The Formation Mechanism and Step Coverage Quality of Tetraethylorthosilicate-SiO₂ Films Studied by the Micro/Macrocavity Method

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ABSTRACT

The formation mechanism and step-coverage quality of SiO_2 films formed by the pyrolysis of tetraethylorthosilicate (TEOS) were studied, using a novel experimental technique called the "multi-layered micro/macrocavity method." The growth rate profiles at millimeter (macrocavity) and submicron (microtrench) sales deposited under a total pressure ranging from 2 to 760 Torr were simultaneously analyzed. The step coverage approaches conformal deposition either with decreasing volume-to-surface ratio (V/S) of the macrocavity reaction zone or with increasing total pressure. Combining these results with the growth-rate profiles of the macrocavity shows that two kinds of intermediate species participate in deposition. One is a high-activity species with a surface sticking probability near 1, and the other is a low-activity. A nonlinear increase of the growth rate with the macrocavity V/S ratio indicates that a polymerization reaction occurs in the growth rate uniformity with the operating conditions.

Film thickness profiles on silicon wafers and in microtrenches is of great interest in the field of very large scale integrated (VLSI) technology. As the minimum feature size design rule of dynamic random access memory (DRAM) chips decreases, the film thickness uniformity becomes increasingly important for achieving high-quality, micrometer-sized dielectrics, metal wires, and contact electrodes.

While chemical vapor deposition (CVD) processes are known for their potential applications of fabricating various kinds of uniform thin films, and although numerous attempts have been made to explain and improve the quality of thin films, the mechanisms that determine the film thickness profile and step coverage quality are still not well understood. Watanabe and Komiyama¹ proposed a novel technique for studying these processes, called the "micro/ macrocavity (MMČ) method," that includes measurement of deposition profiles in a millimeter-sized cavity with micrometer-sized trenches.2 They applied the MMC technique to study the step coverage during SiH₄:O₂ thermal chemical vapor deposition (CVD), and demonstrated that it provides substantial information about the deposition kinetic mechanism. The cavity used in their experiments was composed of two silicon wafer substrates with trenches separated by spacers. With the intention of improving experimental accuracy and distinguishing between the individual effects of gas-phase and surface reactions in CVD processes, an advanced MMC method has been developed by Hong³ and the authors of this work. The new method uses a stack of MMC cells that are separated by millimetersized spacers (Fig. 1). The features of the "multilayered MMC method" are to obtain a lot of data changing macrocavity spacing "W" with one deposition run. This can avoid ambiguity that there are some scatters in deposition conditions to repeat deposition runs changing the spacings.

 SiO_2 films formed by pyrolysis of tetraethylorthosilicate (TEOS) have been widely used as insulating films in VLSI technology and intensively studied.⁴⁻⁹ SiO_2 films formed from TEOS are recognized to have thickness and step coverage uniformity superior to those from the other chemical systems.^{4,5} Although extensive experimental studies have been devoted to achieving improved film thickness and step coverage uniformity on silicon wafers,^{6,7} the theoretical interpretation of deposition profiles including step coverage quality has not been reported thus far. Desu and Kalidindi investigated the kinetic mechanism of TEOS-SiO₂ film formation with a low pressure CVD system by an analysis of growth-rate profiles along the gas stream direc-

^{*} Permanent address: Mitsubishi Electric Corporation, Central Research Laboratory, 1-1, Tsukaguchi Honmachi 8-chome, Amagasaki, Hyogo 661, Japan. tion, and presented a theoretical kinetic model for the deposition.¹⁰⁻¹² They did not, however, analyze the wafer and microtrench (step coverage) growth-rate profile and did not comment on the possibility of predicting operating conditions that would guarantee conformal film deposition.

This paper deals with the chemical reaction kinetics and simulation of the step-coverage quality of $TEOS-SiO_2$ films studied by the MMC method. In order to understand systematically the mechanism of the deposition profile, experiments were done under total gas pressures ranging from 2 to 760 Torr. A comprehensive model of deposition kinetics is also presented.

Mathematical Model

Figure 1 shows a multilayered MMC cell which contains several silicon wafers separated by spacers with the open ends perpendicular to the gas stream. The space between two silicon substrates is an order of a millimeter and is hereafter called a macrocavity. Micrometer-sized trenches, fabricated by VLSI lithographic technology, are called microcavities.

First of all, the deposition rate profile in a macrocavity is analyzed based on a simple TEOS deposition model, shown in Fig. 2.^{10,11} We assume that a reactant species (*e.g.*, TEOS) and/or an intermediate species (*e.g.*, TEOS derivatives) ac-



Microcavity

Fig. 1. Schematic structure of the multilayered micro/macrocavity cell. The wafers are separated by spacers of varying diameters.

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Fig. 2. A simple deposition model of SiO₂ film formation by pyrolysis of TEOS. The symbols k_s and k_g represent surface and gas-phase reaction-rate constants, respectively.

cumulated in the gas phase of a CVD reactor diffuses into the macrocavity and subsequently deposits on the wafer. The surface deposition flux is represented by k_sC , where k_s and C stand for the total surface reaction-rate constant and gas-phase species concentration, respectively. Also, the kinetic theory of gases gives the flux as a function of sticking probability, η

$$J = -k_s C$$
$$= -\frac{1}{4} v \eta C \qquad [1]$$

where v is the thermal mean velocity of the molecular considered. The mass conservation equations for the reactant and intermediate species are represented by

$$D \frac{d^2 C_{\text{TEOS}}}{d^2 x} - \left(k_{\text{g}} + k_{\text{s}} \frac{2}{W}\right) C_{\text{TEOS}} = 0$$
 [2]

$$D_{i} \frac{d^{2}C_{i}}{d^{2}x} - k_{si} \frac{2}{W} C_{i} + k_{g} C_{TEOS} = 0$$
 [3]

where D is the diffusion coefficient of TEOS, k_g is the gasphase reaction rate constant corresponding TEOS dissociation, W is the width of the macrocavity (2/W is an S/V ratio), and the subscript i refers to the intermediate species.



Fig. 3. The relation between step coverage quality and sticking probability of a deposition species using a direct-simulation Monte Carlo method applied to the trench. The inset shows how the step coverage quality is defined.



Fig. 4. Schematic diagram of the experimental apparatus, where TMC represents a thermal mass flow-controller.

The boundary conditions for Eq. 2 and 3 are

at
$$x = 0$$
 $\frac{dC}{dx} = 0$
 $\frac{dC_i}{dx} = 0$
at $x = L$ $C = C_0$ [4]
 $C_i = C_{i0}$

Solving Eq. 2 and 3 with these boundary conditions gives the concentration profiles for C and C_i

$$C = C_0 \frac{\cosh(\phi_1 x/L)}{\cosh \phi_1}$$
[5]

$$C_{i} = -\frac{\phi_{3}^{2}}{\phi_{1}^{2} - \phi_{2}^{2}} C_{0} \frac{\cosh(\phi_{1}x/L)}{\cosh\phi_{1}}$$

+
$$\left(C_{i0} + \frac{\phi_3^2}{\phi_1^2 - \phi_2^2} C_0\right) \frac{\cosh(\phi_2 x/L)}{\cosh \phi_2}$$
 [6]

$$\phi_1 = L \sqrt{\frac{k_g + k_s \frac{2}{W}}{D}}$$
[7]

$$\phi_2 = L \sqrt{\frac{k_{\rm si} \frac{2}{W}}{D_{\rm i}}}$$
[8]

$$\phi_3 = L \sqrt{\frac{k_g}{D_i}}$$
 [9]

The growth rate, GR, is the sum of TEOS and intermediate species surface flux and is represented by

$$GR = k_s C + k_{si} C_i$$

= $A_1 \cosh(\phi_1 x/L) + A_2 \cosh(\phi_2 x/L)$ [10]

Equation 10 indicates that the deposition profile consists of two approximately straight lines with slopes of ϕ_1/L and and ϕ_2/L , respectively, on a semilogarithmic plot, according to the model shown in Fig. 2. The ratio of the gas-phase reaction rate to diffusion coefficient, k_g/D , can be estimated by measuring the film thickness profile. Consequently, the values of k_g and k_s for the key components can be evaluated in this analysis because the value of D can be reliably estimated. Then, using Eq. 1 k_s gives η with an estimate of v. In turn, the growth rate can be converted to Jand, consequently, the concentration of growth species C can be estimated. The concentration level suggests

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| CVD conditions | Total pressure [Torr] | TEOS partial pressure [Torr] | Deposition temperature [K] | $D_{	ext{teos}}$ a $[ext{m}^2/	ext{s}]$ | TEOS mean free path [m] | Residence time [s] |
|----------------|--------------------------|------------------------------------|----------------------------------|--|-------------------------------|-----------------------|
| VLPCVD | 2 | 0.12 | 973 | 1.32×10^{-2} | $3.6	imes10^{-5}$ | 0.26 |
| LPCVD | 8 | 0.4 | 973 | $3.30	imes10^{-3}$ | $9.0	imes10^{-6}$ | 0.11 |
| MPCVD | 60 | 1.2 | 973 | $4.40 	imes 10^{-4}$ | $1.2	imes10^{-6}$ | 0.44 |
| APCVD | 760 | 0.6 | 973 | $3.47	imes10^{-5}$ | $9.5	imes10^{-8}$ | 2.7 |

* Estimated by Chapman-Enskog's equation.

whether the key component is the reactant or the intermediate species.

Accurate estimation of the surface sticking probability is achieved by considering the deposition profile in the macrocavity and that in the microcavity. Analytical methods for interpretation of the film thickness profile in a microcavity has been described. $^{13-15}$ In order to evaluate the profile in a microcavity, we employed a direct simulation Monte Carlo method which considers gas-phase collisions, but not surface migration. Step coverage quality is governed by η and by the geometry of a microtrench. Figure 3 shows typical results of a Monte Carlo simulation (similar method to Ref. 13) in which the step coverage (St) for the microcavity was calculated. The step-coverage quality is governed by sticking probability of the particle and a trench aspect ratio. Note that nonconformal deposition profiles occur in the presence of a species with y larger than about 0.1. While the deposition profile in a macrocavity results from gas-phase and surface reactions of the deposition species in the cavity, the profile in a microcavity can be analyzed without considering gas-phase reactions. Analysis of a microcavity placed in a well-defined macrocavity volume makes it possible to estimate and understand the contribution of the intermediate species generated in the gas phase.

Experiments

The experimental apparatus is schematically shown in Fig. 4. A horizontal quartz tube reactor having a diameter of 15 mm was used. The tube reactor was mounted on a resistant-heated pedestal and kept at 973 K (temperature was monitored by a thermocouple). The length of the isothermal zone was about 150-mm. The multilayered MMC cell was placed about 3.0 cm apart, starting at the beginning of the isothermal zone in the reactor tube. The cell was held by Ni wires so that the cell could be positioned several millimeters apart from the inside wall of the quartz reactor (the widest spacer is positioned at the bottom). TEOS gas was carried by a stream of N₂ through a bubbler to the reactor tube. The TEOS gas introduced into the reac-



Fig. 5. Dependence of step coverage quality on macrocavity width under VLPCVD conditions, where the step coverage of microtrench was measured at the center of a macrocavity.

tor was condensed by a cold-trap located after the reactor, and the TEOS weight was measured. The experimentally measured TEOS concentration agreed well with concentrations calculated from the bubbler temperature and pressure. The gas flow rate was controlled by a calibrated mass flow controller and the pressure was adjusted by a valve located between the reactor and the evacuation pump. The total pressure was adjusted from 2 to 760 Torr by adding N₂. Deposition conditions are summarized in Table I. Deposition under total pressures of 2, 8, 60, and 760 Torr are abbreviated as VLPCVD, LPCVD, MPCVD, and APCVD conditions, respectively.

The thickness profiles in the macrocavity in a direction perpendicular to the gas stream were measured by an optical surface-profiler. The step-coverage quality of the microcavity at the center of the macrocavity was observed by a scanning electron microscope (SEM). The MMC cells were composed of square silicon wafers (10 mm \times 10 mm) separated by spacers (0.1, 0.2, 0.3, 0.55, 1.1, and 2.2 mm) as shown in Fig. 1. The microtrenches were typically 1.8 μ m wide and 2.5 μ m deep.

Analysis and Discussion

Experimental results and interpretation under various CVD conditions.—We analyzed the deposition kinetic mechanism by simultaneously analyzing the deposition profiles and step coverage quality under various total pressures.

VLPCVD (very low-pressure CVD).—Figure 5 shows St at the center of the macrocavity, *i.e.*, x = 0, vs. W of the macrocavity, which indicates that St is a strong function of W. If only one species participates in deposition, St should be independent of W as well as the gas-phase concentration of



Fig. 6. Experimental and theoretical growth-rate profiles in the macrocavity under VLPCVD conditions. The fitted curve is the sum of a hyperbolic cosine function and a constant.



Fig. 7. Experimental and theoretical growth-rate profiles in the macrocavity under MPCVD conditions.

the deposition species. The change of step-coverage quality can be understood in terms of the change in the relative contribution of multiple deposition species. At least two species (*e.g.*, TEOS and an intermediate molecule) participate in deposition. An *St* value less than 1.0 strongly indicates the existence of a high-activity species with η greater than 10^{-1} (see Fig. 3).

A typical growth rate profile in the macrocavity (W = 0.55 mm) is shown in Fig. 6. Though Fig. 6 only shows data measured in one-half of the macrocavity, the entire profile was symmetric in the x-direction about the center line. This symmetry indicates that the dominant mass-transport mechanism is diffusion. Notable features of the profile are a very steep profile near the edge of the macrocavity and a flat profile near the center. The steep profile is associated with rapid deposition of a high-activity intermediate spe-



Fig. 8. Experimental and theoretical growth-rate profiles for W = 0.3 mm in the macrocavity under MPCVD conditions, where the theoretical curves A and B assume that the deposition species are TEOS and a high-activity intermediate species with $\eta = 1.0$, respectively.



Fig. 9. Dependence of step coverage quality on the macrocavity width under MPCVD conditions.

cies and the flat profile represents slow deposition of either TEOS or a low-activity intermediate species. The deposition profile was fit by the hyperbolic cosine function given by Eq. 6 and is shown in Fig. 6. Fitting the data near the edge yields $k_s/D 1.2 \times 10^4$ [1/m] for the high-activity intermediate species. Assuming that the *D* and *v* of the intermediate species are equal to those of TEOS (estimated to be 1.32×10^{-2} [m²/s] and 315 [m/s], respectively), η for the high-activity species can be calculated from Eq. 1 as

$$\eta = \frac{4k_s}{v}$$
 [11]

Substituting the values of k_s and v, η is 2.0; accounting for experimental and analytical errors, η is about unity. The steep profile is reasonably attributed to a high-activity intermediate species accumulated outside the macrocavity. When the growth-rate profile is fit by a single hyperbolic cosine function (*i.e.*, when the dominant deposition mechanism is surface reaction of the high-activity intermediate species that has $\eta = 1$), no deposition will occur near the center of the macrocavity, as shown in the lower fitting curve in Fig. 6. Since the flat profile with a significant growth rate must be fitted as $k_s/D = 0$, it is reasonable to assume that the growth-rate profile near the center is governed by a low-activity species, (*e.g.*, TEOS or another intermediate species), transported by diffusion from outside of the cavity.

We summarize the previous discussion as follows. The formation of TEOS-SiO₂ films is caused by at least two kinds of deposition species. One species is a high-activity intermediate with a sticking probability near unity, and another is a low-activity species.

MPCVD (medium-pressure CVD).—Figure 7 shows the growth-rate profiles in the macrocavity. The MPCVD growth rate exhibits a shallower profile than under



Substrate

Fig. 10. A proposed deposition model of TEOS-SiO₂ films, where the high- and low-activity intermediate species undergo reversible reactions in the gas phase.

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Fig. 11. Growth-rate profiles in the macrocavity under APCVD conditions.

termediate with a sticking probability on the order of 10^{-5} dominates the transport in the macrocavity and reacts to convert to a high-activity intermediate species in the gas VLPCVD conditions. We consider whether this profile is due to the high-activity intermediate or the low-activity species as discussed for VLPCVD. Contrary to the experimental data, a very steep profile is predicted if only one species with an η of 1.0 is assumed to deposit (Fig. 8, curve B). The growth-rate profile corresponding to the high-activity intermediate species is experimentally unmeasurable under MPCVD or APCVD conditions since its concentration rapidly approaches 0 within about 0.1 mm from the open end of the macrocavity.

Whether TEOS is responsible for the shallow profile or not is clarified by evaluating the TEOS concentration as follows. The growth rate is the sum of various reaction paths. Consequently, the experimental growth rate divided by the concentration of TEOS gives the maximum possible surface reaction-rate constant $k_{\rm s\,max}$. The fraction of TEOS molecules consumed in the reactor in the present experiments was not larger than 5%. Therefore, $k_{\rm s\,max}$ was calculated using the concentration of TEOS entering the reactor. The contribution of TEOS to the total growth rate is given by the first term of Eq. 10

$$GR = A \cosh\left(\sqrt{\frac{2k_s}{WD}}X\right)$$
 [12]

Substituting the values of k_{smax} , W_{smax} and D in Eq. 12 determines the coefficient in the hyperbolic cosine function. When W is 3 mm



Fig. 12. Relation between the growth rate and the macrocavity width under APCVD conditions.



Fig. 13. Dependence of the step coverage quality on the macrocavity width under APCVD conditions, where the film thickness profile is nearly conformal, independent of W.

$$\sqrt{\frac{2k_{\rm s}}{WD}} \le \sqrt{\frac{2k_{\rm s\,max}}{WD}} = 56.6 \, [1/m]$$
 [13]

As shown in Fig. 8, even the possible maximum k_s gives much flatter profiles than the experimental ones. TEOS is not responsible for the shallow profile.

We conclude that the profile observed under MPCVD conditions is neither due to the high-activity intermediate species nor to TEOS. Consequently, another low-activity intermediate species should be active under MPCVD conditions. Curve fitting by a hyperbolic cosine function gives a total surface reaction-rate constant, $k_{\rm s\,total}$, for this intermediate species

$$k_{\text{s total}} = k_{\text{s}} + k_{\text{g}} \frac{W}{2}$$

= 1.2 × 10⁻³ [m/s] (W = 0.3 mm) [14]

Separating the contribution of k_s and k_g by evaluating the dependence of the profile on the value of W was not attempted because of the number of fitting parameters involved.

Since $k_{\rm s\,total}$ gives $\eta_{\rm max} = 1.5 \times 10^{-5}$ for $k_{\rm g} = 0$, the step coverage quality should be conformal according to Fig. 3. Nevertheless, the step coverage values experimentally measured are, surprisingly, as small as 0.70 to 0.77 as shown in Fig. 9. This fact shows that a species with a large η dominates the deposition. A possible mechanism to explain this apparent discrepancy is that the low-activity in-



Fig. 14. A possible reaction mechanism by pyrolysis of TEOS in CVD systems, polymerization reactions in which the high-activity intermediate species react with TEOS in the gas phase.

| | m () | Step coverage, St [-] ^a | | | | | |
|----------------|---------|------------------------------------|------|------|------|---|--|
| CVD conditions | [Torr] | <i>W</i> [mm] = 0.1 | 0.2 | 0.3 | 0.4 | 0.55 | |
| VLPCVD | 2 | 0.76 | 0.62 | 0.55 | 0.52 | 0.50 | |
| LPCVD MPCVD | 8 60 | 0.92 | 0.70 | 0.81 | 0.73 | $\begin{array}{c} 0.71 \\ 0.75 \end{array}$ | |
| APCVD | 760 | 0.92 | | 0.98 | | 0.91 | |

^a Mean value of observed St.

phase. Combined with the results under VLPCVD conditions, this suggests that there are two key intermediates, high- and low-activity, and these species undergo reversible reactions to change to one another as schematically shown in Fig. 10.

APCVD (atmospheric-pressure CVD).—Figure 11 shows the growth-rate profiles under APCVD conditions. Different from the profiles observed under VLPCVD and MPCVD conditions, there are steep profiles near the edge of the macrocavity and a flat profile near the center. The low-activity intermediate which was a diffusing species under MPCVD conditions may be responsible for the steep nearedge profile, because the decreased diffusion coefficient at increased pressure makes the growth-rate profile steeper (see Eq. 5 and 7). This theory can be confirmed by fitting the near-edge profile in a similar manner to the analysis of VLPCVD and MPCVD. The parameters that best fit the data for W = 0.3 mm are

$$k_{\rm s \ total} = 1.9 \times 10^{-3} \ [{\rm m/s}]$$
 [15]

$$\eta_{\rm max} = 2.4 \times 10^{-5}$$
 [16]

Equations 15 and 16 compare well with those of the lowactivity intermediate species as shown in Eq. 14. The flat profile near the center indicates the existence of species with much lower activity than that of the low-activity intermediate species. TEOS is the most probable candidate for this species.

A quantitative analysis of the role played by TEOS was made by considering its concentration level in the macrocavity. Here we treat all the intermediate species dissociated from TEOS as a group. Since the concentration profile is nearly flat around the center of the macrocavity, the low-activity intermediate species that diffuses into the region is negligible. Equations 3 and 10 can therefore be simplified as

$$k_{\rm g} \frac{W}{2} C_{\rm TEOS} - k_{\rm si} C_{\rm i} = 0 \qquad [17]$$

$$GR_{\text{center}} = \left(k_{\text{s}} + k_{\text{g}}\frac{W}{2}\right)C_{\text{TEOS}}$$
 [18]

A plot of the growth rate at the center vs. W, (the linear region near W = 0 in Fig. 12) distinguishes the contribution of direct deposition of TEOS, $k_{\rm s}C_{\rm TEOS}$, from that of deposi-



Fig. 15. Schematic of concentration profiles in the direction perpendicular to the wall, where C_L and C_H represent the concentration of the low- and high-activity intermediate species, respectively. Concentration axis is along X-axis.

tion via intermediate species, $k_{\rm g}C_{\rm TEOS}$ W/2, according to Eq. 18. The surface reaction rate constant, sticking probability, and gas-phase reaction rate constant for TEOS are estimated as

$$k_{\rm s\,TEOS} = 1.4 \times 10^{-5} \,\,[{\rm m/s}]$$
 [19]

$$\eta_{\rm TEOS} = 1.8 \times 10^{-7}$$
 [20]

$$k_{\rm g\,TEOS} = 0.15 \, [1/s]$$
 [21]

The fraction of direct deposition of TEOS, X_{TEOS} , can be expressed as

$$X_{\text{TEOS}} = \frac{k_{\text{s}} C_{\text{TEOS}}}{k_{\text{s}} C_{\text{TEOS}} + \frac{W}{2} k_{\text{g}} C_{\text{TEOS}}}$$
$$= \frac{1}{1 + 5400W}$$
[22]

For example, when W = 0.55 mm, the fraction of direct deposition of TEOS is about 0.25 and that of deposition of intermediates is about 0.75. In spite of the deposition due to the intermediates, including the high-activity ones, the step coverage is nearly conformal, regardless of *W*, as shown in Fig. 13. This apparent discrepancy is discussed in detail later.

Modeling of SiO_2 film deposition from TEOS.—The growth rate increases nonlinearly with increasing W (see Fig. 12). This nonlinearity suggests that TEOS reacts with an intermediate species, since increased W facilitates gasphase reactions. A deposition model (Fig. 14) was constructed to account for this reaction of TEOS and intermediates as well as transport of these species into the MMC layers and subsequent deposition. This model is consistent with the idea that two groups of intermediates, with different activities, dominate the film formation process. The deposition model is substantiated by other studies: sol-gel kinetic studies have revealed some probable intermediate



Fig. 16. Theoretical step coverage quality fitted to experimental St values under various CVD conditions.

| Table III. Contributions of TEOS and the intermediate species to growth-rate profiles in the |
|--|
| macrocavity and the step coverage quality. |

| | | Growth-rate prof | ile in macrocavity | Step coverage | | |
|-------------------|--|---|--|---|---|---|
| CVD conditions | TEOS | High-activity intermediate species | Low-activity intermediate species | TEOS | High-activity intermediate species | Low-activity intermediate species |
| VLPCVD | Not significant | Mostly depleted near the edge by horizontal diffusion | Dominant diffusing species | Not significant | Dominant (easily reaches surface) | Dominant (easily reaches surface) |
| MPCVD | Not significant | Completely depleted near the edge by horizontal diffusion | Dominant diffusing species | Not significant | Dominant (slightly depleted by vertical diffusion with reaction) | Dominant (easily reaches surface) |
| APCVD | Dominant diffusing species near the center | Completely depleted near the edge by horizontal diffusion | Dominant diffusing species near the edge (gradually depleted) | Dominant at small W Not significant at large W | Mostly depleted by vertical diffusion with reaction | Dominant (easily reaches surface) |

molecules that appear in this model;^{16,17} ethylene was detected as a by-product in reduced pressure CVD systems;^{6,18} a small amount of fluid and solid substances were observed around the outlet of the reactor tube in the present experiments, indicating polymerization reactions.

Interpretation and simulation of step coverage quality under various CVD conditions.-The step coverage quality observed in various CVD conditions is summarized in Table II. To improve analytical accuracy, the data including low-pressure CVD are shown in this section. The step coverage quality seems to improve either with decreasing spacing W(W/2 is volume-to-surface ratio) or with increasing total pressure. It is understood that increasing fraction of TEOS direct deposition with decreasing W, according to Eq. 22, results in the step coverage improvement. An interesting effect is that the contribution of the high-activity intermediate species to SiO₂ film deposition decreases with increasing total pressure. An attempt was made to quantitatively understand the step coverage quality by taking into account the concentration gradient of the high-activity intermediate species in the direction perpendicular to the substrate surface. Figure 15 shows a schematic of typical profile of the gas-phase concentration of the high-activity intermediate species. There are more high-activity intermediate species in the center and less at the wall surface because of its rapid surface reaction, while there is little concentration gradient for the low-activity intermediate species. The mass conservation is represented by

$$D_{\rm H} \frac{d^2 C_{\rm H}}{dZ^2} = k_{\rm gH} C_{\rm H} - k_{\rm gL} C_{\rm L}$$
 [23]

$$k_{\rm gH} = k_{\rm g0H} C_{\rm TEOS}$$
 [24]

at
$$Z = \frac{W}{2} - D_{\rm H} \frac{dC_{\rm H}}{dZ} = k_{\rm s} C_{\rm H}$$
 [25]

and *Z* represents vertical coordinates and subscripts H and L refer to the high- and low-activity intermediates, respec-

$$k_{a H} = 2.1 \times 10^6 C_{TEOS} [1/s] (C_{TEOS} [mol/m^3])$$



Fig. 17. Deposition kinetic model for TEOS-SiO₂ films, where the gas-phase reaction-rate constant, k_{gH} , depends on the concentration of TEOS.

tively. The gas-phase reaction rate constant $k_{\rm gH}$ could be expressed as Eq. 24 using a parameter $k_{\rm g0H}$ independent of the concentration, because particular attention should be given to the dependence of $k_{\rm gH}$ on the TEOS concentration (see Fig. 14). Solving Eq. 23 with the boundary condition given by Eq. 25 yields

$$C_{\rm H} = - \frac{\frac{k_{\rm gL}}{k_{\rm gH}} k_{\rm sH} C_{\rm L}}{\sqrt{D_{\rm H} k_{\rm gH}} \sinh\left(\frac{W}{2} \sqrt{\frac{k_{\rm gH}}{D_{\rm H}}}\right) + k_{\rm sH} \cosh\left(\frac{W}{2} \sqrt{\frac{k_{\rm gH}}{D_{\rm H}}}\right)} \times \cosh\left(\sqrt{\frac{k_{\rm gH}}{D_{\rm H}}}Z\right) + \frac{k_{\rm gL}}{k_{\rm gH}} C_{\rm L} \quad [26]$$

where the concentration of the low-activity intermediate, $C_{\rm L}$, is constant. The concentration of the high-activity intermediate species depends on p, which is given by

$$p = \frac{W}{2} \sqrt{\frac{k_{gH}}{D_{H}}}$$
[27]

When p > 1, the concentration at the wall becomes negligible. Decreasing $D_{\rm H}$ under APCVD conditions can enhance the conversion of the high-activity intermediate species into the low-activity species before the high-activity one reaches the wall. This is the most probable reason for improvement of the step coverage quality under APCVD conditions, as we evaluate numerically later in this work.

Equation 26 was used to simulate the step coverage quality. Using $J_{\rm H} = k_{\rm sH}C_{\rm H}$ and $J_{\rm L} = k_{\rm sL}C_{\rm L}$, the ratio of the flux of high-activity intermediate species to low-activity ones to the wall, $J_{\rm H}/J_{\rm L}$, is represented by

$$\frac{J_{\rm H}}{J_{\rm L}} = \frac{\frac{k_{\rm sH}k_{\rm gL}}{k_{\rm sL}k_{\rm gH}}}{1 + \frac{k_{\rm sH}}{k_{\rm gH}}\sqrt{\frac{k_{\rm gH}}{D_{\rm H}}} \coth\left(\frac{W}{2}\sqrt{\frac{k_{\rm gH}}{D_{\rm H}}}\right)}$$
[28]

Assuming that the step coverage quality due to the low-activity intermediate species is 1.0, *St* is given by

$$St = \frac{J_{\rm L} + J_{\rm H}St_{\rm H}}{J_{\rm L} + J_{\rm H}} = \frac{1 + \frac{J_{\rm H}}{J_{\rm L}}St_{\rm H}}{1 + \frac{J_{\rm H}}{J_{\rm L}}}$$
[29]

where $St_{\rm H}$ is the step coverage quality due to the high-activity intermediate species with an η of 1.0. The direct Monte Carlo simulation method, in which the mean-free path length is taken into consideration, was employed to determine the values of $St_{\rm H}$ under various total pressures. The results show that the values of $St_{\rm H}$ under VLPCVD, LPCVD, MPCVD, and APCVD conditions are 0.34, 0.23, 0.06, and 0, respectively. Substituting these values of $St_{\rm H}$ into Eq. 29, St can be calculated, using three dimensionless numbers

$$rac{k_{
m sH}}{k_{
m sL}}$$
, $rac{k_{
m gH}}{k_{
m gL}}$, and $rac{W}{2}\sqrt{rac{k_{
m gH}}{D_{
m H}}}$

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Figure 16 shows that all the experimental step coverage quality data agrees well with the simulation using Eq. 28 and 29 when

$$\frac{k_{\rm sH}}{k_{\rm sL}} = 2.4 \times 10^5$$
 [30]

$$\frac{k_{\rm gH}}{k_{\rm gL}} = 1.0 \times 10^4$$
 [31]

$$\frac{W}{2}\sqrt{\frac{k_{\rm gH}}{D_{\rm H}}} = 8.2 \times 10^2 W$$
 [32]

 $(k_{\rm gH}$ was estimated at $P_{\rm TEOS}$ = 1.0 Torr). Up to the saturation of St the width of macrocavity is predominantly governed by the dimensionless number

$$rac{W}{2}\sqrt{rac{k_{
m gH}}{D_{
m H}}}$$

When $k_{\rm sH}/k_{\rm sL}$ is large or $k_{\rm gH}/k_{\rm gL}$ is small, St spproaches 0.

Role of deposition species in growth-rate profiles.—The contribution of the three deposition species (TEOS, lowand high-activity intermediate species) to the macroprofile and the step coverage quality are summarized in Table III. (The role of TEOS in step coverage quality was described based on Eq. 22). The role of each species depends on the operating conditions.

Quantitative description of SiO₂ film-deposition kinetics.—An estimate for the rate constant of each reaction path described in Fig. 14 can be made by Eq. 11, 30, 31, and 32 together with the mean value of Eq. 14 and 15

$$k_{\rm s \ total} = k_{\rm s} + k_{\rm g} \frac{W}{2}$$

= 1.6 × 10⁻³ [m/s] (W = 0.3 mm) [33]

The results are shown in Fig. 17, which indicates that each of the high- and low-activity intermediate species can be characterized by separate rate constants. This "two-group model" correctly predicts the step coverage quality and growth rates observed in the present experiments.

Concluding Remarks

The growth-rate profile and step coverage quality of TEOS-SiO₂ films were studied. A novel experimental technique based on a multilayered MMC method was used to investigate the film-deposition kinetics and the formation mechanism of the step coverage quality. A generalized interpretation for the film formation was developed by observing film formation under a wide range of total pressure. The concentration profiles in the macrocavity and microtrench were simulated by means of mass conservation equations and a direct simulation Monte Carlo method for the direction parallel and perpendicular to the wall.

The experimental results indicate that low- and high-activity intermediate species participate in the film deposition. The high-activity intermediate has a sticking probability of 1.0 and gives a sharply decreasing concentration profile in the macrocavity. The low-activity intermediate has a sticking probability near 0 and results in a shallow concentration profile. These two intermediate species undergo reversible reactions in the gas phase, each converting to the other. A nonlinear increase of the growth rate with increasing volume to surface ratio (width of macrocavity) suggests that additional reactions of intermediate molecules to TEOS (*i.e.*, a polymerization reaction) occurs in the gas phase. The sticking probabilities for the highand low-activity intermediate species were estimated to be 1.0 and 8.5×10^{-6} , respectively. While the sticking probability for TEOS direct deposition was estimated at 1.8 \times 10⁻⁷, the contribution to the deposition is negligibly small in practical systems. For modeling purposes, TEOS can be categorized in the same group as the low-activity intermediate species. The step coverage quality observed under various CVD conditions were consistently simulated with the deposition model presented. The improvement of step coverage quality with increasing total pressure is attributed to the decreasing concentration of the high-activity intermediate species near the substrate surface. The reason for this decrease is the conversion of the high-activity intermediate species to the low-activity species during diffusion toward the surface. The deposition kinetic model and the formation mechanism of the step coverage quality presented consistently explain all the phenomena observed.

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