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Modeling of Low-Pressure CVD Processes

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ABSTRACT

The spread in layer thickness within a series of wafers simultaneously covered in an LPCVD process will, in general, have two distinct causes. First, a spread across a wafer may occur if the deposition process is carried out in a diffusion controlled growth regime. Second, a gradual depletion in the flow direction may cause a spread within the length of the boat carrying the wafers. The latter phenomenon can be approximated with a mathematical model. This approach reveals that the thickness spread within a batch will be acceptably small if the gas flow velocity exceeds a certain value, determined by the batch and wafer size, and also by the apparent order of the kinetics of the LPCVD process.

The ability to grow uniform films on a large number of substrates in a single run is making the technique of low pressure CVD increasingly more popular in IC technology. In the field of microelectronics silicon nitride, silicon oxide, and polysilicon layers with thickness variations of less than, typically, 5% for batches of over one hundred wafers of 100 mm diam are now commonly grown in LPCVD reactors. The total thickness spread in a batch will be the result of two factors; the variation of the layer thickness across one wafer and, as a consequence of their different positions in the reactor, the differences between the mean film thicknesses on each wafer.

A uniform coverage of a wafer can be achieved by choosing process conditions such that, near the substrate, the diffusion process by which the reactive compounds are transported to the growth surface proceeds much faster than the material consumption by the actual growth reaction. In this case, the deposition process is surface controlled. It has been demonstrated (1) that the state of first-order process is then characterized by very small values of the Sherwood number

$$\mathrm{Sh} = kd/D$$

where k is the mass transfer coefficient of the reaction, d a relevant length of the order of the wafer spacing, and D the diffusion coefficient of the reactive species in the low pressure ambient. When $\mathrm{Sh} >> 1$, the deposition process is diffusion limited, whereas for $\mathrm{Sh} << 1$ the growth rate is determined by the surface reaction. The gain achieved by reducing the pressure in a CVD reactor from 1 atm to a few tenths of a Torr results from the corresponding increase of the diffusion coefficient by three orders of magnitude (see Fig. 1). As a consequence, gas phase diffusion ceases to be rate determining for most reaction systems, and hence local variations in the gas phase concentration due to the geometry in the reactor will be negligibly small. Under these circumstances the growth rate is governed by the surface reaction, and homogeneously heated substrates (even irregularly shaped objects) will be uniformly covered.

A sufficiently small Sh number, however, in general will not guarantee that all wafers in a batch will be covered with a layer of the same thickness. A gradual depletion of the gas phase in the flow direction will often cause a tapered thickness profile over the batch. In this paper attention is focused on a quantitative understanding of this effect in order to minimize the overall thickness spread obtained in LPCVD.

Experimental and Results

The low pressure CVD of polysilicon from silane was selected as a vehicle for the present investigation. The reactor was a commercially available type, viz., an LPCVD I reactor from Applied Materials Incorporated, fitted with a Roots blower. The experimental conditions have been described in detail previously (1). It should be noted that a flat temperature profile was created in the reactor, such that the temperature over the length of the boat was constant at 625°C to within 1°C.

Key words: polysilicon, kinetics, thickness spread.

Figure 2 shows typical variations in the observed growth rate with the wafer position, with the input concentration of silane as parameter. At low input concentrations a strong depletion is found, which gradually diminishes with increasing partial silane pressures. The growth rate profiles tend to flatten, until the silane gas phase concentration near the front end becomes so high that homogeneous gas phase reactions lead to an increased deposition on the first wafers. This effect is accompanied by a nonuniform deposition on the wafers, as has been established in a previous study (1). For the present investigation the experimental conditions were chosen such that this phenomenon could not occur. Figure 2 also shows a retarded growth rate at the first five wafers, which is attributed to the fact that the gas at this position is not yet completely at reactor temperature. To compensate for this effect we have used estimated values of $G(O)$ (the growth rate at the first wafer) by extrapolating the growth rate profiles to $z = 0$.

Since the LPCVD reactor used was equipped with a Roots blower whose pumping speed could be adjusted, it was possible to perform growth experiments at different gas flows but at the same reactor pressure. It appears that the gas flow also plays an important role in the process, as is demonstrated in Fig. 3. In this figure extrapolated $G(O)$-values are plotted *vs.* the gas flow, for various partial silane input pressures. This

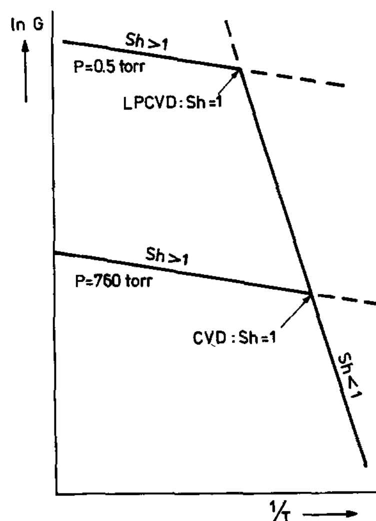


Fig. 1. General growth rate curve of a CVD process. The situation shown is for a process operating at atmospheric and at reduced pressures.

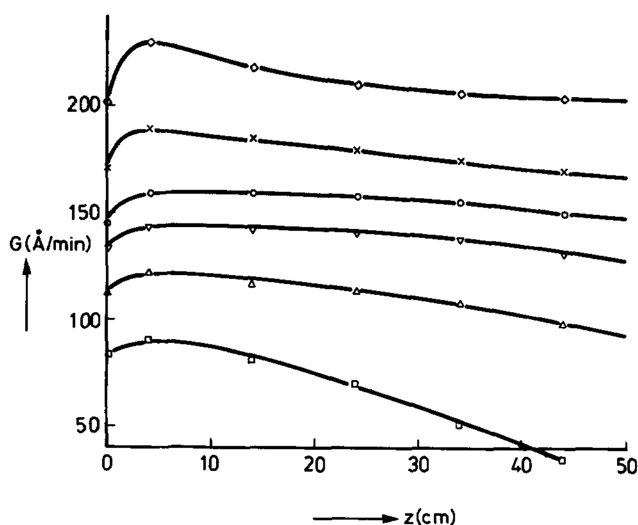


Fig. 2. Measured growth rate profiles of polysilicon for various silane/nitrogen input ratios. The total gas flow is 400 cm³/min (STP), the pressure in the reactor is 0.5 Torr. Wafer spacing is 1 cm. p_{SiH_4} = 200(◇), 150(×), 100(○), 75(▽), 50(△), and 25 mTorr(□).

shows that a minimum gas flow is required to ensure that at $z = 0$ the adjusted input concentration can be maintained. It will be clear that in our case unambiguous conclusions may be drawn only when gas flows of at least 400 cm³/min are applied.

To describe the influence of the depletion of the gas phase on the growth rate profile, as shown in Fig. 2, it is necessary to understand the kinetics of the deposition process. To this end extrapolated G(O) values, obtained at various silane input pressures and gas flows, have been collected in Fig. 4. We achieved the best fit for the points in Fig. 4 (solid curve) applying a relation of the kind

$$F(p) = \frac{A\, p_{SiH_4}{}^{1/2}}{1 + B\, p_{SiH_4}{}^{1/2}} \quad [1]$$

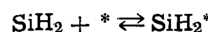
This can be understood from a simple model of the deposition of (poly)silicon. Following the approach of Claassen *et al.* (2), the following reactions are considered:

1. Dissociation of SiH_4 in the gas phase

$$SiH_4 \rightleftarrows SiH_2 + H_2$$

having equilibrium constant K_1.

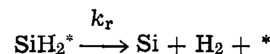
2. Adsorption of SiH_2



$$SiH_2 + * \rightleftarrows SiH_2{}^*$$

with equilibrium constant K_2. The asterisks denote a free surface site.

3. Reaction of $SiH_2{}^*$ to produce a lattice Si-atom



$$SiH_2{}^* \xrightarrow{k_r} Si + H_2 + *$$

where k_r is the reaction rate constant.

The reaction rate of 3 can now be written as

$$v_r = k_r \cdot [SiH_2{}^*] = k_r \cdot K_2 \cdot [*] \cdot p_{SiH_2} \quad [2]$$

and [*] can be estimated using

$$[*] = 1 - [SiH_2{}^*] = 1 - K_2[*]\, p_{SiH_2} \quad [3]$$

To express p_{SiH_2} in the input partial pressure p_{SiH_4} we introduce the degree of dissociation of the gaseous SiH_4, therefore $p_{SiH_2} = \alpha p_{SiH_4}$, which upon insertion in 3 yields

$$[*] = \frac{1}{1 + K_2\, \alpha p_{SiH_4}} \quad [4]$$

and with Eq. [2] we obtain

$$v_r = \frac{k_r K_2\, \alpha p_{SiH_4}}{1 + K_2\, \alpha p_{SiH_4}} \quad [5]$$

α can be expressed in K_1 using

$$K_1 = \alpha^2 p_{SiH_4}/(1 - \alpha) \quad [6]$$

which for small values of α (p_{SiH_4} not too small) reduces to $\alpha \simeq (K_1/p_{SiH_4})^{1/2}$. The reaction rate [5] thus becomes

$$v_2 = \frac{k_r K_2 K_1{}^{1/2}\, p_{SiH_4}{}^{1/2}}{1 + K_2 K_1{}^{1/2}\, p_{SiH_4}{}^{1/2}} \quad [7]$$

which corresponds to the observed growth kinetics as expressed in Eq. [1].

It is remarked that when hydrogen is used as carrier gas expression [6] should read

$$K_1 = \frac{\alpha p_{SiH_4} \cdot p_{H_2}}{(1 - \alpha) p_{SiH_4}} \quad [8]$$

hence

$$v_2 = \frac{k_1 K_1 K_2\, p_{SiH_4}}{K_1 + p_{H_2} + K_1 K_2\, p_{SiH_4}} \quad [9]$$

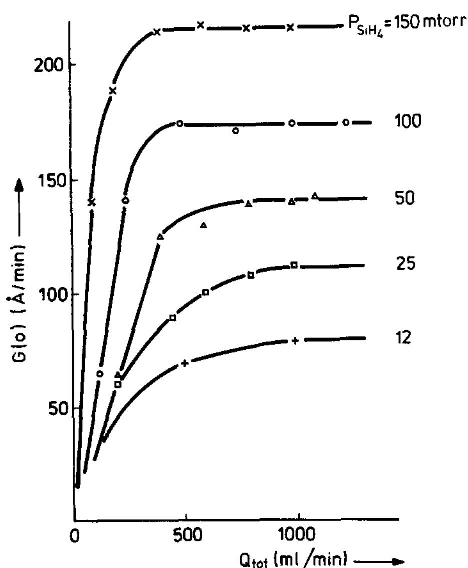


Fig. 3. Growth rate at the first wafer (extrapolated) as a function of the gas flow for different silane/nitrogen input ratios; the pressure is 0.5 Torr.

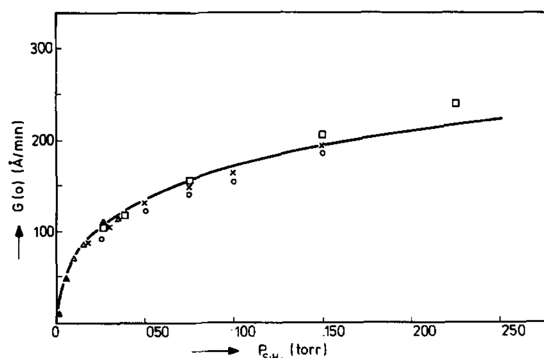


Fig. 4. Growth rate at the first wafer (extrapolated) as a function of silane partial pressure, obtained at various gas flows and input ratios (□: p = 0.75 Torr, Q = 1000 cm³/min. ×: p = 0.50 Torr, Q = 1000 cm³/min. ○: p = 0.50 Torr, Q = 400 cm³/min. △: p = 0.10 Torr, Q = 400 cm³/min. ▲: p = 0.50 Torr, Q = 1000 cm³/min.

Figure 4 shows that at silane input pressures of 0.2 Torr and higher relation [7] ceases to match the experimental results. As mentioned before, Van den

Brekel and Bollen (1) have proved that at such high input concentrations gas phase nucleation occurs, leading to an increased deposition rate at the first wafers and to a different set of reactions.

The measured kinetics of the growth process can now explain the differing shapes of the growth rate profiles, as in Fig. 2. At low input concentrations the system is much more sensitive to depletion than at higher inputs of reactive species $dg_1/dp_1 > dg_2/dp_2$ for $p_1 < p_2$. This is shown in a slightly different manner in Fig. 5, where the growth rate, relative to the growth rate at the first wafer ($z = 0$), is plotted as a function of the longitudinal position in the reactor: compare curve □ with curve x.

The growth rate profile is also dependent on the gas flow, as is demonstrated by the upper three curves in Fig. 5, obtained at equal input concentrations of silane. The decrease of the growth rate with z is seen to diminish with increasing gas flow velocity. This influence can be understood on the basis of the dimensionless number, the so-called Péclet number

$$\text{Pe} = vd/D$$

where v is the flow velocity. It will be appreciated that the gas phase concentration will be nearly constant along the length of the reactor if, even at the last wafer, the supply of the reactive compound via the gas flow is large compared with the consumption taking place at all reactive surfaces.

For a better understanding of the process a mathematical model has been developed in order to calculate the reactive species concentration and the growth rate as a function of z.

Mathematical Model

We will discuss now a simple mathematical model that describes the growth rate profiles for various experimental conditions. In the model, see Fig. 6, it is assumed that the gas flow is parallel to the axis of the reactor, that it has a constant velocity v in the flow region ($b < r < a$, where a = reactor radius and b = wafer radius), and that its velocity is equal to zero between the wafers. This assumption is justified under the conditions normally present in LPCVD reactors, as has been discussed (1). In the stationary situation that we are considering here the reactive gas concentration C (relative to an equilibrium value) must satisfy a convection-diffusion equation

$$\Delta C - \frac{v}{D}\frac{\partial C}{\partial z} = 0, \quad b < r < a \qquad [10a]$$

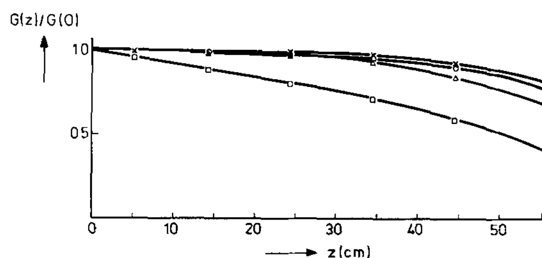


Fig. 5. Normalized growth rates as a function of z, measured at different values of Pe and P_t. These values have been estimated using $D = 0.1\ (T/300)^2 \cdot 760/p$ cm²/sec. From Fig. 4 a value for k of the order of 1 cm/sec is derived, when G(0) is expressed in at/sec/cm².

	p_t (Torr)	p_{SiH_4} (Torr)	v(cm/sec)	D(cm²sec⁻¹)	Pe
×:	0.1	0.03	1700	6850	0.25
○:	0.5	0.03	850	1370	0.62
△:	0.5	0.03	350	1370	0.25
□:	0.1	0.005	1700	6850	0.25

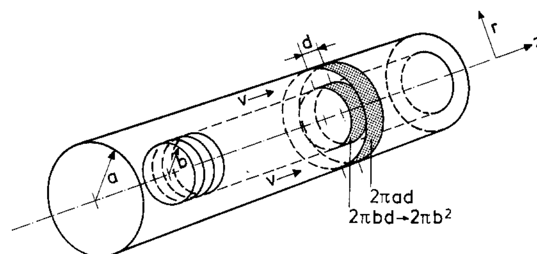


Fig. 6. Schematic view of the LPCVD reactor. V is the gas flow velocity, a the radius of the tube, b the wafer radius, and d the slice stacking distance.

where

$$\Delta \equiv \frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}$$

is the Laplace operator in cylindrical coordinates and D the diffusion coefficient of the reactive species. For $0 < r < b$ the convective term in [10a] drops out and then we have for C Laplace's equation

$$\partial C = 0 \qquad [10b]$$

At the reactor wall and at the wafer surfaces the boundary condition is

$$D\frac{\partial C}{\partial n} = F(C) \qquad [11]$$

Here it is understood that $\partial/\partial n$ represents the derivative along the normal vector in the direction of the interior of the reactor, F is an expression for the growth rate with property $F(0) = 0$.

An analytical solution of the problem can be obtained when $F(C)$ is linear in C, implying first order kinetics (3). However, for the deposition reaction of polysilicon this appears not to be the case (see Eq. [1]). We therefore direct attention to Eq. [10a] and [10b] and try to determine a simplified solution. Since the process is in the reaction limited mode, one may assume that the concentration in the gas phase will hardly vary along the radial direction. We now define

$$u(z) = 2\,\frac{\int_b^a r\,C(r,z)\,dr}{a^2 - b^2} \qquad [12]$$

From Eq. [10a] we then derive a differential equation for u

$$\frac{d^2u}{dz^2} - \frac{v}{D}\frac{du}{dz} + \frac{z}{a^2 - b^2}\left[a\frac{\partial C}{\partial r}\bigg|_{r=a} - b\frac{\partial C}{\partial r}\bigg|_{r=b}\right] = 0 \qquad [13]$$

By application of Gauss' theorem to Eq. [10b] we find, to a first approximation

$$D\frac{\partial C}{\partial r}\bigg|_{r=b} = \frac{2\pi b^2}{2\pi bd} F(C(b,z)) \qquad [14]$$

For reaction-controlled conditions we may further assume approximately

$$C(a,z) = C(b,z) = u(z) \qquad [15]$$

By writing $\zeta = z/d$, and realizing that $w = uC_0$, where $C_0 = u(0)$, we finally arrive at the following differential equation for w

$$\frac{d^2w}{\partial\zeta^2} - \text{Pe}\frac{dw}{d\zeta} - z\frac{d}{D}\,\frac{ad + b^2}{a^2 - b^2}\,\frac{F(C_0)\,F(wC_0)}{C_0\,F(C_0)} = 0 \qquad [16]$$

We have computed solutions of Eq. [16] numerically for various values of Pe and C_0. The relative growth rates $(G(z)/G(O))$ obtained from this have been plotted in Fig. 7. By introducing a new independent variable η, defined by

$$\eta = p\zeta \qquad [17]$$

where p is a constant, Eq. [16] is converted into

$$p^2 \frac{d^2w}{d\eta^2} - p\,\mathrm{Pe}\,\frac{dw}{d\eta} - Q\,\frac{F(wC_0)}{F(C_0)} = 0 \qquad [18]$$

where

$$Q = 2\,\frac{d}{D}\,\frac{ad + b^2}{a^2 - b^2}\,\frac{F(C_0)}{C_0}$$

The scale factor p is now chosen such that $p = Q/\mathrm{Pe}$. It is known (4) that for small p the first term of Eq. [18] vanishes except for the very end of the reactor tube, which means that Eq. [18] may be simplified to

$$\frac{dw}{d\eta} + \frac{F(wC_0)}{F(C_0)} = 0 \qquad [19]$$

This result shows that w, apart from C_0, only depends on p, which means that the diffusivity does not play any role in w. This was experimentally verified by the two upper curves in Fig. 5.

A further examination of Eq. [16] reveals that there exists a unique solution $w(\zeta)$ with $w(0) = 1$ that strictly decreases for $0 < \zeta < \zeta_0$ (gradual depletion), whereas $w(\zeta) \equiv 0$ for $\zeta \geq \zeta_0$ (full depletion).

Discussion

The growth rate profiles as calculated for different values of Pe, D, and p_{SiH_4} show that the spread in layer thickness within a batch reduces with increasing Pe and p_{SiH_4}. The relatively small gradients that are caused by the depletion of the gas phase can therefore be neutralized easily by increasing the flow velocity. If the capacity of the vacuum pump does not allow an increase in the gas flow, the effect of a small depletion may, in practice, readily be neutralized by creating a proper temperature gradient in the LPCVD reactor.

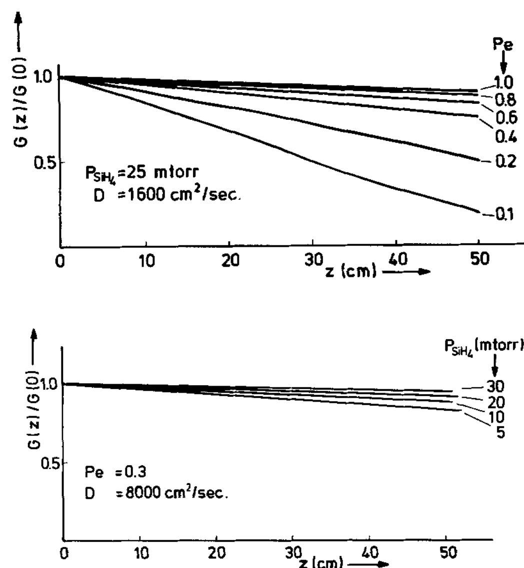


Fig. 7. Calculated relative growth rates for various values of Pe and p_{SiH_4}. Total pressure is 0.43 Torr for (a, top) and 0.09 Torr for (b, bottom).

Comparison of Fig. 5 and 7 reveals that there is a fair agreement between measurements and simulations. Measured and computed growth rate profiles corresponding to comparable degrees of depletion at $z = 50$ are found to have virtually the same combination of Pe and p_{SiH_4}.

The results show that high flow rates favor uniform growth rate profiles, the effect is more effective the higher p_{SiH_4} is. This can be appreciated from the decreasing apparent order of the reaction for higher input values, as shown in Fig. 4. This is also expressed by the simultaneous occurrence of both the gas flow velocity and the input concentration in the denominator of the factor p.

It should be noted that the calculated curves for very low input values deviate from the measured curves. This is due to the use of Eq. [1], which is less valid in the low input range, where the approximation with regard to α is no longer justified. In practice it was found that the order of the surface reaction shifts to unity for small input values, while the employed mathematical relation, Eq. [1], then counts with a half order. Charlier (3), who solved the problem for first-order kinetics, showed that in that case the shape of the growth rate profiles is no longer convex (as in Fig. 5), but concave, with the larger part of the depletion taking place in the first half of the reactor. This explains why the last part of the experimental curves for small input values, where the local concentration is decreased so far that the reaction approximates first order, shows a strong discrepancy with the calculated value, because the depletion is underestimated in that case.

The measured profiles (Fig. 5) have a slightly different shape compared to the calculated ones. For $z > 35$ cm the actual growth rate appears to be somewhat smaller than in the computed profiles. This effect is attributed to the abruptly changing flow conditions at the end of the row of slices. This was demonstrated by experiments where a long and a short row of wafers were coated, (boat filled up to $z = 75$ and 25 cm, respectively) all other conditions being kept constant. The growth rate at position $z = 25$ cm, was found to be 10-15% higher for the large batch. For the calculations an infinitely long tube and row of wafers is assumed. Consequently this effect is not taken into account in the model.

Summarizing, one may state that using the model as described in this paper, it has been possible to establish clearly the influence of common LPCVD parameters like gas flow, input partial pressure, total pressure, and the kinetics of the deposition process on the growth rate profile. Therefore, optimization of LPCVD processes that are applied in IC technology has now become easier.

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