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Systematic Classification of LPCVD Processes

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Abstract. A simple classification scheme of low pressure chemical vapor deposition processes is discussed which is based on only three different one-dimensional models of the radial film thickness distribution on silicon wafers processed in a conventional horizontal hot-wall reactor. Comparing theoretical predictions of these models with experimental results obtained from various LPCVD processes, a good qualitative agreement can be stated. For better quantitative accuracy additional effects must be taken into account. The stoichiometrically induced radial flow for deposition reactions not preserving the mole number of involved gaseous species is very important for the parameter evaluation as well as model identification.

1. INTRODUCTION

Low pressure chemical vapor deposition (LPCVD) processes are widely used for preparation of various kinds of thin film coatings in microelectronics and many other branches of industry. Corresponding to their great practical importance a lot of detailed experimental as well as theoretical investigations of diverse deposition processes have been published up to now. For example, the publications on layer deposition from gaseous Si-H compounds contributed by Wahl [1], Kleijn [2], Jensen [3], Meyerson [4], Hitchman [5], Coltrin [6], Yeckel [7], Duverneuil [8], and Couderc [9] should be mentioned here. Nevertheless, the efficient use of LPCVD processes in the industrial sphere demands for more simplified as well as universally applicable basic models describing common characteristics of whole groups of LPCVD processes and allowing model predictions suitable for a "scale up" of the process equipment.

In 1991 Schlote et al. [10] have proposed to use only three different diffusion-reaction models in order to analyze radial film thickness distributions on silicon wafers processed in a conventional horizontal hot-wall reactor and to classify LPCVD processes. Applying these one-dimensional (1D) models to microscopic cavity structures, too, one of them predicts an abrupt decrease of the deposition rate within narrow trenches for depositions controlled by the by-product mechanism. Recently, this "rate jump" phenomenon including the underlying by-product model could be experimentally verified for SiO₂ films deposited from a TEOS/O₂ gas mixture [11] and for in-situ phosphorus doped Si or SiGe films [12]. Meanwhile, the proposed three-model classification has also been adopted by Raupp et al. [13] for their comparative analysis of the characteristic step coverage behavior in LPCVD.

The paper presented summarizes shortly the essential results of the previous modeling and discusses possible as well as necessary supplements for improved accuracy of the models.

2. CLASSIFICATION SCHEME

For a systematic classification of LPCVD processes only three different basic models will be necessary, if the analysis of any given process is restricted to some essential features and if all other specific properties depending on the individual deposition reaction used are neglected. These features are summarized in Tab. 1. In order to assign a given LPCVD process to the corresponding basic model we have to check both the sensitivity of the radial thickness distribution with respect to the wafer arrangement and the thickness uniformity within microscopic trench structures.

Tab. 1: Three-model classification of LPCVD processes

Basic model Controlling component	Simplified reaction scheme (without complete stoichiometry)	Sensitivity regarding wafer arrangement	Trench coverage at low rate constant	Example
Standard Primary reactant PR(g)	$PR(g) \xrightarrow{q} F(s)$	low	uniform	SiH_2Cl_2 / NH_3 $\longrightarrow Si_3N_4$ $SiH_4 \longrightarrow aSi$
Intermediate product IP(g)	$PR(g) \xrightarrow{k} IP(g) \xrightarrow{q} F(s)$	high, caged boat necessary	uniform	TEOS/ $POCl_3/O_2$ $\longrightarrow PSG$
By-product BP(g)	$PR(g) \xrightarrow{q} BP(ads)$ $\updownarrow$ $BP(g) \xrightarrow{k} PR(g)$ (by-product formation) $PR(g) \longrightarrow F(s)$ (deposition reaction)	high, caged boat necessary	nonuniform, rate jump	TEOS/ O_2 $\longrightarrow SiO_2$

The mathematical background including employed simplifications and restrictions has been explained in detail in the previous publication [10].

Tab. 2 presents the normalized radial thickness (growth rate) distributions obtained from a one-dimensional calculation of the spatial distribution of the respective controlling component (primary reactant PR, intermediate product IP, or by-product BP). In contrast to [10], the thickness distributions have been normalized with respect to the wafer center here.

Tab. 2: Normalized radial distributions of the growth rate ($I_0(x), I_1(x)$: modified Bessel function of zeroth and first order, respectively)

Basic model	Thickness distribution $R(\rho)/R(0)$	Coefficient A', A'' , respectively	Square of Thiele modulus, a^2
Standard	$I_0(a\rho)$		$\frac{2qr_1^2}{dD}$
Intermediate product	$\frac{1 - A' I_0(a\rho)}{1 - A'}$	$\frac{1 - \frac{d_0}{d}}{\left(1 + \frac{kd_0}{2q}\right) I_0(a) + \frac{Da}{r_1 q} I_1(a)}$	$\frac{2qr_1^2}{dD} + \frac{kr_1^2}{D}$
By-product	$\frac{1 + A''}{1 + A'' I_0(a\rho)}$	$\frac{\frac{d}{d_0} - 1}{\left(1 + \frac{kd_0}{2q}\right) I_0(a) + \frac{Da}{r_1 q} I_1(a)} *$ $* \frac{1}{\frac{2q}{kd_0} + \frac{K_2}{c_0} \left(\frac{2q}{kd_0} + \frac{d}{d_0}\right)}$	$\frac{2qr_1^2}{dD} + \frac{kr_1^2}{D}$

Between the concentration of controlling component, c , and the growth rate, R , the following relationships have been assumed to be valid (for explanation of symbols see notations):

Standard model: $R = \gamma q c$ c : concentration of primary reactant (1)

Intermediate product model: $R = \gamma q c$ c : concentration of intermediate product (2)

By-product model: $R = \gamma \frac{K_1}{K_2 + c}$ c : concentration of by-product (3)

A sufficient radial uniformity can be reached either for small values of the Thiele modulus (standard processes) or for a wafer arrangement within a "caged" wafer boat observing the following geometrical condition between wafer spacing d_0 , wafer radius r_1 , and cage radius r_2 :

$$d_0 = 2(r_2 - r_1) \quad (4)$$

In the latter case valid for intermediate product as well as for by-product processes, the coefficients A' , A'' in the corresponding distribution functions are equal to zero (not depending on the value of Thiele modulus).

3. EXPERIMENTAL INVESTIGATIONS

The thickness distributions of various LPCVD films have been measured along a wafer diameter by means of an automatic ellipsometer PLASMOS SD 2000. Mean values were formed from both the thickness values assigned to the same radial position and normalized with respect to the thickness in the wafer center. These mean values have been fitted using the Levenberg-Marquardt method [14]. Adjustable fitting parameters are the Thiele modulus, a , as well as the coefficients, A' (intermediate product model) and A'' (by-product model), respectively.

Fig. 1 exhibits measured (marker symbols) and fitted (continuous line) radial thickness distributions for Si_3N_4 films deposited from $\text{SiH}_2\text{Cl}_2/\text{NH}_3$ gas mixtures as well as amorphous Si films deposited from SiH_4 . For the fitting procedure corresponding to the standard model the inner regions $0 \leq \rho < 0.8$ (Si_3N_4) and $0 \leq \rho < 0.6$ (aSi) have been selected because of certain systematic deviations of the measurement points from the theoretical functions in the vicinity of the wafer edge.

Fig. 1: Radial thickness distribution of LPCVD films deposited with "cage-less" wafer arrangements. Various wafer spacings as indicated at the curves (normalized to $d_0 = 11$ mm)

Fig. 2 presents corresponding results for LPCVD processes which need a wafer arrangement within a caged boat for sufficient uniformity of the deposited films. The deposition of phosphosilicate glass (PSG) films from the TEOS/ POCl_3/O_2 reaction system is controlled by an intermediate product mechanism, whereas the deposition of undoped SiO_2 layers from TEOS/ O_2 gas mixtures have to be assigned to the by-product model. This distinction is supported by the trench coverage behavior discussed in detail elsewhere [11].

Fig. 2: Radial thickness distributions of PSG and SiO_2 films, respectively. Caged boat with various wafer spacings as indicated at the curves. Optimum wafer spacing $d_0 = 11$ mm.

4. DISCUSSION

4.1. Modification of thickness distributions in the vicinity of wafer edge

Comparing the agreement between the fitted curves and the measurement points for the selected examples in Fig. 1 and 2, marked deviations can be observed particularly for the SiH_4 -based deposition of amorphous silicon within the range of radial position $0.6 < \rho < 1$. For the other deposition reactions similar deviations also exist, but they are smaller and more restricted to the immediate vicinity of the wafer edge. This phenomenon has been discussed as overlapped deposition controlled by two species simultaneously [8, 15].

On the other hand, the application of an one-dimensional modeling itself also causes characteristic deviations between measured and fitted thickness distributions in the outer region of a wafer. These deviations should drastically increase for larger ratios of wafer spacing to wafer radius. Fig. 3 presents an experimental verification of that "2D effect" for some PSG depositions performed with different caged wafer boats (different optimum wafer spacings d_0).

Obviously, the 2D modification of the thickness distributions is much more distinct for distributions characterized by a small or a negative curvature in the wafer center than for distributions with positive curvature. Thus the large deviations observed in the case of aSi films seem to be caused mainly by the parallel intermediate product mechanism as discussed in [8] and not by the 2D effect.

In connection with the intentional restriction to 1D models within this paper there is only the possibility to exclude measurement points in the outer wafer region from the fitting procedure.

Fig. 3: Influence of geometrical dimensions on the radial thickness distribution of TEOS-based (left diagram) and SiH_4 -based PSG films (right diagram). Caged wafer boats for different optimum wafer spacings d_0 . Normalized wafer spacings d/d_0 as indicated at the curves.

4.2. Modification by stoichiometrically induced convection

The theoretical treatment of the conventional horizontal LPCVD reactor mostly proceeds on the assumption that the forced convection flow feeding the deposition reaction is concentrated in the annular region between wafer boat and reactor tube while the intrawafer regions are free of any convection. This assumption will be false, if the number of moles of reactants consumed by the given deposition reaction is not equal to the number of gas moles produced. In this case an additional radial flow will be stoichiometrically induced. This induced convection is directed outwards for deposition reactions producing and inwards for deposition reactions consuming a surplus of gas moles, respectively. Depending on the direction of diffusion with respect to the direction of induced flow the reactant transportation through the gas phase can be hindered (antiparallel orientation) or can be forced (parallel orientation).

Involving induced convective effects in the intrawafer region Velander and White [16] have already tried to explain the radial thickness distribution of TEOS-based SiO_2 films in 1987. Their investigation could not completely convince because they have assigned the deposition from TEOS to the standard mechanism but not to the by-product model. Using PSG and SiO_2 films deposited from $\text{TEOS}/\text{POCl}_3/\text{O}_2$ and TEOS/O_2 gas mixtures as examples we will demonstrate that the correct assignment of given LPCVD process to the basic models is of deciding importance in order to explain the influence of induced convection.

An useful test for the reliability of any fitting procedure and the consistency of parameter evaluation can be obtained by checking the dependence of the Thiele modulus squared, a^2 , as a function of the reciprocal wafer spacing, d_0/d (for the sake of convenience normalized with respect to d_0). Referring to the last column in Tab. 2 we get the linear functions:

$$a^2 = \frac{qr_1^2}{d_0 D} \cdot \frac{d_0}{d} \quad (\text{standard model}) \quad (5)$$

$$a^2 = \frac{kr_1^2}{D} + \frac{qr_1^2}{d_0 D} \cdot \frac{d_0}{d} \quad (\text{cage models}) \quad (6)$$

Equ. (6) valid for deposition processes with intermediate or by-product mechanism provides an intercept $kr_1^2/D > 0$ in contrast to equ. (5).

Using the fitting results of Fig. 1 and 2 the obtained values of squared Thiele modulus, a^2 , are plotted versus the normalized reciprocal wafer spacing, d_0/d in Fig. 4. The experimental values of the Thiele modulus derived from the functions in the left diagram (standard processes) for the wafer spacing $d = d_0 = 11$ mm (Si_3N_4 : 0.225, aSi: 0.116) correlate reasonably to values directly calculated from the process conditions in consideration of the assumed first order kinetics as well as the neglected axial reactant depletion (Si_3N_4 : 0.122, aSi: 0.046). For the calculation the diffusivity values $3.0\text{E}3$ cm^2/s (Si_3N_4) and $1.5\text{E}3$ cm^2/s (aSi), respectively, have been used.

The values of the both cage processes cannot be arranged in a single straight line corresponding to equ. (6) (right-hand side of Fig. 4). Obviously a discontinuity exists at $d = d_0$ and the a^2 values for smaller wafer spacings ($d < d_0$) must be arranged in a straight line separated from another one for greater spacings ($d > d_0$). Both straight lines of each kind of layer differ only in the slope and show approximately a common intercept. Note that for PSG films the slope is higher in the range $d < d_0$ than for $d > d_0$, the reverse order is valid for SiO_2 films.

As a first approximation (small change of the number of gas moles after reaction and low degree of radial thickness nonuniformity) the influence of the induced radial convection can be expressed by a correction term $p \geq 0$ in the linear functions for the squared Thiele modulus:

$$a^2 = \frac{qr_1^2}{d_0D} (1 \pm p) \frac{d_0}{d} \quad (7)$$

$$a^2 = \frac{kr_1^2}{D} + \frac{qr_1^2}{d_0D} (1 \pm p) \frac{d_0}{d} \quad (8)$$

$$\text{with } p \sim |\beta - 1| \cdot x \quad (9)$$

The correction term p tends to zero for a stoichiometric ratio of product gas to reactant gas $\beta \approx 1$ or for a small mole fraction of controlling species $x \ll 1$. If the diffusion works in the same direction as the induced convection, the sign of p will be negative. In the opposite case the positive sign has to be used. Note that the direction of the induced radial flow is defined by the deposition reaction considered (outwards for TEOS-based depositions). The radial diffusion flow is always an inward flow for the standard mechanism. But for both the cage models the direction of diffusion of controlling component (intermediate or by-product) will change, if the wafer spacing goes from the region $d < d_0$ (inwards for intermediate, outwards for by-product) to the region $d > d_0$ (outwards for intermediate, inwards for by-product). The various situations are sketched in Fig. 5.

Now the behavior of the dependencies $a^2 = f(d_0/d)$ exhibited in Fig. 4 becomes understandable, it demonstrates the correctness of classification carried out for TEOS-based SiO_2 and PSG films (by-product and intermediate product model) and provides an additional explanation of possible differences between experimental and calculated values of the Thiele modulus in the case of the standard model.

The negative slope of both the linear functions assigned to the SiO_2 deposition in Fig. 4 cannot be completely explained at the moment. At least one of the functions must have a positive slope corresponding to the simplified analysis discussed above. Taking the 2D effect illustrated in the preceding paragraph into account it is highly probable that the values of the Thiele modulus obtained particularly in the case $d \geq d_0$ are too low even if measurement points in the outer wafer region have been neglected. But this systematic error influences the results in the same direction for both cage models and does not hide the distinction between them.

Fig. 4: Squared Thiele modulus versus normalized reciprocal wafer spacing.

Left-hand side: Depositions corresponding to standard model

Right-hand side: Depositions controlled by intermediate (PSG) or by-product mechanism (SiO_2)

Fig. 5: Shift and splitting of the relation $a^2 = f(d_0/d)$ caused by stoichiometrically induced convection (schematically). The dotted lines in both diagrams represent the initial situation without any convection. The left diagram shows the influence of an inward, the right one of an outward flow.

SM, IP, BP: Standard, intermediate, by-product model.

5. CONCLUSIONS

Starting from a simple classification scheme of LPCVD processes, which is based on three different 1D models of the radial thickness distribution, possible supplements providing a better quantitative accuracy as well as a deeper insight have been discussed. Although a simplified mathematical description appropriate to practical purposes has still to be elaborated, the present results allow to make the following conclusions:

1. The basic idea of the three-model classification of LPCVD processes does not have to be changed.
2. The induced convection caused by deposition reactions changing the net number of gas moles must be taken into account. Since the direction of induced radial flow is given by the stoichiometry of the reaction, the characteristic behavior of the Thiele modulus squared as a function of the reciprocal wafer spacing can be used for model identification instead of the rate jump phenomenon within narrow trenches.
3. Some deviations between the experimental and theoretical radial thickness distributions occur in the vicinity of the wafer edge, which could be caused by the application of 1D models. In order to reduce this systematic error measured values taken from that region are to be neglected for an evaluation of 1D model parameters.

It cannot be excluded that the actual mostly more complicated chemistry of a given deposition process involves more than one of the three basic models. Especially, thickness distributions corresponding to the intermediate or the by-product mechanism seem to be frequently overlapped by ordinary depletion effects governed by the standard model. Nevertheless, a dominant model type should be definable on the basis of the proposed classification characteristics.

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Notations

R	deposition rate, cm s^{-1}
γ	molar volume of deposited layer, $\text{cm}^3 \text{mol}^{-1}$
c, c_0	concentration of primary reactant, intermediate product or by-product, respectively, mol cm^{-3}
K_1	adsorption kinetics constant in equ. (3), $\text{mol}^2 \text{cm}^{-5} \text{s}^{-1}$
K_2	adsorption kinetics constant, mol cm^{-3}
k	rate constant of homogeneous reaction, s^{-1}
q	rate constant of heterogeneous reaction, cm s^{-1}
r_1, r_2	radius of wafer and cage, respectively, cm
ρ	normalized radial position ($= r/r_1$)
d, d_0	wafer spacing and optimum wafer spacing for cage processes, cm
D	diffusivity of process dominating component, $\text{cm}^2 \text{s}^{-1}$
β	stoichiometric ratio of product gas to reactant gas
x	mol fraction of controlling species

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