The deposition of silicon (Si) from silane (SiH₄) was studied in the silane pressure range from 0.5 to 100 Pa (0.005 to 1 mbar) and total pressure range from 10 to 1000 Pa using N₂ or He as carrier gases. The two reaction paths, namely, heterogeneous and homogeneous decomposition could be separated by varying the amount of wafer area per unit volume (wafer-distance variation) and the SiH₄ partial pressure as well as the total pressure. Rate constants were derived by fitting the experimental results. The heterogeneous reaction path could be described by only the adsorption rate constants of reactive species and the desorption rate constant of hydrogen using a Langmuir-Hinshelwood mechanism. Hydrogen and phosphine were found to suppress the deposition rate at low silane pressures. At high silane pressures or high total pressures the unimolecular decomposition of silane dominates. The unimolecular rate constant was found to be one to two orders larger than literature values based on RRKM analyses of high pressure rate data. The relative efficiency of SiH₄-N₂ and SiH₄-He collisions compared with SiH₄-SiH₄ collisions in the unimolecular gas-phase decomposition of SiH₄ has been investigated. Helium was found to be a weak collider compared to silane and nitrogen.

Polycrystalline silicon plays an important role in the semiconductor industry, namely, in integrated circuits (IC), thin film transistors (TFT), solar cells, and sensors. An extensive review of many scientific aspects and applications of polysilicon is given in Ref. 1.

In general polysilicon is deposited in hot-wall tube reactors where loads of 50 to 100 wafers are processed in one run. The depositions are performed using 100% SiH₄ or 25% SiH₄ diluted in an inert gas at SiH₄ partial pressures of between 10 and 30 Pa (0.1 to 0.3 mbar) at 625°C. Under these conditions the growth rate is dominated by a Langmuir-Hinshelwood type of heterogeneous SiH₄ decomposition with H₂ release from Si-H bonds as the rate determining step. In this paper values of the unimolecular rate constant and of the collision efficiency of the carrier gases He and N₂ are derived by making use of the effect that, due to the high reactivity of gas-phase reaction products, the growth rate becomes dependent on wafer spacing. We used this phenomenon for the separation of homogeneous and heterogeneous contributions to the total growth rate.

**Experimental**

**Deposition.**—The depositions were carried out on oxidized 3 in. wafers in a three-zone hot-wall horizontal tube reactor with 12 cm inner diameter. The length of the heating element is 90 cm with a flat temperature zone of 30 cm. The quartz wafer-carrier with slots at 5 mm spacing was positioned radially symmetrically in the reactor. The first and last five slot positions are always loaded with 3 in. wafers. In the experiments we varied the wafer spacing, gas flow rate, gas composition, and pressure. For the experiments presented in Fig. 2, 3, 4, 9, 10, and 11, the wafer spacing was varied alternatingly at 5 and 15 mm with the same run.

In this paper we report on a study of the decomposition of SiH₄ at low and medium pressures as well as the influence of the carrier and dopant gases. Special attention is paid to the unimolecular gas-phase decomposition of SiH₄ into SiH₃, for which, in general, values were used, which up to now were derived by means of RRKM analyses of experiments at much higher pressures and/or lower temperature than generally applied in low pressure chemical vapor deposition (LPCVD) of polysilicon. In this paper values of the unimolecular rate constant and of the collision efficiency of the carrier gases He and N₂ are derived by making use of the effect that, due to the high reactivity of gas-phase reaction products, the growth rate becomes dependent on wafer spacing. We used this phenomenon for the separation of homogeneous and heterogeneous contributions to the total growth rate.

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The experiments were performed in the temperature range from 525 to 700°C, this paper deals mainly with the experiments at 625°C. The temperature at the wafer-carrier position was calibrated by in situ thermocouple measurements and by using solid phase epitaxy of an amorphous layer, created by implantation of Si in monocrystalline silicon wafers, as a temperature monitor. All experiments were performed with a so-called flat temperature profile at the carrier position. The wafer temperature was found to be independent of the pressure. With experiments at 500 Pa (5 mbar) we found that the temperature at the wafer position was no longer constant when the flow was larger than 1 slm. Therefore, the total flow was kept below 1 slm in the 500 and the 1000 Pa experiments.

All gases except SiH₄ had contamination levels below 1 ppm. The purity of SiH₄ was 99.995%.
Growth-rate measurements.—Growth rates were measured by weighing and by measuring the height of an etched step. The weighing method yields global growth rates whereas step-height measurements give information about the local growth rate and uniformity within the wafer. As a standard procedure the growth rates were measured at different positions in the wafer carrier, with various flow rates and various interwafer spacings.

In a horizontal hot-wall reactor, where Si wafers are placed in series with respect to the gas flow, the growth rate will decrease in the axial direction due to depletion of the reactant. The undepleted growth rate, \( r_0 \), for high Péclet values can be determined by plotting the growth rate, \( r_1 \), at position \( x \) against the ratio \( A_e/MF \) according to Eq. 1:

\[
  r = r_0 [1 - \nu(1 + (e - 1)(p_{\text{inlet}}/p_{\text{tot}}))A_e r_0 MF^{-1}] \tag{1}
\]

where \( A_e \) is the total hot surface area (wafers, wall, cantilever, carrier) upstream the position where \( r \) is measured, \( MF \) is the mass flow of SiH\(_4\), \( \nu \) is the overall order of the reaction, \( p_{\text{inlet}} \) is the inlet partial pressure of SiH\(_4\), \( p_{\text{tot}} \) is the total pressure, and \( e \) is the number of gaseous molecules formed by the decomposition of one molecule of reactant.

Other authors ignored the hot surface area upstream the flat zone. Although this area does not play a significant role in low depletion cases it cannot be ignored in most of the practical cases, and it is, in our opinion, the source of the lower activation energy of about 150 kJ mol\(^{-1}\) generally reported for LPCVD hot-wall silicon-deposition systems. We found an apparent activation energy of 180 kJ mol\(^{-1}\) in the temperature range 550-650°C, which is in agreement with values reported for single-wafer systems and molecular-beam reactors and in hot-wall reactors under conditions of low depletion.

We determined the effective wall area upstream the flat zone by measuring the growth rate on silicon wafers placed close to the wall. The effective area of the entrance region was found to be 1200 cm\(^2\).

The growth rates were also measured by varying the wafer spacing within the same run. When a surface reaction is the rate-determining step the growth rate is independent of the wafer spacing. However, when the gas-phase reaction leading to highly reactive components becomes important the growth rate will become a function of the density of surface area per unit volume. Gas-phase reactions have been reported for the deposition of silicon from SiH\(_4\), Si\(_2\)H\(_6\), Si\(_3\)H\(_5\), and Si\(_2\)H\(_4\) as major constituents contribute to the total deposition rate at high pressures.

When gas-phase reactions become important, extrapolation according to Eq. 1 is no longer valid because the loss in the entrance region is no longer determined by the effective wall area alone but also by the effective entrance volume. It is more convenient then to measure the loss in the entrance region for each run. The loss can be calculated by weighing and by measuring the height of an etched step. The Si growth, studied in the pressure range presented in Fig. 5, can be divided into three regions:

Region 1: SiH\(_4\) partial pressures below 10 Pa. In this region the growth rate within the wafer is uniform, with edge/center ratios between 1 and 1.01, and independent of wafer spacing. The Si growth is moderately reduced by the addition of H\(_2\) and strongly suppressed by PH\(_3\).

Results and Discussion

Growth rate.—The results of growth-rate measurements at various positions, flow rates, and wafer spacings are presented in Fig. 1 through 4. In Fig. 1 the wafer spacing was kept constant at 10 mm and the total pressure remained at 133 Pa using N\(_2\) as a carrier gas. The undepleted growth rates, \( r_0 \), were obtained by extrapolation to the zero axis. In Fig. 2, 3, and 4 the wafer spacing was varied in order to separate surface and gas-phase decomposition of SiH\(_4\). The undepleted total growth rates for 10 mm wafer spacing are presented in Fig. 5, along with results with the addition of PH\(_3\). Also included in Fig. 5 are some data points (open circular markers) obtained previously in another reactor with N\(_2\) and H\(_2\) as carrier gases.

Fig. 1. Growth rate for various SiH\(_4\) input partial pressures. Area/flow is the total growing surface area upstream of the position where growth is measured divided by the input flow of SiH\(_4\). Total pressure is 133 Pa, carrier gas is nitrogen, wafer spacing is 10 mm, area per unit volume 159 m\(^{-1}\). Deposition temperature is 625°C.

Fig. 2. Growth rate vs. slot position in the wafer carrier for various SiH\(_4\) input pressures. Total pressure equals the SiH\(_4\) input pressure. Slot spacing is 5 mm. Input is undiluted SiH\(_4\). Wafer spacing: open markers 15 mm, filled markers 5 mm, area per unit volume 138 and 244 m\(^{-1}\), respectively. SiH\(_4\) flow is 88 sccm. Deposition temperature is 625°C. (△, ○) \( p_{\text{SiH}_4} \) input 133 Pa; (■, ●) \( p_{\text{SiH}_4} \) input 80 Pa; (□, ■) \( p_{\text{SiH}_4} \) input 60 Pa.

expressed as the ratio between the thickness at 2 mm from the wafer edge and the thickness in the center of the wafer is shown.

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Region 1: SiH\(_4\) partial pressures below 10 Pa. In this region the growth rate within the wafer is uniform, with edge/center ratios between 1 and 1.01, and independent of wafer spacing. The Si growth is moderately reduced by the addition of H\(_2\) and strongly suppressed by PH\(_3\).
Region 2: SiH₄ partial pressures in the range of 10-35 Pa. In this region the growth rate is uniform for undoped polysilicon. The influence of H₂ for H₂-partial pressures in the range of 10-100 Pa is small to negligible, the suppression by PH₃ is moderate. The growth rate does not depend on wafer spacing in the case of undoped polysilicon layers whereas in the case of phosphorus-doped layers the growth rate is wafer spacing dependent. With the addition of PH₃ the uniformity decreases not only in a relative sense compared to undoped layers, but also the absolute difference between edge- and center-growth rate increases, indicating that the growth of polysilicon is not a simple addition of a heterogeneous and homogeneous contribution.

Region 3: SiH₄ partial pressures above 35 Pa. The growth becomes nonuniform, the edge/center growth-rate ratio increases. The growth rate is dependent on the partial pressure of the carrier gas but also depends on the wafer spacing.
ing. H₂ addition has no influence on growth rate. The suppression of growth due to PH₃ is small to negligible.

In order to study the effect of the carrier gas on the growth rate, experiments were carried out using N₂ and He as carrier gases up to pressures of 1000 Pa (10 mbar); see Fig. 3 and 4.

**Heterogeneous surface decomposition.**—In order to explain the observations in the three regions we propose considering the following sets of reactions

\[ \text{SiH}_4 + (\ast)d \rightarrow \text{SiH}_3^+ + H^+ \quad \text{(R-1)} \]

\[ \text{SiH}_4^+ \rightarrow \text{SiH}_3^+ + H^+ \quad \text{(SiH}_4\text{H}_4 \text{H}) \quad \text{(R-1a)} \]

\[ \text{H}_2 \text{\rightarrow SiH}_4^+ + H^+ \quad \text{(SiH}_4\text{H}_4 \text{H}) \quad \text{(R-1b)} \]

\[ 2\text{SiH}^+ \rightarrow 2\text{Si} + H_2 + 2^* \quad \text{(R-2a)} \]

\[ 2^* \rightarrow H_2 + 2^* \quad \text{(R-2b)} \]

(*d) indicates a dual site, i.e., two free sites at neighboring positions. The parentheses in (SiH)_4.H indicate that the Si atom is bonded to the substrate with more than one bond and is therefore more or less immobile. There is no basic difference between (SiH)_4.H and H^+ except that in (SiH)_4.H the H^+ is bonded to the Si atom which originates from the gas-phase precursor. The exact sequence of decomposition is not known but from temperature-programmed desorption (TPD) measurements and secondary ion mass spectroscopy (SIMS), it appears that SiH_4.H and SiH^+_4 are important intermediates in the surface decomposition of SiH_4. It is known from reaction freezing experiments followed by TPD or laser induced desorption (LID) that at normal pressures Lifschitz decomposition conditions only the high temperature monohydride peak can be detected. At large coverage the release of H_2 from (SiH)_4.H and H^+ was found to be a process which is first order in H^+.x^2 due to Sill^4 and SigH^6, which suggests a low mobility of the chemisorbed hydrogen atom.

Our growth rate data in region 1 could be reasonably well described by a one-site chemisorption model using Klein's model parameters with a correction of 20% for k_2. A dual-site chemisorption model, however, has been demonstrated to give a better fit over a larger pressure range. Because we believe that dissociative chemisorption is more likely, in this paper the dual-site adsorption model is adopted to fit our growth rate data.

The surface decomposition for other silanes and silylenes, which are formed by gas-phase reactions as shown further on, is proposed to be similar to the surface decomposition of SiH_4.

The chemisorption reactions can be summarized as

\[ \text{Si}_i \text{H}_j + (\ast)d \rightarrow \text{SiH}_j(\ast)d \quad \text{(R-3a)} \]

\[ \text{(SiH}_j\text{H})^{+\ast} + (y-z-x) \rightarrow x \text{SiH}_3^+ + (y-z-x)H^+ + z/2 H_2 \quad \text{(R-3b)} \]

where (SiH_jH)^+ indicates that SiH_j occupies a site, either through dissociative adsorption, or by realizing a bond per molecule, or by shielding of neighboring sites. Shielding becomes of importance when the chemisorbed species has a much larger diameter than the substrate atom.

In the case of SiH_3, SiH_2, and SiH_j, formed due to gas-phase reactions, it has been suggested that the reactive sticking probability is high regardless of surface occupancy. It has been demonstrated for SiH_3 that it can adsorb in more than one monolayer, supporting the above assumption. It is known from gas-phase experiments that SiH_4, SiH_2, and SiH_j inserts with near unit probability in Si-H bonds in SiH_4, SiH_2, and SiH_j. A similar interaction reaction to surface Si-H bonds is likely.

The following scheme is suggested for the reaction with occupied surface

\[ \text{Si}_i \text{H}_j + H^+ \rightarrow (\text{SiH}_i\text{H}_j)^{+\ast} \quad \text{(R-4a)} \]

\[ (\text{SiH}_i\text{H}_j)^{+\ast} \rightarrow H^+ + x \text{Si} + y/2 H_2 \quad \text{(R-4b)} \]

\[ (\text{SiH}_i\text{H}_j)^{+\ast} + (\ast)s \rightarrow H^+ + (\text{SiH}_j\text{H}_i)^{+\ast} \quad \text{(R-4c)} \]

In words this means that the species adsorbed to occupied surface (R-4a) may either directly decompose (R-4b) without any interaction with surface sites or it may do so after interaction with free surface sites, R-4c, followed by R-3b. The suppression by PH_3 may be represented by the reactions

\[ \text{PH}_3 + (\ast)s \rightarrow \text{PH}_3^{+\ast} \quad \text{(R-5a)} \]

\[ \text{PH}_3^{+\ast} + 3* \rightarrow P + 3H^* \quad \text{(R-5b)} \]

The suppression of the surface reaction in region 1 by H_p, may proceed through reverse reactions like R-1b, R-2a, b, or R-3b and then through surface hopping H_p may occupy surface sites, or interact directly with free surface sites.

The overall result is represented by

\[ H_p + (\ast)s \rightarrow 2H^* \]

It is of importance to note that SiH_2, SiH_2, SiH_2, PH_3 compete with SiH_4 for the same surface sites through the reactions R-3a, b, R-4c, and R-5a, b. Therefore, even if gas-phase products adsorb independently of occupancy, they may still interact in a subsequent step with free surface sites which would normally be available to SiH_4 chemisorption.

The essence of this competition is that the deposition of Si through the various reaction paths is not a simple addition of individual growth rates. Gradually when the gas-phase reactions become of more importance they will take over the role of SiH_4 due to their higher reaction probability. This effect leads to the conclusion that even if gas-phase reactions may already be significant they do not necessarily enhance the growth rate because of a simultaneous suppression of the SiH_4 surface decomposition. It is this effect that, in our opinion, determines the kinetics in region 2. The effect can be understood from Eq. 2 and 3 and is discussed in detail in the Section on Fitting of rate constants to experiments.

The gas-phase reactions, R-6, producing SiH_3, SiH_2, SiH_2, and SiH_2 are discussed in the Section on gas-phase reactions and collision efficiency.

**The Langmuir-Hinshelwood growth rate equations.**—The contribution to the deposition of Si by chemisorption reactions R-1a, R-3a and R-4a is given by

\[ r = \sum_k x_k \text{K}_k [\text{SiH}_i\text{H}_j](\theta_0)^y + x_k \text{K}_k [\text{SiH}_j\text{H}_i](1 - \theta_0) \quad \text{(2)} \]

where k_i and k_j are the adsorption rate constants on free and occupied surface sites, respectively, of species i, where species i is of the type SiH_j. It was assumed for SiH_3 and SiH_2 that k_i = 0, for SiH_4 and SiH_2 we assumed k_i = k_j. \theta_0 is the fraction of free surface sites, and a_0 is the number of sites involved in the first step of chemisorption.

Equation 3 for the fraction of free surface sites \theta_0 can be derived by assuming that H^+ is the most abundant surface species and by assuming steady-state condition for H^+.

\[ dH^+/dt = \Sigma \text{R}_n = 0 \quad \text{where R}_n \text{stands for all the H}^+ \text{and (SiH}_4\text{H}_4) \text{producing and destroying reactions and by setting } * + H^+ = 1 \text{ we get } * = 1/(1 + H^+)^x \text{which leads to} \quad \text{(3)} \]

\[ \theta_0 = (1 + \Sigma x_k \text{K}_k [\text{SiH}_i\text{H}_j](\theta_0)^\gamma - 1)^{-1} \]

K = k/k_0, with k_0 the desorption rate constant of H_p, n is the sum of H^+ and a new (SiH^+_iH^+_j) formed during the total decomposition sequence of species i.

In \((A, H^+)\), A stands for either Si or P. In the particular case of H_p, A is no element which can be modeled by setting \( x = 0 \). For SiH_4 and SiH_2 we have set \( n = (x + 2) \) which is for SiH_4 in agreement with the reaction sequence R-1 to R-2.

Because SiH_4 and SiH_2 adsorb and decompose
The change in reciprocal growth rate $A(r)^{-1}$ was measured for $p_{\text{SiH}_4} = 5 \text{ Pa}$ and is shown in Fig. 7. The change in slope from 1 to 0.5 for increasing temperature is, in our opinion, related to the mobility of $\text{H}^*$ on the surface. Surface mobility is a thermally activated process and also dependent on the surface coverage, which generally increases with decreasing temperature. The desorption of $\text{H}_2$ from surface Si-H bonds at high coverage is a first-order process.\textsuperscript{4,43-44} We think it may become a second-order process at higher temperatures and lower surface coverage due to increasing surface mobility.\textsuperscript{49} This is in agreement with Schulze et al.\textsuperscript{49} who attribute a symmetric TPD peak at low surface coverage to a second-order desorption process with a desorption energy of 240 kJ mol$^{-1}$. At high surface coverage they find the desorption to be first order with a desorption energy of 200 kJ mol$^{-1}$. An energy change of about 160 kJ mol$^{-1}$ can be derived from the Arrhenius plot in Fig. 8 for the low temperature region where $A(r)$ is linear with $p_{\text{H}_2}$. For the poly-Si growth rate at very low surface coverage given by

$$r_{0.5} = k_{1}[\text{SiH}_4]$$

activation energies in the range of 30–80 kJ mol$^{-1}$ have been reported.\textsuperscript{4,5,23,27,30-32} Using this range the enthalpy change for $\text{H}_2$ chemisorption on a $\text{H}^*$ covered Si surface can then be calculated to be in the range from 160 to 190 kJ mol$^{-1}$. This is in agreement with $\Delta H$ values reported in the literature ranging from 150 to 200 kJ mol$^{-1}$.\textsuperscript{43-45} Adopting the value of 190 kJ mol$^{-1}$ for desorption of H$_2$ from a “Si-$\text{H}^*$” surface,\textsuperscript{43,44} we calculated the barrier to chemisorption of H$_2$ to be in the range from 5 to 35 kJ mol$^{-1}$, which is in agreement with the 18 kJ mol$^{-1}$ reported by Raifi et al.\textsuperscript{50} The barrier for the H$_2$ insertion reaction with SiH$_4$ is also reported to fall within this range.\textsuperscript{28,34,37,46}

The reduction of growth due to H$_2$ has also been reported by Claassen et al.\textsuperscript{36} and by Hottier et al.\textsuperscript{51} Hottier also reports a first-order influence of H$_2$ at low temperature and a one-half order at high temperature.

Based on the calculations by Giling\textsuperscript{29} one would also expect a substantial effect of H$_2$ on our experimental conditions. Others found no influence of H$_2$.\textsuperscript{5,37,46} Those who reported no H$_2$ influence have either carried out their experiments in region 2, where we also measured no influence, or the amount of added H$_2$ was too small so that the effect was within experimental error. We think that the absence of H$_2$ effects in region 2 and 3 was due to the fact that the surface is too close to H$_2$ saturation. Liehr\textsuperscript{5} reported that H$_2$ adsorbs only slightly to Si, even at high

$$\Delta(r)^{-1} = 2k_{30}[\text{H}_2]/k_1k_{1,4}[\text{SiH}_4]$$

where $k_{1,4} = k_1 + k_2 + k_3 + k_4$. The change in slope from 1 to 0.5 for increasing temperature is, in our opinion, related to the mobility of H$^*$ on the surface. Surface mobility is a thermally activated process and also dependent on the surface coverage, which generally increases with decreasing temperature. The desorption of H$_2$ from surface Si-H bonds at high coverage is a first-order process.\textsuperscript{4,43-44} We think it may become a second-order process at higher temperatures and lower surface coverage due to increasing surface mobility.\textsuperscript{49} This is in agreement with Schulze et al.\textsuperscript{49} who attribute a symmetric TPD peak at low surface coverage to a second-order desorption process with a desorption energy of 240 kJ mol$^{-1}$. At high surface coverage they find the desorption to be first order with a desorption energy of 200 kJ mol$^{-1}$. An energy change of about 160 kJ mol$^{-1}$ can be derived from the Arrhenius plot in Fig. 8 for the low temperature region where $A(r)$ is linear with $p_{\text{H}_2}$. For the poly-Si growth rate at very low surface coverage given by

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temperatures. The difference between Liehr's experiment and ours is that Liehr's experiments were performed on a clean Si surface whereas ours were performed on a H* covered surface. A lower barrier for H$_2$ chemisorption to a H* covered surface may explain the difference. The lower barrier reported for H$_2$ reaction with SiH$_4$ compared to a bare Si atom is indicative.

In summary our conclusions at the end of this section are:

In region 1 growth is moderately suppressed by H$_2$. Seemingly contradicting literature results on this topic are explained in terms of surface coverage.

Gas-phase reactions and collision efficiency.—Gas-phase reactions become important at higher SiH$_4$ pressures.

The unimolecular reaction R-6 proceeds through SiH$_4$-M collisional excitation, where M may be any gas-phase molecule, including SiH$_4$ itself.

\[
\text{SiH}_4 \leftrightarrow \text{SiH}_3 + \text{H} + \text{SiH}_4 \quad \text{[R-6]}
\]

Disilane, trisilane, and higher silanes are formed through insertion reactions of silylene with gas-phase silanes.

In our further discussion only SiH$_3$, Si$_2$H$_6$, and Si$_3$H$_8$ formation is taken into account because these are, besides SiH$_4$, the most abundant Si containing gas-phase species. Other reaction paths proposed by Coltrin et al.,

including higher silanes and silylenes, are now ignored, because any other path than the ones mentioned is controlled by the silylene formation in reaction R-6. Transport to the surface of silylene using higher silanes as an intermediate do not basically change the growth rate contribution along the homogeneous path.

In order to study the gas-phase reactions we have varied the total pressure and the partial pressure of SiH$_4$. The undepleted growth rates were derived in the manner presented in Fig. 2, 3, and 4. Fig. 9 (pure SiH$_4$), Fig. 10 (N$_2$ carrier), and Fig. 11 (He carrier).

A considerable effect of wafer spacing on the growth rate is observed, indicating the homogeneous gas-phase formation of reactive species. The unimolecular decomposition of SiH$_4$ in the pressure range we have studied is, according to RRKM analyses, in the low pressure limit regime, where the growth is dominated by the bimolecular reaction

\[
\text{SiH}_4 + M \xrightarrow{k_6} \text{SiH}_3 + M
\]

where M can be any gas-phase molecule including SiH$_4$ itself. The subsequent decomposition of the energized SiH$_3$ is given by

\[
\text{SiH}_3 \xrightarrow{k} \text{SiH}_2 + \text{H}_2
\]

where SiH$_3$ is the activated complex. In the low pressure limit the basic equation for the decomposition rate constant is given by

\[
k_0 = \lambda Z \frac{Q}{Q_0} \frac{p_{\text{tot}}}{RT} \exp \left( -\frac{E_0}{RT} \right)
\]

Where Z is the collision number given by

\[
Z = N_s \sigma_{\text{SiH}_4} \langle 8\pi RT/M_m \rangle^{1/2} \Theta^{1/2}
\]

\[
\text{He carrier gas}
\]

\[
\text{N}_2 \text{ carrier gas}
\]

\[
\text{SiH}_4 \quad \text{1000 Pa}
\]

\[
\text{SiH}_4 \quad \text{1000 Pa}
\]

\[
\text{SiH}_4 \quad \text{500 Pa}
\]

\[
\text{SiH}_4 \quad \text{500 Pa}
\]

\[
\text{SiH}_4 \quad \text{50 Pa}
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Table I. Lennard-Jones collision parameters.

<table>
<thead>
<tr>
<th>M</th>
<th>Mol. weight (g/mol)</th>
<th>( \sigma ) (nm)</th>
<th>( \sigma_{\text{SiH}_4} ) (nm)</th>
<th>( M_{\text{red}} ) (kg/mol)</th>
<th>( Q^* )</th>
<th>( Z_{\text{SiH}_4, M} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4</td>
<td>0.255</td>
<td>0.532</td>
<td>3.55E-3</td>
<td>0.73</td>
<td>3.54E8</td>
</tr>
<tr>
<td>N(_2)</td>
<td>28</td>
<td>0.397</td>
<td>0.403</td>
<td>14.96E-3</td>
<td>0.87</td>
<td>3.04E8</td>
</tr>
<tr>
<td>SiH(_4)</td>
<td>32, 12</td>
<td>0.408</td>
<td>0.408</td>
<td>22.71E-3</td>
<td>0.97</td>
<td>2.81E8</td>
</tr>
</tbody>
</table>

\( N_a \) is Avogadro’s number, \( \sigma_{\text{SiH}_4, M} \) is an effective collision diameter, and \( M_{\text{red}} \) is the reduced mass given by

\[
M_{\text{red}} = \frac{M_{\text{SiH}_4} M_{\text{M}}}{M_{\text{SiH}_4} + M_{\text{M}}} \quad [8]
\]

\( Q^* \) is the partition function of the activated complex using the ground state of SiH\(_4\) for the zero of energy. \( Q \) is the partition function for the active degrees of freedom of the reactant SiH\(_4\), \( k \) is the collision efficiency, \( E_z \) is the minimum energy required for decomposition.

In order to compare \( k \) for different combinations we calculated the collision number for the various combinations. The approach proposed by Troe et al.\(^{60}\) for the Lennard-Jones collision correction, \( Q^* \), was used, see Table I.

In the case of a SiH\(_4\)-M mixture we can model the rate constant for gas-phase decomposition as

\[
k = \sum_{M} k_i[M_i] \quad [13]
\]

For those cases where \( \lambda Z \) depends on \( M \), the total pressure \( P_{\text{tot}} \) in Eq. 9 is replaced by

\[
p_{\text{tot}} = p_{\text{SiH}_4} + \sum\lambda \rho_{M_i} \quad [14]
\]

where

\[
\lambda' = \lambda Z_{\text{SiH}_4, M}/Z_{\text{SiH}_4, \text{SiH}_4} \quad [15]
\]

It can be concluded from Fig. 9, 10, and 11 for the gas-phase contribution to the total growth rate that \( k_{\text{SiH}_4, \text{SiH}_4} < k_{\text{SiH}_4, \text{SiH}_2} < k_{\text{SiH}_4, \text{M}} \). Since the collision number for He-SiH\(_4\) is larger than for N\(_2\)-SiH\(_4\) and SiH\(_2\)-SiH\(_4\), the lower gas-phase contribution to the total growth rate has to be attributed to a lower collision energy transfer efficiency of He with SiH\(_4\).

The lower efficiency found for He in this work agrees with results in other works where He was shown to be one of the weaker colliders in unimolecular reactions.\(^{41}\)

Conclusions of this section are:

- In region 3 the growth is dominated by gas-phase reactions.
- The growth rate results can be explained by SiH\(_4\)-M collisions where M may be any gas molecule including SiH\(_4\) itself.
- The collision efficiency of He in the gas-phase reaction is lower than that of SiH\(_4\) and N\(_2\).

**Fitting of rate constants to experiments.**—In order to calculate rate constants from our experimental results we adopted a few rate constants from the literature and present the values for \( T = 898 \) K and a total pressure of 100 Pa assuming \( \lambda' = 1 \), see Table II. The constants that were fitted to the experiments are summarized in Table III.

The reactive sticking coefficient of SiH\(_4\) at zero coverage, \( \gamma_{\text{SSiH}_4, \text{SiH}_4} \), was fitted to the low pressure side of region 1 where it is most sensitive to it. The value is in good agreement with those reported by Kleijn \((6e-4)\), Gates \((2-5e-4)\),\(^{15}\) and Buss \((1e-3)\).\(^{46}\)

\( k_6 \) was fitted to the medium and high pressure side of region 1 which is insensitive to \( k_6 \) and \( \gamma_{\text{SSiH}_4, \text{SiH}_4} \) was fitted in region 1 where it is most significant. The effect of temperature on H\(_2\) suppression of growth rate has already been discussed above. \( k_{\text{SiH}_4} \) is very high and would correspond to an unrealistic reactive sticking coefficient of 2. However, qualitatively the high value agrees with 0.6 reported by Yu et al.\(^{11}\) Our assumption that the SiH\(_4\), H\(_2\) chemisorption on phosphorus sites is similar to chemisorption on silicon sites is possibly too much of a simplification. Also the adsorption and desorption reactions suggested in R-5 may be too simplified. No attempts were made in this paper to improve the model for PH\(_3\) chemisorption. \( c \) and \( \gamma_{\text{SSiH}_4} \) are most significant in region 2. A value for \( c \ll 1 \) seems reasonable since the activation energy for surface hopping is much lower than for direct desorption.\(^{45}\) The value for \( n \) is realistic because it means that nearly all H atoms in SiH\(_4\) leave the surface as H\(_2\) through H*. Also the low value for \( c \) indicates that the reaction path \( R-4b \) is negligible.

Region 3 is governed by \( k_{\text{SiH}_4} \) and the collision efficiencies. The rate constants adopted in Table II also determine the fitting of these parameters. Modification of the rate constants in Table II may change the relative contributions of SiH\(_3\), SiH\(_2\), and SiH\(_4\). In extreme cases \( k_{\text{SiH}_4} \) for \( P_{\text{tot}} = 100 \) Pa may vary from 4.6e-1, i.e., if all gas-phase products deposit as SiH\(_3\), to 2.3e-1 if all products deposit as SiH\(_2\). The value for \( k_{\text{SiH}_4} \), which fits to our experiments is in good qualitative agreement with values found by Jeckel et al.\(^{18}\) They reported values in the range of 5.6e-1 to 7.3e-1 s\(^{-1}\) for 100 Pa total pressure by fitting \( k_{\text{SiH}_4} \) to the experimentally found edge nonuniformity. If we calculate \( k_{\text{SiH}_4} \) from \( k_6 \) using Jasinsky’s and Inoue’s values\(^{45,46}\) and thermochemistry,\(^{13}\) we obtain 5.2e-1 using Jasinsky’s value and 2.9e-1 using Inoue’s value. These calculated values are also in good agreement with this work. A big disagreement is found with respect to RRKM analyses by Roenigk et al. \((8.7e-3 \text{ at } 100 \text{ Pa})\)\(^{22}\) and Meyerson et al. \((4.3e-3 \text{ at } 100 \text{ Pa})\).\(^{21}\)

The low efficiency for He is typical for this element\(^{41}\) but was not confirmed by Jasinsky’s\(^{49}\) room-temperature measurement. Moffat’s RRKM analyses\(^{25}\) show no He influence for their best fit but with a slight modification of the assumptions they demonstrate that the RRKM analysis can predict a considerable lower efficiency for He.

Using the rate constants in Tables II and III, we calculated the growth rates and these are presented as solid lines in Fig. 5, 9, 10, 11, and 12. In Fig. 12 the calculated individual contributions to the growth rate of SiH\(_3\), SiH\(_2\), and SiH\(_4\) are presented. The suppression of the SiH\(_4\) contribution by higher silanes is clearly demonstrated in Fig. 12.

**Table II. Kinetic parameters obtained from the literature.**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value at 898 K and 100 Pa total pressure</th>
<th>Remarks</th>
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</table>
| \( k_{1,2,3,4} \) | 5.5 m s\(^{-1}\) | Adsorption rate constants were calculated using \( k_{1,2,3,4} = \frac{1}{\lambda} \frac{c}{\rho_{\text{SiH}_4}} \gamma_{\text{SSiH}_4, \text{SiH}_4} \) with \( c = 4 - 2 \) \[Ref. 4, 46]\).
| \( k_{2,3,4} \) | 199 m s\(^{-1}\) | \( \gamma_{\text{SiH}_4, \text{SiH}_4} = 1 \), see text. |
| \( k_{3,4} \) | 119 m s\(^{-1}\) | Calculated from \( k_4 \) using thermochemistry calculations by Kleijn.\(^{15}\) |
| \( k_{4,5} \) | 7.8e2 s\(^{-1}\) | Calculated from room temperature measurements by Jasinsky et al.\(^{13}\) assuming \( E_z = 0 \) and \( k_5 \) is proportional to \( T^4 \) and the order in total pressure 1 for SiH\(_4\) and 0.5 for SiH\(_2\) and SiH\(_3\).\(^{23}\) |
| \( k_{4,5} \) | 5.5e2 s\(^{-1}\) | |
| \( k_{4,5} \) | 1e5 m\(^3\)/mol s | |
| \( k_{4,5} \) | 1.2e8 m\(^3\)/mol s | |
The fits to Fig. 10 and Fig. 11 could be improved if we assume the effective total pressure as $p_{\text{eff}} = (1 + \alpha)p_{\text{H}_{2}} + (p_{\text{tot}} - p_{\text{H}_{2}})\lambda$. The physical interpretation of the fitting parameter $\alpha$ would be that other reaction paths independent of the total pressure exist, e.g., $\text{SiH}_{4}-\text{SiH}_{2}$ collisions directly leading to reactive products like, e.g., $\text{SiH}_{4}$ or $\text{SiH}_{2}$.

**Conclusions**

The growth rate of polysilicon at LPCVD conditions can be modeled by contributions of heterogeneous and homogeneous decomposition reactions.

At low pressures where the contribution by the homogeneous gas-phase reaction is negligible the growth rate is suppressed by $\text{H}_{2}$ and strongly suppressed by $\text{PH}_{3}$. At higher pressures the contribution by $\text{SiH}_{4}$ is also suppressed by reactive products formed due to gas-phase reactions such as $\text{SiH}_{2}$ and $\text{SiH}_{6}$.

The heterogeneous decomposition of $\text{SiH}_{4}$ can be described by only two rate constants, namely, the adsorption rate constant of $\text{SiH}_{2}$ and the desorption rate constant of $\text{H}_{2}$.

Many reaction parameters can be used to fit the experimental results but by adopting independently achieved constants from the literature, the number of parameters to be fitted can be kept to a minimum.

The gas-phase decomposition reaction $\text{SiH}_{4} \rightarrow \text{SiH}_{2} + \text{H}_{2}$ has a much higher rate constant than was obtained from RRKM analyses.

The collision efficiency of $\text{He}$ in gas-phase reactions is lower than the collision efficiency of $\text{N}_{2}$ and $\text{SiH}_{4}$.

Kinetic parameters have been extracted which enable us to predict the total growth rate for a wide range of pressure conditions, carrier gases, dopants, and loadings.

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Electrochemical Detection of Defects in Ge/GaAs Structures
by an Anodic Dissolution Method under Illumination

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ABSTRACT

Detection of crystal defects in Ge/GaAs structure has been studied by an electrochemical etching under illumination. Germanium film grown by the plasma-assisted epitaxy method with hydrogen on a semi-insulating GaAs substrate is anodically dissolved in a NaOH solution. Hillocks connected with the structural defect are then detected and their densities are estimated. Results obtained suggest that the defects in the Ge film originate from plasma ion bombardment, related to those in the GaAs substrate.

Semiconductor crystalline films with heterostructure have been recently made by several different epitaxial growth methods. Detection of crystal defects in such films is very important and particularly necessary for the characterization of the film used in optoelectronic devices. For bulk semiconductor material, chemical etching is one of the most convenient techniques available for the detection. However, for films with a thickness less than 1 μm, the conventional chemical etching method cannot be used because of high etching rates.

Yamamoto et al. have reported an electrochemical etching method in which the surface of n-type GaAs and InP is anodically dissolved under illumination and crystal defects are detected as etch hillocks. The hillock formation results from decreases in the dissolution rate of the surface under which defects are located because of rapid recombination of holes. Etched depth in this case is less than 1 μm.

The purpose of this paper is to present results concerning crystal defects of an epitaxially grown germanium film and its substrate.

In connection with our study of low temperature epitaxial film growth technology, we formed epitaxially Ge films on GaAs using a hydrogen plasma sustained by radio frequency (RF) excitation and detected the crystal defects of the film and the GaAs substrate, using the above-mentioned etching method. To obtain additional data, defects of Ge wafers were investigated in the same way as stated above.

Experimental

The sample holder and the apparatus used for anodic dissolution of Ge and GaAs are schematically illustrated in Fig. 1a and b, respectively.

The electrolyte used here was an NaOH solution with the concentration of 1 mol/liter at room temperature. The sample holder was an L-shaped glass tube used to illuminate the sample surface from its normal direction. As seen from the figure, a sample was fixed on the cross section of the tube, and the sample edge was covered carefully by an electronic grade wax, picene, to limit current flow to only the