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

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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 I 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.¹⁻¹⁷ 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

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Fig. 1. Schematic diagram of a conventional hotwall multiwafer LPCVD reactor.

Table I. Geometrical features and operating conditions of an industrial-scale reactor.

Reactor length ^a	L	0.75 m
Reactor tube radius	R_t	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 ^b	A_d/V_d	168.8 m ⁻¹
Number of wafers	NRWF	150
Total pressure	P	25 Pa
Temperature	T	900 K
Silane inlet flow rate	Q_{SiH_4}	400 sccm

^a 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.¹⁶ 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 interwafer 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 area-to-tube surface area ratio α 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 interwafer zone is similar to that developed by Roenigk and Jensen² 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 axial coordinate in the annular zone, while the other set allows the concentration profiles along the radial coordinate in the interwafer zone. to be calculated. Multicomponent diffusion effects are accounted for by the Stefan-Maxwell equations.²¹ 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.²²

To integrate the complete set of differential equations with corresponding boundary condition, 6th-order orthogonal collocation²³ is applied in both the r -direction of the interwafer 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.²⁴ 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

$$\overline{R_{Si}} = \frac{2 \int_0^{R_W} R_{Si}(r) r dr}{R_W^2} \quad [1]$$

Fig. 2. Schematic representation of the wafer section as considered in the one-dimensional, two-zone reactor model. The annular and interwafer zone consist of (NRWF-1) annular and interwafer spaces, respectively.

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

Interwafer zone

$$\frac{1}{r} \frac{d}{dr} (r N_i^w) = \frac{2}{\Delta} \sum_{m=1}^{ns} \nu_{m,i} r_{a,m} + \sum_{k=1}^{ng} \nu_{k,i} r_{v,k} \quad [1]$$

$$\frac{dy_i^w}{dr} = \sum_{j=1}^{NG} \frac{y_i^w N_j^w - y_j^w N_i^w}{C_i D_{i,j}} \quad [2]$$

$$\sum_{i=1}^{NG} y_i^w = 1 \quad [3]$$

$$r = 0 \quad N_i^w = 0 \quad [4]$$

$$r = R_w \quad y_i^w = y_i^a \quad [5]$$

Annular zone

$$\frac{dN_i^a}{dz} = \frac{2}{R_t^2 - R_w^2} \left(R_t (1 + \alpha) \sum_{m=1}^{ns} \nu_{m,i} r_{a,m} + R_w N_i^w \Big|_{r=R_w} \right) + \sum_{k=1}^{ng} \nu_{k,i} r_{v,k} \quad [6]$$

$$\frac{dy_i^a}{dz} = \sum_{j=1}^{NG} \frac{y_i^a N_j^a - y_j^a N_i^a}{C_i D_{i,j}} \quad [7]$$

$$\sum_{i=1}^{NG} y_i^a = 1 \quad [8]$$

$$z = 0 \quad N_i^a = u_0 C_i y_{i,0}^a \quad [9]$$

$$z = L \quad \frac{dy_i^a}{dz} = 0 \quad [10]$$

with $R_{Si}(r)$ the silicon growth rate at radial position r calculated according to

$$R_{Si}(r) = \frac{M_{Si}}{\rho_{Si}} \sum_{m=1}^{ns} \nu_{m, Si} r_{a,m}(r) \quad [2]$$

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.^{19,20} It consists of four elementary gas-phase reactions coupled to ten elementary surface reactions (see Table III). The description of the surface reaction of Si_2H_6 , reaction 7, which leads to gaseous SiH_4 and an adsorbed SiH_2^* species, is chosen on the basis of temporal analysis of products (TAP) experiments, as described by Weerts *et al.*²⁶ 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_2H_6), disilene (H_2SiSiH_2), and silylsilylene (H_2SiSiH), hydrogen adatoms form the only kinetically significant surface species. Higher silanes, such as Si_3H_8 or Si_4H_{10} , 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.²⁰ 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.^{20,27} 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).

Gas-phase reactions ^a	A s^{-1} or $m^3 \text{ mol}^{-1} s^{-1}$	E_a kJ mol^{-1}	
$\text{SiH}_4 \rightleftharpoons \text{SiH}_2 + \text{H}_2$	$1.28 \times 10^{10} f_1$	$215.8 + g_1$	[1]
$\text{SiH}_4 + \text{SiH}_2 \rightleftharpoons \text{Si}_2\text{H}_6$	$3.53 \times 10^9 f_2$	$163.3 + g_2$	[2]
$\text{Si}_2\text{H}_6 \rightleftharpoons \text{H}_3\text{SiSiH}_3$	$9.68 \times 10^9 f_3$	$180.6 + g_3$	[3]
$\text{H}_3\text{SiSiH}_3 \rightleftharpoons \text{H}_2\text{SiSiH}_2$	$6.02 \times 10^4 f_4$	$4.2 + g_4$	[4]

Surface reactions	A s^{-1} , $m^3 \text{ mol}^{-1} s^{-1}$, or $m^3 \text{ mol}^{-1}$	E_a kJ mol^{-1}	
$\text{SiH}_4 + 2^* \rightarrow \text{SiH}_3^* + \text{H}^*$	3.89×10^4	0.0	[5]
$\text{SiH}_2 + ^* \rightarrow \text{SiH}_2^*$	1.76×10^7	0.0	[6]
$\text{Si}_2\text{H}_6 + ^* \rightarrow \text{SiH}_3^* + \text{SiH}_2^*$	1.23×10^9	0.0	[7]
$\text{H}_3\text{SiSiH}_3 + 2^* \rightarrow 2\text{SiH}_3^*$	1.25×10^7	0.0	[8]
$\text{H}_2\text{SiSiH}_2 + 2^* \rightarrow 2\text{SiH}_2^*$	1.25×10^7	0.0	[9]
$\text{SiH}_3^* + ^* \rightarrow \text{SiH}_2^* + \text{H}^*$	instantaneous		[10]
$\text{SiH}_2^* + ^* \rightarrow \text{SiH}^* + \text{H}^*$	instantaneous		[11]
$\text{SiH}^* + ^* \rightarrow \text{Si}(s) + \text{H}^*$	instantaneous		[12]
$\text{H}^* \rightleftharpoons \text{H} + ^*$	4.47×10^{11}	188.4	[13] ^b
$\text{H}^* + \text{H}^* \rightleftharpoons \text{H}_2 + ^*$	8.99×10^{-18}	-360.6	[14] ^c

^a The Arrhenius parameters listed apply to the forward steps of reactions 1, 3, and 4 and to the reverse step of reaction 2. Empirical pressure falloff corrections²⁰ f_i and g_i are given by $f_i = p_{\text{eff}}^{B_{i,1}}$ and $g_i = B_{i,2} \ln p_{\text{eff}} + B_{i,3} (\ln p_{\text{eff}})^2$ with p_{eff} defined as: $p_{\text{eff}} = \sum_i \lambda_i p_i$, where p_i and λ_i are the partial pressure and collisional deactivation efficiency of gas-phase component i , respectively. In the present work λ_{H_2} equals 0.3, whereas for all silicon hydrides λ_i is taken equal to 1.0. The coefficients $B_{1,1}$, $B_{2,1}$, and $B_{3,1}$ are 1.0013, $-3.55 \times 10^{-2} \text{ kJ mol}^{-1}$, and $1.23 \times 10^{-2} \text{ kJ mol}^{-1}$ for reaction 1; 1.0953, 1.21 kJ mol^{-1} , and $1.80 \times 10^{-1} \text{ kJ mol}^{-1}$ for reaction 2; 1.1076, 1.97 kJ mol^{-1} , and $1.55 \times 10^{-1} \text{ kJ mol}^{-1}$ for reaction 3; and 1.0001, $7.86 \times 10^{-5} \text{ kJ mol}^{-1}$, and $8.37 \times 10^{-5} \text{ kJ mol}^{-1}$ for reaction 4.

^b The Arrhenius parameters listed apply to hydrogen adatom excitation.

^c The values listed are the pre-exponential factor and the change in standard enthalpy for the dissociative adsorption of molecular hydrogen. The corresponding equilibrium coefficient is expressed in Van't Hoff form.

reverse steps are calculated from thermodynamics.^{28,29} The necessary thermodynamic data for gas-phase chemical species are given in Table IV.

The calculation of the heterogeneous net production rates of the above-mentioned gas-phase species, represented by the first terms on the right side of Eq. 1 and 6 in Table II, is less straightforward. The complexity of the surface reaction network does not allow a straightforward derivation of closed kinetic expressions relating the silicon deposition rates from the individual silicon-containing gas-phase species to gas-phase concentrations only. Writing the mass balance for hydrogen adatoms in terms of the concentration of vacant surface sites, yields a third-order equation in L_* , the concentration of vacant surface sites, which is solved numerically. L_* is subsequently used to calculate the heterogeneous net production rates of the silicon-containing gas-phase species following the law of mass action for the rates of adsorption reactions.

Origin of Nonuniform Growth

Model predictions.—Figure 3 shows the total silicon growth rate, the growth rate due to gas-phase intermediates, and the individual growth rates from silane, silylene,

Table IV. Thermodynamic data for chemical species considered in the gas phase.^{28,29} Standard state 1 atm.

Gas-phase species	H_{298} (kJ mol^{-1})	S_{298} ($\text{J mol}^{-1} \text{ K}^{-1}$)	$C_{p,298}$ ($\text{J mol}^{-1} \text{ K}^{-1}$)
H_2	0.0	130.5	28.9
SiH_4	34.3	204.2	43.1
SiH_2	269.0	206.7	34.8
Si_2H_6	79.9	273.6	79.9
H_3SiSiH_3	312.1	282.4	69.0
H_2SiSiH_2	264.0	273.2	70.7

Fig. 3. Radially averaged silicon growth rate (—), total silicon 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. (+) SiH_4 , ($\square$) SiH_2 , and ($\triangle$) Si_2H_6 , calculated with the one-dimensional two-zone model presented in Table II and the reaction network given in Table III. Conditions: $Q_{\text{SiH}_4} = 400 \text{ sccm}$, 100% SiH_4 , $P = 25 \text{ Pa}$, and $T = 900 \text{ K}$.

and disilane vs. the axial reactor coordinate for the conditions listed in Table I. The plotted growth rates concern radially averaged values (see Eq. 1). The total silicon growth rate decreases from $2.0 \times 10^{-10} \text{ m s}^{-1}$ on the first wafer to $1.4 \times 10^{-10} \text{ m s}^{-1}$ on the last wafer of the load, corresponding to an axial nonuniformity of roughly 35%, which is calculated from the radially averaged growth rates at the entrance and exit of the wafer section according to

$$\text{Axial nonuniformity} = 2 \frac{\overline{R_{\text{Si}}}|_{z=0} - \overline{R_{\text{Si}}}|_{z=L}}{\overline{R_{\text{Si}}}|_{z=0} + \overline{R_{\text{Si}}}|_{z=L}} \quad [3]$$

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 SiH_2 and Si_2H_6 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 H_2SiSiH_2 and H_3SiSiH_3 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

$$\text{Local radial nonuniformity} = \frac{R_{\text{Si}}(r) - R_{\text{Si}}|_{r=0}}{R_{\text{Si}}|_{r=0}} \quad [4]$$

Fig. 4. Silicon growth rate (—), total silicon growth rate due to gas-phase intermediates (---), individual silicon growth rates from the most abundant silicon-containing gas-phase species (····), and growth rate nonuniformity (- · - ·) vs. the radial coordinate of the interwafer zone. (□) SiH_4 , (○) SiH_2 , and (+) Si_2H_6 , calculated with the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH_4 , $P = 25$ Pa, $T = 900$ K, and $X_{\text{SiH}_4} = 53.5\%$.

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.*¹³ 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 shapes 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 homo-

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

geneous 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_v^f ($\text{mol m}^{-3} \text{s}^{-1}$), equal to the product of the unimolecular reaction rate coefficient k_1 (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_v (s^{-1}), equal to the product of the bimolecular rate coefficient k_2 ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$) 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_{s, SiH_2} and $k_{s, \text{Si}_2\text{H}_6}$ (m s^{-1}) being the products of the rate coefficients k_6 and k_7 ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$) of Table III and the concentration of vacant surface sites, L_* (mol m^{-2}). The latter is practically uniform in each interwafer space, because it is predominantly determined by heterogeneous decomposition of silane and desorption of hydrogen. Table V lists the calculated values for the conditions prevailing in the interwafer space with a silane conversion of 53.5%. The value of L_* under these conditions amounts to $1.65 \times 10^{-6} \text{ mol m}^{-2}$, *i.e.*, the surface coverage of vacant sites amounts to about 14.6%. As the surface coverages of adsorbed silicon hydrides are assumed to be negligible, the surface coverage of H^* amounts to about 85%, implying that the surface is mostly covered with hydrogen adatoms

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

r_v^f	$9.32 \times 10^{-6} \text{ mol m}^{-3} \text{s}^{-1}$
k_v	1302.2 s^{-1}
k_{s, SiH_2}	29.175 m s^{-1}
$k_{s, \text{Si}_2\text{H}_6}$	2.029 m s^{-1}
L_*	$1.65 \times 10^{-6} \text{ mol m}^{-2}$
$D_{\text{SiH}_2, \text{m}}$	$0.688 \text{ m}^2 \text{s}^{-1}$
$D_{\text{Si}_2\text{H}_6, \text{m}}$	$0.431 \text{ m}^2 \text{s}^{-1}$

^a Conditions: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH_4 , $P = 25$ Pa, $T = 900$ K, $X_{\text{SiH}_4} = 53.5\%$, $C_{\text{SiH}_2}^a = 3.406 \times 10^{-8} \text{ mol m}^{-3}$ and $C_{\text{Si}_2\text{H}_6}^a = 1.978 \times 10^{-7} \text{ mol m}^{-3}$.

under deposition conditions. For values of L_* under other conditions see Weerts *et al.*²⁰

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)

$$-\frac{D_{\text{SiH}_2, \text{m}}}{r} \frac{d}{dr} \left(r \frac{dC_{\text{SiH}_2}}{dr} \right) = r_v^f - k_v C_{\text{SiH}_2} - \frac{2}{\Delta} k_{s, \text{SiH}_2} C_{\text{SiH}_2} \quad [5]$$

$$-\frac{D_{\text{Si}_2\text{H}_6, \text{m}}}{r} \frac{d}{dr} \left(r \frac{dC_{\text{Si}_2\text{H}_6}}{dr} \right) = k_v C_{\text{SiH}_2} - \frac{2}{\Delta} k_{s, \text{Si}_2\text{H}_6} C_{\text{Si}_2\text{H}_6} \quad [6]$$

with $D_{i, \text{m}}$ denoting the effective molecular diffusion coefficient of species i 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

$$r = 0 \quad \frac{dC_i}{dr} = 0 \quad [7]$$

$$r = R_w \quad C_i = C_i^a \quad [8]$$

with the superscript a 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^{25,31}

$$C_{\text{SiH}_2} = \frac{r_v^f}{k_v + \frac{2}{\Delta} k_{s, \text{SiH}_2}} + \left(C_{\text{SiH}_2}^a - \frac{r_v^f}{k_v + \frac{2}{\Delta} k_{s, \text{SiH}_2}} \right) \frac{I_0 \left(\phi_{\text{SiH}_2} \frac{r}{R_w} \right)}{I_0(\phi_{\text{SiH}_2})} \quad [9]$$

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

$$\phi_{\text{SiH}_2} = R_w \sqrt{\frac{k_v + \frac{2}{\Delta} k_{s, \text{SiH}_2}}{D_{\text{SiH}_2, \text{m}}}} \quad [10]$$

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

$$C_{\text{SiH}_2}^{\text{SSA}} = \frac{r_v^f}{k_v + \frac{2}{\Delta} k_{s, \text{SiH}_2}} \quad [11]$$

The first term inside the brackets of Eq. 9, $C_{\text{SiH}_2}^a$, 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^{25,31}

$$C_{\text{Si}_2\text{H}_6} = \frac{k_v C_{\text{SiH}_2}^{\text{SSA}}}{2k_{s, \text{Si}_2\text{H}_6}} + \left(\frac{k_v}{D_{\text{Si}_2\text{H}_6, \text{m}}} (C_{\text{SiH}_2}^a - C_{\text{SiH}_2}^{\text{SSA}}) R_w^2 \right) \frac{I_0 \left(\phi_{\text{SiH}_2} \frac{r}{R_w} \right)}{I_0(\phi_{\text{SiH}_2})} + \left(C_{\text{Si}_2\text{H}_6}^a - \frac{k_v C_{\text{SiH}_2}^{\text{SSA}}}{2k_{s, \text{Si}_2\text{H}_6}} - \frac{k_v}{D_{\text{Si}_2\text{H}_6, \text{m}}} (C_{\text{SiH}_2}^a - C_{\text{SiH}_2}^{\text{SSA}}) R_w^2 \right) \frac{l_0 \left(\phi_{\text{Si}_2\text{H}_6} \frac{r}{R_w} \right)}{l_0(\phi_{\text{Si}_2\text{H}_6})} \quad [12]$$

with $\phi_{\text{Si}_2\text{H}_6}$ the Thiele modulus defined as

$$\phi_{\text{Si}_2\text{H}_6} = R_w \sqrt{\frac{2k_{s, \text{Si}_2\text{H}_6}}{\Delta D_{\text{Si}_2\text{H}_6, \text{m}}}} \quad [13]$$

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

$$C_{\text{Si}_2\text{H}_6}^{\text{SSA}} = \frac{k_v C_{\text{SiH}_2}^{\text{SSA}}}{\frac{2}{\Delta} k_{s, \text{Si}_2\text{H}_6}} \quad [14]$$

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, whereas the dashed lines show the same profiles obtained using the analytical expressions and values listed 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 after substitution into Eq. 10 and 13 to $\phi_{\text{SiH}_2} = 13.7$ and $\phi_{\text{Si}_2\text{H}_6} = 4.3$. Due to the large value of ϕ_{SiH_2} , the second term on the right side of Eq. 9 is small compared to the first term for small values of the radial coordinate. Hence, the silylene concentration in the center of the interwafer space equals $C_{\text{SiH}_2}^{\text{SSA}}$ and mass-transport effects are absent. It is important to note that the steady-state concentration of silylene is determined solely by the uniform concentration of silane. The shape of the silylene concentration profile is determined by the values of ϕ_{SiH_2}

Fig. 6. Concentration of silylene (+) and disilane (O) vs. the radial coordinate in an interwafer space. Full lines: 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. Conditions: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH_4 , $P = 25$ Pa, $T = 900$ K, and $X_{\text{SiH}_4} = 53.5\%$. (Dashed lines closely follow solid lines.)

and $C_{\text{SiH}_2}^{\text{SSA}}$ and, hence, by the time scale of silylene consumption through surface as well as gas-phase reactions, provided the effective molecular diffusion coefficient, $D_{\text{SiH}_2, \text{m}}$, and the silylene production rate, r_v^i , remain the same. Two extreme situations can now be distinguished. In the absence of silylene consumption, i.e., $\phi_{\text{SiH}_2} = 0$, silylene is uniformly distributed throughout the interwafer space and a flat concentration profile results at the level prevailing in the annular zone, $C_{\text{SiH}_2}^{\text{a}}$. In case silylene consumption proceeds extremely fast, i.e., in the limit $\phi_{\text{SiH}_2} \rightarrow \infty$, 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 ϕ_{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 ϕ_{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 $\phi_{\text{Si}_2\text{H}_6}$, 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 $C_{\text{Si}_2\text{H}_6}^{\text{a}}/I_0(\phi_{\text{Si}_2\text{H}_6})$, since the other terms inside the brackets are in an absolute sense much smaller than $C_{\text{Si}_2\text{H}_6}^{\text{a}}$. The expression for the disilane concentration at $r = 0$ thus becomes

$$C_{\text{Si}_2\text{H}_6}|_{r=0} = C_{\text{Si}_2\text{H}_6}^{\text{SSA}} + \frac{C_{\text{Si}_2\text{H}_6}^{\text{a}}}{I_0(\phi_{\text{Si}_2\text{H}_6})} \quad [15]$$

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

$$\left(\frac{C_{\text{SiH}_2}}{C_{\text{Si}_2\text{H}_6}} \right)_{r=0} = \frac{C_{\text{SiH}_2}^{\text{SSA}}}{C_{\text{Si}_2\text{H}_6}^{\text{SSA}} + \frac{C_{\text{Si}_2\text{H}_6}^{\text{a}}}{I_0(\phi_{\text{Si}_2\text{H}_6})}} \quad [16]$$

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 (NRWF) 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 conversion, namely, 53%. In this way the effects of changing gas-phase composition on the effective molecular diffusion coefficients $D_{\text{SiH}_2, \text{m}}$ and $D_{\text{Si}_2\text{H}_6, \text{m}}$ 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

Fig. 7. Silicon growth rates from silylene (—) and disilane (---) vs. the radial coordinate of the interwafer zone. Calculated using the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH_4 , $P = 25$ Pa, $T = 900$ K, and $X_{\text{SiH}_4} = 53\%$. (+) $\Delta = 0.00843$ m, (O) $\Delta = 0.00605$ m, and (□) $\Delta = 0.00431$ m.

concentration profiles, since the adsorption rate coefficients k_6 and k_7 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 $2/\Delta$ of the interwafer zone, the growth rates from both silylene and disilane in the center of the interwafer space and, hence, the corresponding concentrations of silylene and disilane, $C_i|_{r=0}$, decrease. For silylene this concentration equals the steady-state concentration, $C_{\text{SiH}_2}^{\text{SSA}}$, given by Eq. 11, which indeed decreases with decreasing interwafer spacing. Note that the corresponding silylene concentration in the annular space, $C_{\text{SiH}_2}^{\text{a}}$, 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 $C_{\text{Si}_2\text{H}_6}^{\text{SSA}}$, Eq. 14, and the annular concentration $C_{\text{Si}_2\text{H}_6}^{\text{a}}$ and an increase in the Thiele modulus $\phi_{\text{Si}_2\text{H}_6}$, Eq. 13. The decreases in $C_{\text{SiH}_2}^{\text{SSA}}$ and $C_{\text{Si}_2\text{H}_6}^{\text{SSA}}$ 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 $C_i|_{r=0}$, 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.^a

Δ (m)	0.00431		0.00843	
	Surface (%)	Gas phase (%)	Surface (%)	Gas phase (%)
SiH ₄	98.4	1.6	96.8	3.2
SiH ₂	91.0	9.0	83.8	16.2
Si ₂ H ₆	98.4	1.6	96.9	3.1

^a 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: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH₄, $P = 25$ Pa, $T = 900$ K, $X_{\text{SiH}_4} = 53\%$.

uted to an increase in the corresponding Thiele modulus, ϕ_{SiH_2} , Eq. 10, whereas for disilane the increases in both ϕ_{SiH_2} and $\phi_{\text{Si}_2\text{H}_6}$ are responsible. Generally, a smaller value for the interwafer spacing results in a smaller time scale of silylene and disilane consumption relative to that of their diffusional mass transport. Hence, the consumption of silylene and disilane molecules entering the interwafer space takes place over a shorter distance from the wafer edge, thereby reducing the layer over which the concentration gradient occurs.

Figure 7 shows an increasing ratio between the growth rates from silylene and disilane, $R_{\text{SiH}_2}/R_{\text{Si}_2\text{H}_6}$, in the central part of the interwafer space with decreasing interwafer spacing, meaning that the growth rate from disilane decreases more strongly than that from silylene. This effect can be explained in terms of the ratio between the gas-phase concentrations of silylene and disilane, see Eq. 16. The steady-state concentration of silylene and the Thiele modulus of disilane, see Eq. 11 and 13, change as a result of changing interwafer spacing only. The steady-state concentration of disilane on the other hand, Eq. 14, changes not only as a result of changing interwafer spacing but also as a result of a varying steady-state concentration of silylene. Due to the stronger decrease in $C_{\text{Si}_2\text{H}_6}^{\text{SSA}}$ than in $C_{\text{SiH}_2}^{\text{SSA}}$ with decreasing Δ and due to the exponential character of the modified Bessel function I_0 incorporating the disilane Thiele modulus, the denominator of Eq. 16 more strongly decreases upon decreasing Δ than does the numerator. In this way it is shown that with decreasing interwafer spacing the ratio of silylene concentration to disilane concentration in the center of the interwafer space increases and, hence, the relative contribution of silylene to the silicon growth rate.

The radial variations in the growth rates from silylene and disilane significantly reduce at larger interwafer spacings. In case $\Delta = 0.00431$ m, the growth rate from silylene at the edge of the wafer is 5.5 times that in the center of the wafer. In case $\Delta = 0.00843$ m this factor amount to 3.3. With respect to disilane, factors of 11.1 and 4.0 are obtained, respectively. Nevertheless, the net effect on the growth rate profile is quite small. Due to the relatively small contribution to the silicon growth rate of silylene and especially of disilane, the decrease in the radial growth nonuniformity is almost negligible. The latter, calculated from the silicon growth rates in the center and at the edge of the interwafer space according to

$$\text{Radial nonuniformity} = \frac{R_{\text{Si}}|_{r=R_w} - R_{\text{Si}}|_{r=0}}{R_{\text{Si}}|_{r=0}} \quad [17]$$

decreases only slightly from 6.6% where $\Delta = 0.00431$ m to 6.3% for $\Delta = 0.00843$ m. A further increase in interwafer spacing certainly leads to more uniform growth rates along the radial coordinate; however, an improvement in radial uniformity by an increase in interwafer spacing occurs at the cost of the wafer packing density. An increase in interwafer spacing from 0.00431 to 0.00843 m already means a reduction in the total number of silicon wafers from 175 to 90. The smaller interwafer surface-to-volume ratio on the other hand lowers the silane conver-

sion and, thus increases the average silicon growth rate in the wafer section, see Table VII. The higher average growth rate, however, is attended with a smaller axial growth rate nonuniformity as defined by Eq. 3.

Effect of Reactor Tube Radius

Table VIII shows the effect of reactor tube radius on the silane conversion and radially averaged silicon growth rate at both reactor entrance and outlet and on the axial growth rate nonuniformity for the conditions listed in Table I. Since the silane volumetric flow rate, Q_{SiH_4} , is kept constant during the simulations, the superficial gas velocity in the annulus decreases with increasing tube radius, thereby increasing the mean residence time of the gas mixture in the wafer section. Consequently, the average silane conversion increases and the average silicon growth rate thus decreases. Moreover, the decrease in superficial gas velocity increases the relative importance of molecular diffusion in respect of convection, leading to a smaller value of the mass Peclet number, $Pe = uL/D_{\text{SiH}_4,\text{in}}$. In this way axial variations in the silane concentration are reduced more effectively and a more uniform silicon growth rate is obtained along the length of the wafer section. This is also reflected by the values for the axial nonuniformity calculated using Eq. 3. The contribution of the gas-phase intermediates to the growth rate is quite small and practically insensitive to a change in tube radius. It decreases from 5% at the entrance to 3% at the exit for a tube radius of 0.18 m and from 4 to 1% in case the tube radius amounts to 0.14 m. The more pronounced decrease at the smaller tube radius is related to the more pronounced decrease in silane concentration for the same radius (see Table VIII). These percentages correspond to the lumped growth rate contributions from silylene and disilane; those from the Si₂H₄ isomers are typically less than 1%. The radially averaged growth rates from silylene and disilane increase with increasing radius, which seems to be in contradiction with the corresponding increasing silane conversion (see Table VIII). However, the occurrence of higher concentrations of silylene and disilane despite the lower concentration of silane is explainable on the basis of a smaller surface-to-volume ratio, $2R_t/(R_t^2 - R_w^2)$, of the annular zone. Table IX lists disappearance contribution percentages for the most important silicon-containing

Table VII. Effect of the interwafer spacing on the silane conversion, the radially averaged silicon growth rate, and the axial growth rate nonuniformity.^a

Δ (m)	X_{SiH_4} (%)		R_{Si} (10^{-10} m s ⁻¹)		axial nonuniformity (%)
	Entrance	Exit	Entrance	Exit	
0.00431	50.4	69.6	1.92	1.27	41
0.00605	44.7	62.4	2.11	1.54	31
0.00843	39.4	55.2	2.29	1.79	25

^a Calculated using the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: $Q_{\text{SiH}_4} = 400$ sccm, 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.^a

R_t (m)	X_{SiH_4} (%)		R_{Si} (10^{-10} m s ⁻¹)		axial nonuniformity (%)
	Entrance	Exit	Entrance	Exit	
0.14	41.2	67.1	2.18	1.36	46
0.16	47.8	66.3	2.00	1.40	35
0.18	51.9	66.0	1.89	1.42	28

^a Calculated using the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH₄, $P = 25$ Pa, $T = 900$ K.

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

R_t (m)	0.14		0.18	
	Surface (%)	Gas phase (%)	Surface (%)	Gas phase (%)
SiH ₄	76.8	23.2	61.2	38.8
SiH ₂	39.2	60.8	26.1	73.9
Si ₂ H ₆	79.3	20.7	67.6	32.4

^a 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: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH₄, $P = 25$ Pa, $T = 900$ K, $X_{\text{SiH}_4} = 54\%$.

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 intermediates, taking place through gas-phase reactions only, starts to overcome the consumption of these species through surface reactions. Consequently, the gas-phase intermediates are present at higher concentration levels.

Figure 8 shows the effect of reactor tube radius 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. In order to eliminate gas-phase composition effects, all growth rate profiles apply to interwafer spaces having a similar silane conversion, namely, 54%. Furthermore, recall that the shapes of the growth rate profiles shown in Fig. 8 fully reflect the shapes of the corresponding concentration profiles.

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

wafer space. For the conditions considered, the silylene concentration in the center of the interwafer space equals the steady-state concentration of silylene given by Eq. 11, which is merely a function of gas-phase composition and interwafer spacing. The latter is not changed during the simulations. Since the plotted growth rate profiles all apply to the same concentration of silane and a similar gas-phase composition, the silylene concentration in the center of the interwafer space, $C_{\text{SiH}_2}^{\text{SSA}}$, and the corresponding growth rate from silylene remain constant. There is no dependence on the radius of the reactor tube. Based on the expression for the steady-state concentration of disilane, Eq. 14, a constant value for the disilane concentration in the center of the interwafer space and for the corresponding growth rate from disilane would then be expected as well. However, it has been shown that the Thiele modulus of disilane (see Eq. 13) is too small to completely eliminate mass-transport effects in the center of the interwafer space and justify the application of the steady-state approximation to this species at this position. Since the steady-state concentration and Thiele modulus of disilane remain unchanged, the concentration of disilane in the center (see Eq. 15) changes merely as a result of changing disilane concentration in the annular space, $C_{\text{Si}_2\text{H}_6}^a$. It thus increases with increasing reactor tube radius.

Based on the foregoing considerations it follows that the ratio between the concentrations of silylene and disilane in the center of the interwafer space decreases with increasing tube radius, *i.e.*, with decreasing annular surface-to-volume ratio. Consequently, the ratio between the growth rates from silylene and disilane reduces as well (see Fig. 8). Moreover, the radial growth rate nonuniformity, being completely determined by the radial variations in the growth rates from silylene and disilane, changes with changing reactor tube radius. It almost doubles from 4.4% when $R_t = 0.14$ m to 8.6% when $R_t = 0.18$ m due to the higher concentrations of silylene and disilane in the case of the larger radius. A smaller reactor tube radius promotes radial uniformity of the growth rate in the interwafer zone but worsens the uniformity of the growth rate along the length of the wafer section (see Table VIII). The latter, however, can be improved by an increase of the total flow rate and/or temperature profiling.

Conclusions

The performance of an industrial-scale LPCVD reactor can be simulated for the deposition of undoped polycrystalline 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 silane 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 silane. 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-

Fig. 8. Silicon growth rates from silylene (—) and disilane (---) vs. the radial coordinate of the interwafer zone. Calculated using the one-dimensional, two-zone model presented in Table II and the reaction network given in Table III. Conditions: $Q_{\text{SiH}_4} = 400$ sccm, 100% SiH₄, $P = 25$ Pa, $T = 900$ K, and $X_{\text{SiH}_4} = 54\%$. (□) $R_t = 0.14$ m, (+) $R_t = 0.16$ m, and (○) $R_t = 0.18$ m.

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 silylene 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 silylene 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 preferred as it occurs at the cost of wafer packing density.

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LIST OF SYMBOLS

A	pre-exponential factor, reaction dependent
A_d	total deposition surface area, m^2
C_i	gas-phase concentration of component i , $mol\ m^{-3}$
C_i	total gas-phase concentration, $mol\ m^{-3}$
D_{ij}	binary molecular diffusion coefficient, $m^2\ s^{-1}$
$D_{i,m}$	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	reaction rate coefficient, reaction dependent
k_s	surface reaction rate coefficient, $m\ s^{-1}$
k_v	pseudo-first-order gas-phase reaction rate coefficient, s^{-1}
L	reactor length, m
L_*	concentration of vacant surface sites, $mol\ m^{-2}$
M_{Si}	molar mass of solid silicon, $kg\ mol^{-1}$
ng	number of gas-phase reaction steps
ns	number of surface reaction steps
NG	number of gas-phase components
N_i	molar flux of component i with respect to fixed coordinates, $mol\ m^{-2}\ s^{-1}$
P	total pressure, Pa
P_i	partial pressure of component i , Pa
$Pé$	mass Peclet number
Q_{SiH_4}	inlet volumetric flow rate of silane at standard conditions, scm
r	radial coordinate, m
r_v	volumetric reaction rate, $mol\ m^{-3}\ s^{-1}$
r_a	areal reaction rate, $mol\ m^{-2}\ s^{-1}$
R_t	reactor tube radius, m
R_w	wafer radius, m
R_{Si}	silicon deposition rate or growth rate, $m\ s^{-1}$
T	temperature, K
u	molar average velocity, $m\ s^{-1}$
V_g	gas-phase reaction volume, m^3
X_{SiH_4}	conversion of silane
y_i	molar fraction of component i
z	axial coordinate, m
Greek	
α	boat area/tube area
Δ	interwafer spacing, m
λ	collisional deactivation efficiency
ν	stoichiometric coefficient
ρ_{Si}	density of solid silicon, $kg\ m^{-3}$
ϕ_i	Thiele modulus of component i

Superscripts

a	annular region
f	formation
SSA	steady-state approximation
w	interwafer region
$-$	average

Subscripts

i, j	gas-phase component
k	gas-phase reaction
m	surface reaction
0	inlet
$*$	vacant site

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