed by Eq. 15, decreases due to a simultaneous decrease in the steady-state concentration $C_{SiH_2}^{0}$, and the annular concentration $C_{SiH_2}^{0}$, and an increase in the Thiele modulus $S_{SiH_2}/E$. The decreases in $C_{SiH_2}^{0}$ and $C_{SiH_2}^{0}$ imply that surface reactions are becoming relatively more important compared to gas-phase reactions at smaller interwafer spacing. Table VI lists disappearance contribution percentages for the most important silicon-containing gas-phase species and interwafer spacings of 0.00431 and 0.00843 m, corresponding to interwafer surface-to-volume ratios of 464.0 and 237.2 m⁻¹. Formation contribution percentages are not relevant, since production of these gas-phase species is a matter of gas-phase kinetics only. In order to investigate the effect of interwafer surface-to-volume ratio without interference of silane conversion effects, the contribution percentages were calculated for the interwafer spaces at a silane conversion of 53%. Indeed, with decreasing interwafer spacing, i.e., with increasing interwafer surface-to-volume ratio, the relative contribution of surface reactions to the total consumption of the above-mentioned gas-phase species increases. Moreover, the listed percentages reveal the predominance of the surface reactions over the gas-phase reactions.

Besides $C_{SiH_2}^{0}$, the thicknesses of the layers over which the concentration gradients take place also decrease (see Fig. 7). In the case of silylene this effect can be fully attrib-
Table VI. Effect of the interwafer spacing on the disappearance paths of silane, silylene, and disilane.

<table>
<thead>
<tr>
<th>Δ (m)</th>
<th>Surface (%)</th>
<th>Gas phase (%)</th>
<th>Surface (%)</th>
<th>Gas phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>98.4 1.6</td>
<td>96.8 3.2</td>
<td>91.0 9.0</td>
<td>83.8 10.2</td>
</tr>
<tr>
<td>SiH₂</td>
<td>10.6 1.6</td>
<td>96.9 3.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calculated after solving the complete set of equations of the one-dimensional, two-zone model presented in Table II with the reaction network given in Table III. Conditions: Q_{sil} = 400 scem, 100% SiH₄, P = 25 Pa, T = 900 K, X_{sil} = 53%.

Table VII. Effect of reactor tube radius on the silane conversion, radially averaged silicon growth rate, and axial growth rate nonuniformity.

<table>
<thead>
<tr>
<th>Δ (m)</th>
<th>X_{sil} (%)</th>
<th>R_{rad} (10^{-10} m s⁻¹)</th>
<th>R_{ax} (10^{-10} m s⁻¹)</th>
<th>axial nonuniformity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00431</td>
<td>50.4 69.6</td>
<td>1.92 1.27</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>0.00605</td>
<td>44.7 62.4</td>
<td>2.11 1.34</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>0.00643</td>
<td>39.4 55.2</td>
<td>2.29 1.79</td>
<td></td>
<td>26</td>
</tr>
</tbody>
</table>

*Calculated using the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: Q_{sil} = 400 scem, 100% SiH₄, P = 25 Pa, T = 900 K.

Table VIII. Effect of the reactor tube radius on the silane conversion, radially averaged silicon growth rate, and axial growth rate nonuniformity.

<table>
<thead>
<tr>
<th>Δ (m)</th>
<th>X_{sil} (%)</th>
<th>R_{rad} (10^{-10} m s⁻¹)</th>
<th>R_{ax} (10^{-10} m s⁻¹)</th>
<th>axial nonuniformity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>41.2 67.1</td>
<td>2.18 1.36</td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>0.16</td>
<td>47.8 66.3</td>
<td>2.00 1.40</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>0.18</td>
<td>51.9 66.0</td>
<td>1.89 1.42</td>
<td></td>
<td>28</td>
</tr>
</tbody>
</table>

*Calculated using the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: Q_{sil} = 400 scem, 100% SiH₄, P = 25 Pa, T = 900 K.
gas-phase species and reactor tube radii of 0.14 and 0.18 m, corresponding to annular surface-to-volume ratios of 29.2 and 16.1 m⁻¹. Formation contribution percentages are not relevant, since production of these gas-phase species is a matter of gas-phase kinetics only. In order to investigate the effect of an annular surface-to-volume ratio without interference of silane conversion effects, the contribution percentages were calculated for the annular spaces at a silane conversion of 54%. Clearly, with increasing tube radius, i.e., with a smaller annular surface-to-volume ratio, the relative importance of the gas-phase reactions increases. The production of gas-phase species in the interwafer spaces having a similar silane conversion, namely, 54%. Clearly, with increasing tube radius, i.e., with a smaller annular surface-to-volume ratio, the relative importance of the gas-phase reactions increases. The production of gas-phase species and reactor tube radii of 0.14 and 0.18 m, corresponding to annular surface-to-volume ratios of 29.2 and 16.1 m⁻¹. Formation contribution percentages are not relevant, since production of these gas-phase species is a matter of gas-phase kinetics only. In order to investigate the effect of an annular surface-to-volume ratio without interference of silane conversion effects, the contribution percentages were calculated for the annular spaces at a silane conversion of 54%. Clearly, with increasing tube radius, i.e., with a smaller annular surface-to-volume ratio, the relative importance of the gas-phase reactions increases. The production of gas-phase species only starts to over-

**Table IX. Effect of the reactor tube radius on the disappearance paths of silane, silylene, and disilane.**

<table>
<thead>
<tr>
<th>Rₜ (m)</th>
<th>Surface (%)</th>
<th>Gas phase (%)</th>
<th>Surface (%)</th>
<th>Gas phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>76.3</td>
<td>23.2</td>
<td>61.2</td>
<td>38.8</td>
</tr>
<tr>
<td>SiH₂</td>
<td>39.2</td>
<td>60.8</td>
<td>26.1</td>
<td>73.9</td>
</tr>
<tr>
<td>Si₂H₆</td>
<td>78.3</td>
<td>21.7</td>
<td>67.6</td>
<td>32.4</td>
</tr>
</tbody>
</table>

* Calculated after solving the complete set of equations of the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: Qₛₐᵢₙ = 400 sccm, 100% SiH₄, P = 25 Pa, T = 900 K, Xₛₐᵢₙ = 54%.

Clearly, the reactor tube radius has no influence on the silicon growth rate from silylene in the center of the inter-

The simulations reveal that the radial growth rate nonuniformity across a wafer, typically lying between 4 and 9%, is completely determined by homogeneous reactions, in particular by the radial variations in the growth rates from silylene and disilane. The latter are the most important gas-phase intermediates, with a contribution to the silicon growth rate of typically 1 to 5% at the operating conditions considered. Silylene is formed through homogeneous decomposition of silane and is consumed mainly by heterogeneous decomposition into solid silicon and molecular hydrogen. Consumption of silylene via insertion into silicon is of minor importance. This reaction, however, fully accounts for the formation of disilane. Consumption of disilane is almost completely accounted for by heterogeneous decomposition into solid silicon, molecular hydrogen, and disilane. Only a small fraction of the disilane is converted to silane and silylene. Due to the high reactivity of silylene and disilane on the surface and/or in the gas-phase, significant concentration gradients for these species develop in the radial direction between successive wafers. The shape of these concentration profiles can be described in terms of a (modified) Thiele modulus based on the kinetics of the most impor-

**Conclusions**

The performance of an industrial-scale LPCVD reactor can be simulated for the deposition of undoped polycrys-
talline silicon from silane at industrially relevant operating conditions using a one-dimensional, two-zone reactor model and independently obtained rate equations. The use of an elementary reaction mechanism facilitates the unraveling of the strongly coupled physical and chemical processes in such a reactor.

The simulations reveal that the radial growth rate nonuniformity across a wafer, typically lying between 4 and 9%, is completely determined by homogeneous reactions, in particular by the radial variations in the growth rates from silylene and disilane. The latter are the most important gas-phase intermediates, with a contribution to the silicon growth rate of typically 1 to 5% at the operating conditions considered. Silylene is formed through homogeneous decomposition of silane and is consumed mainly by heterogeneous decomposition into solid silicon and molecular hydrogen. Consumption of silylene via insertion into silicon is of minor importance. This reaction, however, fully accounts for the formation of disilane. Consumption of disilane is almost completely accounted for by heterogeneous decomposition into solid silicon, molecular hydrogen, and disilane. Only a small fraction of the disilane is converted to silane and silylene. Due to the high reactivity of silylene and disilane on the surface and/or in the gas-phase, significant concentration gradients for these species develop in the radial direction between successive wafers. The shape of these concentration profiles can be described in terms of a (modified) Thiele modulus based on the kinetics of the most impor-
tant formation and disappearance reactions of the species under consideration.

With increasing reactor tube radius the radial growth rate nonuniformity increases significantly due to higher net production rates of silylene and disilane in the annular zone. Moreover, the ratio between the growth rates from silane and disilane in the central part of the interwafer zone reduces at larger tube radii. A smaller reactor tube radius promotes the radial uniformity across the wafers but worsens the axial uniformity along the length of the wafer load. The axial variations in the silane concentration and hence, in the silicon growth rate are reduced less effectively due to a decrease in the relative importance of molecular diffusion with respect to convection. However, such variations can generally be countered by imposing a small axial temperature profile and/or increasing the total flow rate.

With increasing interwafer spacing the relative importance of disilane to the silicon growth rate compared to silylene increases. Although the radial variations in the growth rates from silane and disilane significantly reduce at larger interwafer spacings, the net effect on the overall growth rate profile is quite small due to the relatively small contribution of silylene and disilane to the growth rate. A serious improvement in radial uniformity by an increase in interwafer spacing is generally not provided as it occurs at the cost of wafer packing density.

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LIST OF SYMBOLS

- $A_i$: pre-exponential factor, reaction-dependent
- $A_{tota}$: total deposition surface area, $m^2$
- $C_i$: gas-phase concentration of component $i$, mol m$^{-3}$
- $D_{i,m}$: binary molecular diffusion coefficient, $m^2$s$^{-1}$
- $D_{i,m,n}$: effective multicomponent molecular diffusion coefficient, $m^2$s$^{-1}$
- $E_a$: Arrhenius activation energy, J mol$^{-1}$
- $I_0$: modified Bessel function of first kind and order zero
- $k_i$: reaction rate coefficient, reaction dependent
- $k_s$: surface reaction rate coefficient, $m$ s$^{-1}$
- $k_r$: pseudo-first-order gas-phase reaction rate coefficient, s$^{-1}$
- $L$: reactor length, m
- $L_e$: concentration of vacant surface sites, mol m$^{-2}$
- $M_{si}$: molar mass of solid silicon, kg mol$^{-1}$
- $n_g$: number of gas-phase reaction steps
- $n_s$: number of surface reaction steps
- $N_i$: molar flux of component $i$ with respect to fixed coordinates, mol m$^{-2}$ s$^{-1}$
- $P$: pressure, Pa
- $P_a$: partial pressure of component $i$, Pa
- $P_{in}$: inlet volumetric flow rate of silane at standard conditions, sccm
- $r$: radial coordinate, m
- $r_e$: volumetric reaction rate, mol m$^{-3}$ s$^{-1}$
- $r_a$: areal reaction rate, mol m$^{-2}$ s$^{-1}$
- $R$: radius, m
- $R_w$: wafer radius, m
- $R_{wafer}$: wafer radius, m
- $R_{silicon}$: silicon deposition rate or growth rate, m s$^{-1}$
- $u$: molar average velocity, m s$^{-1}$
- $V_p$: gas-phase reaction volume, m$^3$
- $X_{silane}$: conversion of silane
- $x$: molar fraction of component $i$
- $z$: axial coordinate, m

Greek

- $a$: annular region
- $f$: formation
- $SSA$: steady-state approximation
- $w$: interwafer region
- $\bar{w}$: average

Subscripts

- $i,j$: gas-phase component
- $k$: gas-phase reaction
- $m$: surface reaction
- $i$: inlet
- $\varnothing$: vacant site

REFERENCES