Dependence of Oxygen Concentration and Temperature on the Growth Rate Distribution of SiO₂ Solid Film by Chemical Vapor Deposition in the Hexamethyldisiloxane-oxygen System

Misaki HONDA, Yuto YAMASAKI, and Ken-ichiro TANOUE†

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In this paper, the growth rate distribution of SiO₂ solid film by chemical vapor deposition (CVD) under a reduced pressure of 25,000 Pa has been investigated experimentally and numerically. The activation energy of the apparent surface reaction taking no particle formation into consideration was 335 kJ/mol. For all experimental conditions, the experimental results for the growth rate of CVD could be reproduced by the calculation ones before the maximum growth rate when mass transfer could be controlled by the apparent surface reaction. On the other hand, the calculation results for the growth rate of CVD disagreed to some extent with the experimental results after the maximum growth rate when mass transfer could be controlled by diffusion. By the observation of SEM images, the mass transfer in this CVD could include not only surface reaction but also particle formation. It was also suggested that the diffusion coefficient could become the apparent diffusion coefficient with the effect of particle formation. In future work, according to the estimation of the particle formation rate by using a membrane filter, the growth rate distribution could be reproduced by numerical calculation with not only surface reaction but also particle formation.

Key Words
Reduced-pressure CVD, Apparent surface reaction, CFD, SiO₂ particulate film

1. Introduction

The thermal CVD (chemical vapor deposition) method creates a thin film on a heated substrate during chemical reactions from vapor raw material and has been widely used due to its many advantages 1). In order to use thermal CVD for many applications, it is necessary to investigate not only heat transfer with fluid flow but also mass transfer with kinetics of chemical reactions and diffusion coefficient 2) - 6).

There have been two methods of measuring the growth rate on a substrate by thermal CVD 2) - 7). The first method is to measure the mass difference of the substrate in the CVD reactor before and after experiments 2). The second method is to measure the film thickness on the substrate by using SEM (scanning electron microscope) images 7).

In our previous report 8), the growth rate distribution of deposited SiO₂ in the HMDSO (hexamethyldisiloxane, O[Si(CH₃)₃]-O₂ (oxygen) system along the flow axis was measured by the mass difference of the substrates under a pressure of 50,000 Pa. The growth rate had a maximum...
value and then decreased drastically with the distance from the inlet. The calculation results of growth rate distribution with CFD (computer fluid dynamics) did not agree with the experimental results because particle formation could not be ignored in the CVD process under a pressure of 50,000 Pa. Thin film formation of SiC (silicon carbide) by thermal CVD in the SiH₄ (mono-silane)-C₆H₆ (benzene) system was reported by Oyamada et al.⁹ They suggested that the lower the total pressure in the reactor was, the lower the particle formation was⁹.

Therefore, in order to suppress particle formation during SiO₂ CVD in our experimental apparatus⁸, it is necessary to reduce the pressure to less than 50,000 Pa.

In this study, the growth rate distribution of SiO₂ solid film by thermal CVD in the HMDSO-O₂ system under a reduced pressure of 25,000 Pa has been investigated experimentally and numerically. Furthermore, SEM observation of the deposited material on the substrate was also conducted to investigate the surface configuration of the deposited material.

2. Experimental

Fig. 1 shows that the experimental equipment consists of mass flow controllers of nitrogen (N₂) gas and O₂, a reactor, and an aspirator to reduce the reaction pressure. In this study, the path and tank were changed to stainless steel to the extent possible to keep the reduced pressure. In addition, a needle valve for pressure adjustment was installed at the outlet of the reactor. HMDSO in a stainless-steel tank was used as the raw material. The temperature of the liquid HMDSO in the tank was kept at 283 K by a thermostatic chamber (EYELA, UNI COOL BATH NCB - 120). A quartz tube (outer diameter: 13 mm, inner diameter: 10 mm, length: 1000 mm) was used as the reactor, which was heated by an electric furnace (Chugai and Plox Co., Ltd., R32/250/12-P320). In order to evaluate the growth rate of silicon dioxide (SiO₂), 36 short quartz tubes (outer diameter: 9 mm, inner diameter: 7 mm, length: 5 to 20 mm) as the substrate were installed in the heated section (length: 400 mm) in the reactor. Before the experiments, the mass of the short quartz tubes was measured. While N₂ gas was fed into the reactor, the temperature at the outer wall of the reactor was raised to the desirable setting temperature on the outer wall of the tubular reactor Tₒ which was regulated by the thermostat of the electric furnace. When the wall temperature approached Tₒ, the desired mole fraction of HMDSO vapor was supplied to the reactor from the tank by bubbling with another N₂ gas. At the same time, the desired mole fraction of O₂ was also supplied. The mass flow rate of the HMDSO vapor was calibrated beforehand by the bubbling gas flow rate of N₂ and temperature of the liquid material in the tank. Then, the chemical reaction started as the following Eq. (1).

\[
O\left[Si\left(CH_3\right)_3\right]_2 + 12O_2 \rightarrow 2SiO_2 + 9H_2O + 6CO_2
\]  

(1)

The vapor of HMDSO was collected by a cold trap in the liquid N₂ and measured just before the CVD
The total gas flow rate and total pressure were 300 SCCM (standard cubic centimeter per minute) and 25,000 Pa, respectively. The setting temperature was changed from 1273 K to 1473 K. The mole fraction of O\(_2\) was also changed from 0.089 to 0.285. The mole fraction of HMDSO was about 0.0156. The reaction was performed in 100 minutes. After the experiment, the vapor of HMDSO remaining in the reactor was flushed by N\(_2\) gas for 60 minutes. Table 1 shows the experimental conditions.

After the experiments, the growth rate of deposited SiO\(_2\) on the short quartz tube was calculated by the following Eq. (2).

\[
G_{\text{SiO}_2,i} = \frac{m_i - m_{0,i}}{S \Delta t}
\]  

Here, \(G_{\text{SiO}_2,i}\), \(m_i\), \(m_{0,i}\), \(S\), and \(\Delta t\) show the growth rate of deposited SiO\(_2\) of the \(i\)-th quartz tube [kg/m\(^2\)/s], mass of the \(i\)-th quartz tube after the experiments [kg], mass of the \(i\)-th quartz tube before the experiments [kg], inner surface area of the \(i\)-th quartz tube [m\(^2\)], and reaction time (= 6000 s), respectively.

The total mass of deposited SiO\(_2\) was calculated by the following Eq. (3).

\[
\Delta M = \sum_{i=1}^{n} (m_i - m_{0,i})
\]  

The surface configuration of deposited SiO\(_2\) on the short quartz tube at the maximum growth rate was observed by SEM (scanning electron microscope).

### 3. Numerical Simulation

Two-dimensional numerical simulation in the horizontal reactor in the O\([\text{Si(CH}_3_3]_2-O_2-N_2\) system was conducted. The governing equations, calculation domain, and boundary conditions for numerical simulation were reported in our previous report \(^8\). The governing equations and the boundary conditions were discretized by the finite volume method and solved by the THOMAS method. The velocity and pressure profiles were solved by the SIMPLE algorithm. From our previous report \(^8\), \((M_r, M_z) = (100, 12000)\) was adopted as the grid sensitivity of the growth rate distribution along the flow axis.

### 4. Results and Discussion

#### 4.1 Growth rate distribution of the SiO\(_2\) film

Fig. 2 shows both the semi-log plot of the growth rate distribution of the SiO\(_2\) film and normal plot of temperature distribution along the flow axis. In Fig. 2 (a), in which the initial O\(_2\) mole fraction was changed under the condition of \(T_s = 1273\) K, film formation started at the point of about \(z = 0.08\) m under any initial O\(_2\) mole fraction condition. The growth rate and the temperature also increased with the position at \(0.08\) m < \(z\) < \(0.11\) m. In the section after \(z = 0.12\) m, the growth rate decreased exponentially with the distance from the heater inlet. The tendency of the growth rate distribution after \(z = 0.12\) m was almost the same even if the O\(_2\) concentration was changed. We can see that the maximum growth for \(x_{O_2,\text{init}} = 0.089\) was lower than that for \(x_{O_2,\text{init}} = 0.165\) and 0.285.

Mass transfer in CVD has been reported to consist of three rate-limiting processes \(^3\): (i) diffusion of raw material, (ii) gas phase reaction, and (iii) surface reaction. In this study, the gas phase reaction is assumed to be the fastest.
of these three processes, and mass transfer is considered to be composed of (i) diffusion of raw material and (iii) surface reaction. As shown in Fig. 2 (a), at first, as the growth rate increased with temperature, the mass transfer could be controlled by surface reaction. Here, surface reaction refers to the reaction in which the precursor of the deposited material is converted to a solid film on the substrate. On the other hand, in the region after the maximum growth rate, mass transfer could be controlled by diffusion of the precursor \( \text{SiO}_2 \). For this region, the gradient of the growth rate to the distance from the heater inlet on the semi-log plot was utilized to estimate the diffusion coefficient. Here, the temperature of the substrate along the distance from the heater inlet was almost constant.

In Fig. 2 (b), the position of the maximum growth rate moved to the upstream side with increase in \( T_S \) because the surface reaction could be promoted. In the diffusion-controlled region, the growth rate decreased exponentially along the distance from the heater inlet at \( T_S \leq 1373 \text{ K} \). However, the growth rate decreased with large variation along the distance from the heater inlet at \( T_S \geq 1423 \text{ K} \) and \( z > 0.15 \text{ m} \).

Table 2 shows the total mass of deposited SiO\(_2\) on the substrates. From this table, the result is extremely small when \( x_{\text{O}_2,\text{ini}} = 0.089 \). Fig. 3 shows photographs of the formed film immediately at the maximum growth rate for several conditions as listed in Table 1. In Fig. 3 i), ii), and iii), the thin brownish film changed to translucent white as the initial O\(_2\) mole fraction increased. From the results of Table 2 and Fig. 3, it was suggested that the more the initial O\(_2\) mole fraction could cause not only the more the total mass of deposited SiO\(_2\) but also the change in the type of film. As the colors of the substrate were almost translucent at \( x_{\text{O}_2,\text{ini}} = 0.285 \), we assumed that a single crystal of SiO\(_2\) could be formed. In Fig. 3 iii), iv), v), vi), and (vii), when the \( T_S \) increased, the color of the film changed from transparent white to transparent brown and then to fully transparent at \( T_S \leq 1373 \text{ K} \). However, the color of the film changed again to transparent white at \( T_S \geq 1423 \text{ K} \).

This indicates that the difference in the type of film formed by changing the \( T_S \) may be the cause of the above-mentioned tendency in the diffusion-controlled region.

### 4.2 Surface reaction rate constant

The growth rate distribution in the region of the surface reaction rate controlled was applied to the differential reactor model reported by Hatori \textit{et al.} \(^6\) and Kurihara \textit{et al.} \(^8\). From the mass balance equation using this model, the mass flow rate of each component (HMDSO, \( N_2 \), \( O_2 \), \( CO_2 \) and \( H_2O \)) at each quartz short tube was calculated. Next, from the value of the mass flow rate, the mole fraction of HMDSO at each quartz short tube was calculated. The procedure was the same as that in our previous reports \(^6\) \(^8\). Note that the chemical reaction during SiO\(_2\) film coating was assumed to be the first-order chemical reaction of HMDSO and \( O_2 \) in this study. Then, growth rate \( N_{\text{SiO}_2} \text{[mol/m}^2\text{/s]} \) was expressed as follows.

![Fig. 3 Photographs of the formed thin film on the substrate under several conditions as listed in Table 1](image-url)
Here, $C_{\text{HMDSO}}$ [mol/m$^3$] and $C_{\text{O}_2}$ [mol/m$^3$] show the molar concentrations of HMDSO and O$_2$, respectively. Therefore, the surface reaction rate constant $k_S$ [m/s] could be given by

$$k_S = \frac{k_0}{2} \left( \frac{C_{\text{HMDSO}} + C_{\text{HMDSO}}}{2} + \frac{C_{\text{O}_2} + C_{\text{O}_2}}{2} \right).$$

(4)

Fig. 4 shows an Arrhenius plot of the surface reaction rate constant. The surface reaction rate constant could be represented by a single correlation line with a correlation coefficient of 0.62 regardless of the initial O$_2$ mole fraction. The surface reaction rate constant shown in Eq. (6) was obtained.

$$k_s = 8.5 \times 10^{13} \exp \left( \frac{-335000}{R_0 T_{IW}} \right).$$

(6)

Here, $T_{IW}$ [K] is the wall surface temperature. The activation energy value of the surface reaction rate constant $\Delta E$ was 335 kJ/mol.

Even if the $T_i$ was higher than 1373 K, the effective wall temperature range for the surface reaction rate constant was at 1139 K $<$ $T_{IW}$ $<$1219 K. Therefore, we used all experimental conditions for the Arrhenius plots of the surface reaction rate constant.

4.3 Diffusion coefficient

Diffusion coefficient $D$ [m$^2$/s] in CVD was reported by Akiyama et al. and given by

$$D = -\frac{d\ln G_{\text{SiO}_2}}{dz} r^2 u \frac{1}{Sh}.$$

(7)

Here, $d\ln G_{\text{SiO}_2}/dz$ shows the slope of the semi-log plot of the growth rate distribution along the flow axis in the diffusion-controlled region. And $r$, $u$, and $Sh$ show the radius of the quartz short tube, the average gas flow rate in the diffusion-controlled region, and the Sherwood number (= 3.66), respectively.

Fig. 5 shows the dependence of the diffusion coefficient on the average wall temperature in the diffusion-controlled region and on the O$_2$ concentration at about 1260 K. The diffusion coefficient was calculated by using Eq. (7). The keys and lines show the experimental data and the curve-fitting lines of $T_{IW}$. A power 1.75 of temperature was reported by Fuller et al. for polyatomic gas.

The diffusion coefficient of $x_{\text{O}_2,\text{init}} = 0.285$ at about 1260 K was lower than that of $x_{\text{O}_2,\text{init}} = 0.089$ and 0.165. As the colors of the substrate are brownish in Fig. 3 i) and ii), adhesion is poor and the film color is greatly different at $x_{\text{O}_2,\text{init}} = 0.089$ and 0.165. Then, we investigated the growth process at $x_{\text{O}_2,\text{init}} = 0.285$ in this study.

It was found that the diffusion coefficient at 1260 K $\leq T_{IW} \leq 1323$ K differed from that at $T_{IW} \geq 1373$ K. Eq. (8) and Eq. (9) show the diffusion coefficients at 1260 K $\leq T_{IW} \leq 1323$ K and at $T_{IW} \geq 1373$ K, respectively.

$$D = 2.46 \times 10^{-10} T_{IW}^{1.75} (1260 \text{ K} \leq T_{IW} \leq 1323 \text{ K}) \quad (8)$$

$$D = 3.61 \times 10^{-10} T_{IW}^{1.75} (T_{IW} \geq 1373 \text{ K}) \quad (9)$$

The widely spaced dashed line and dashed line with narrow intervals show Eq. (8) and Eq. (9), respectively. The solid line shows Eq. (10) for all temperatures in this study as follows:

$$D = 3.22 \times 10^{-10} T_{IW}^{1.75} (1260 \text{ K} \leq T_{IW} \leq 1423 \text{ K}). \quad (10)$$

Here, we considered the reason that the diffusion coefficient in Eq. (8) was calculated to be smaller than that in Eq. (9). At $T_{IW} \leq 1323$ K, the color of the film on the substrate changed to transparent or transparent white as shown in Fig. 3 (iii) and (iv) as the temperature rose. It was also suggested that the substances produced could change between conditions (iv) and (v). Specifically, it was suggested that the reaction intermediate having a larger molecular...
weight than that of the SiO$_2$ could be generated and deposited at 1260 K $\leq T_a \leq 1323$ K, while SiO$_2$ with sufficiently advanced thermal decomposition could be generated and deposited at $T_a \geq 1323$ K.

Here, the binary diffusion coefficient of components A and B below the atmospheric condition has already been established by the Chapman-Enskog theory, and the diffusion coefficient is expressed by the following Eq. (11)

$$D_{ab} = \frac{0.00018583}{\rho_0 \sigma_{ab} \Omega_{ab}} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} T^3$$

Here, $\rho_0$ [atm], $\sigma_{ab}$, $\Omega_{ab}$, $M_A$ and $M_B$ show the operating pressure, collision radius, collision integral, and molecular weight of component A and B. In this study, component A and component B show carrier gases of N$_2$ and remaining O$_2$, and the reaction intermediate during CVD or SiO$_2$, respectively. If the reaction intermediate having a molecular weight was assumed to be higher than that of SiO$_2$ deposited at 1260 K $\leq T_a \leq 1323$ K, the diffusion coefficient could become smaller than that of the carrier gas and SiO$_2$.

### 4.4 Comparison of the experimental growth rate with the calculated growth rate

Fig. 6 shows a normal plot of the growth rate distribution of the SiO$_2$ film along the distance from the heater inlet, $z$. Plots and lines show the experimental and calculated growth rate distributions. The growth rate is maximum near the heater inlet and decreases as the distance from the heater inlet increases.

**Fig. 6** Calculation results of growth rate distribution along the flow axis for the SiO$_2$ film coating with experimental ones.

- **a) $T_s = 1273$ K**
- **b) $T_s = 1323$ K**
- **c) $T_s = 1373$ K**
- **d) $T_s = 1423$ K**
- **e) $T_s = 1473$ K**
calculated results, respectively. The solid line and the broken line show the calculated results using Eq. (10) and Eq. (8) or Eq. (9), respectively. For all conditions, the experimental results could be reproduced by the calculated results before the maximum growth rate when the mass transfer could be controlled by the surface reaction. However, the calculation results disagreed partially with the experimental results after the maximum growth rate when the mass transfer could be controlled by the diffusion. At $T_s = 1273 \text{ K}$ in Fig 6 a), the calculation results of growth rates using Eq. (8) and using Eq. (10) did not agree with the experimental growth rates at $0.1 \text{ m} < z < 0.3 \text{ m}$. However, they did agree using Eq. (10). In Figs. 6 b) and c), calculation results of growth rates using both Eq. (8) or Eq. (9) and using Eq. (10) agreed wholly with the experimental growth rates except for the maximum growth rate. On the other hand, in Figs. 6 d) and e), the calculation results of growth rates using Eq. (9) and using Eq. (10) were higher than that of the experimental growth rates at $0.1 \text{ m} < z < 0.35 \text{ m}$.

4.5 SEM observation of the deposited material on the substrate at the maximum growth rate

In order to investigate the reason that the growth rate could not be reproduced by calculation at $T_s = 1273 \text{ K}$ and $T_s > 1423 \text{ K}$, SEM observation was conducted. Fig. 7 shows SEM images for the original quartz tube and for the deposited material on the quartz tube at several $T_s$. A few small particles deposited on the substrate at $T_s = 1273 \text{ K}$ (condition iii). The precise particulate film deposited on the substrate at $T_s = 1323 \text{ K}$ (condition iv) and at $T_s = 1423 \text{ K}$ (condition vii). On the other hand, at $T_s = 1473 \text{ K}$ (condition vii), the deposited material had not only precise particulate film but also particles of about 40 $\mu\text{m}$, and the surface morphology was very complex. In comparing these SEM images with the photographs of the substrate as shown in Fig. 3, particles rather than the particulate film could be easily formed when the color of the substrate became white. As particle formation could control mass transfer at $T_s = 1273\text{ K}$ and $T_s > 1423 \text{ K}$, the growth rate could not be reproduced by calculation.

Therefore, it was found that the estimated surface reaction rate in this study could be apparent surface reaction rate with no influence of particle formation. It was also suggested that the diffusion coefficient in Fig. 5 could be the apparent diffusion coefficient with the effect of particle formation. In future work, according to the estimation of the particle formation rate by using the membrane filter, the growth rate distribution could be reproduced by numerical calculation with not only surface reaction but also particle formation.

5. Conclusion

This paper investigated the growth rate of SiO$_2$ solid film on substrates using thermal CVD in a horizontal tubular reactor experimentally and numerically. The following conclusions were obtained.

By using the differential reactor model, the apparent surface reaction rate taking no particle formation into
consideration could be represented by a single correlation line even if the initial mole fraction of O\textsubscript{2} changed. The activation energy of the apparent surface reaction rate constant was 335 kJ/mol.

For all conditions, the experimental results for the growth rate of CVD was reproduced by the calculation ones before the maximum growth rate when the mass transfer could be controlled by the apparent surface reaction. On the other hand, the calculation results for the growth rate of CVD disagreed to some extent with the experimental ones after the maximum growth rate when the mass transfer could be controlled by diffusion of the precursor.

By the observation of SEM images, the mass transfer in this CVD could include not only surface reaction but also particle formation. It was also suggested that the diffusion coefficient could become the apparent coefficient with the effect of particle formation. In future work, according to the estimation of the particle formation rate by using a membrane filter, the growth rate distribution could be reproduced by numerical calculation with not only surface reaction but also particle formation.

\[ \Delta E \] : Activation energy of the surface reaction [J/mol]
\[ \Delta M \] : Total mass of deposited SiO\textsubscript{2} [kg]
\[ \sigma_{AB} \] : Collision radius of molecule A and B in Eq. 11 [Å]
\[ \Omega_{AB} \] : Collision integral in Eq. (11) [-]

Greek symbol
\[ \Delta \] : Inner surface area of the \( i \)-th quartz tube [m\textsuperscript{2}]
\[ S_h \] : Sherwood number [-]
\[ T_S \] : Setting temperature on the outer wall of the tubular reactor which was regulated by the thermostat of the electric furnace [K]
\[ T_{av} \] : Average wall temperature in the diffusion-controlled region [K]
\[ T_{IW,i} \] : Wall temperature of the \( i \)-th substrate [K]
\[ u \] : Average gas flow rate in the diffusion limited zone [m/s]
\[ W_0 \] : Amount of HMDSO supplied [kg/s]
\[ x_{O2} \] : Oxygen mole fraction [-]
\[ z \] : Distance from heater inlet [m]

**Nomenclature**
- \( C_{\text{HMDSO}} \): Molar concentrations of HMDSO [mol/m\textsuperscript{3}]
- \( C_{O2} \): Molar concentration of O\textsubscript{2} [mol/m\textsuperscript{3}]
- \( D \): Diffusion coefficient by Akiyama et al. \textsuperscript{31} [m\textsuperscript{2}/s]
- \( D_{ab} \): Diffusion coefficient by Chapman-Enskog theory \textsuperscript{12} [m\textsuperscript{2}/s]
- \( G_{SiO2} \): Growth rate of deposited SiO\textsubscript{2} of the \( i \)-th quartz tube [m/s]
- \( k_s \): Surface reaction rate constant [kg/m\textsuperscript{2}/s]
- \( M_A \): Molecular weight of A in Eq. (11) [g/mol]
- \( M_B \): Molecular weight of B in Eq. (11) [g/mol]
- \( m_{wi} \): Mass of the \( i \)-th short quartz tube before experiment [kg]
- \( m_i \): Mass of the \( i \)-th short quartz tube after experiment [kg]
- \( M_{SiO2} \): Molecular weight of SiO\textsubscript{2} [kg/mol]
- \( N_{SiO2} \): Growth rate obtained using a differential reactor model [mol/m\textsuperscript{3}/s]
- \( p \): Operating pressure in Eq. (11) [atm]
- \( P \): Operating pressure [Pa]
- \( r \): Radius of the quartz short tube [m]
- \( R_0 \): Universal gas constant (= 8.314 J/mol/K) [J/mol/K]

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