Heat and Mass Transfer Analysis during SiO₂ Film Coating by Thermal CVD

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This paper experimentally and numerically investigates the growth rate of SiO₂ film by thermal CVD from the oxidization of hexamethyldisiloxane in a horizontal tubular reactor. The control steps of the mass transfer were changed from the surface reaction to the diffusion of raw material. By using the differential reactor model, the surface reaction rate was dependent on not only the first order of the hexamethyldisiloxane concentration, but also the power 0.55 of the oxygen concentration. The activation energy of the reaction rate constant was 127 kJ/mol. In the diffusion control step, the apparent diffusion coefficient was obtained by Akiyama's model and dependent on the power 1.75 of the temperature. Except for the diffusion control step, the growth rate distribution was partly reproduced by numerical simulation of heat and mass transfer using the chemical reaction.

Key Words
Chemical Vapor Deposition, SiO₂ Thin Film, Differential Reactor Model, Diffusion-Controlling Step, Numerical Simulation

1. Introduction

The thermal chemical vapor deposition (CVD) 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). For example, it is possible to deposit immediately thin film on a large amount of substrates with complex surface shapes. On the other hand, there is a disadvantage that suitable conditions differ for every raw material due to their mass transfer mechanisms that have chemical reactions 2) 3) 6). In order to present a feasible design criteria for the thermal CVD reactor, it is necessary to understand heat and mass transfer using the chemical reaction.

Monosilane frequently used for SiO₂ film coating has extremely pyrophoric, and tetraethoxysilane has pyrophoric it reacts explosively with water and is toxic to human body. extremely dangerous for laboratory use. On the other hand, hexamethyldisiloxane is suitable for both laboratory and industrial use because it has low reactivity with water, low self-ignition and low flammability, high safety, and easy handling. For these reasons, hexamethyldisiloxane was used in this study. In addition, plasma CVD is often performed in the formation of SiO₂ film using hexamethyldisiloxane. However, large-scale equipment is required to achieve high vacuum. Therefore, the film was formed by the thermal CVD method that enables film formation even at atmospheric pressure.

Heat and mass transfer during thermal CVD have been studied experimentally and numerically 3) 4) 6). Tago et al. used a tubular thermal CVD reactor to form thin films and reported appropriate mass transfer models by kinetic analysis 3. From their model, the raw material reacted to a precursor of the film by the gas phase reaction. Then, the precursor diffused rapidly to the heated substrate. Finally, the film was deposited on the substrate by the surface
reaction. Y. Hatori, K. Tanoue et al. investigated the growth rate of thin films using the thermal CVD method in a horizontal hot-wall tubular reactor experimentally and numerically. They concluded that the control step of mass transfer during CVD changed from a surface reaction to the diffusion of raw material. However, as the mass transfer process during CVD would be changed by the raw material, it is unclear whether the process could be expressed by the mass transfer model of Y. Hatori, K. Tanoue et al.

In this study, the SiO₂ film coating from the vapor of hexamethyldisiloxane was conducted experimentally using a horizontal tube thermal CVD reactor that focused on the effect of the temperature and initial oxygen mole fraction. Furthermore, numerical simulation for heat and mass transfer using the chemical reaction during CVD was conducted and compared with the experimental results.

2. Experimental

Fig. 1 shows the experimental apparatus that consists of a supply section for a carrier gas and a raw material, a reactor and a gas treatment section at the outlet of the reactor. The raw material is stored in a glass tank using hexamethyldisiloxane (HMDSO). The temperature of the liquid material in the tank was controlled 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 partly heated by an electric furnace (Chugai and Plox Co., Ltd., R32 / 250/12-P320). In order to evaluate the deposition rate of silicon dioxide (SiO₂) at each position, short quartz tubes (outer diameter 9 mm, inner diameter 7 mm, length 5 to 20 mm) were installed into the heated section (length = 400 mm) in the reactor.

After the carrier gases of nitrogen (N₂) and oxygen (O₂) were fed into the reactor, the temperature at the outer wall of the reactor was heated up to the desirable setting temperature Tₛ by the electric furnace. When the wall temperature approached Tₛ, the desirable mole fraction of HMDSO vapor was fed into the reactor by bubbling of another nitrogen gas from the tank. The feed rate of the HMDSO vapor was calibrated beforehand by the bubbling gas flow rate of nitrogen. Then, the chemical reaction was started as the following equation.

\[ \text{O[Si(CH₃)₂] + 12O₂} \rightarrow 2\text{SiO₂} + 9\text{H₂O} + 6\text{CO₂} \]  

The vapor of HMDSO was collected by a cold trap in the liquid nitrogen and measured just before the CVD experiment. In order to evaluate the kinetics in SiO₂ film coating, the temperature distribution at the inner wall of the quartz tube along the flow axis was measured using a K type sheath thermocouple without HMDSO vapor. The total pressure and total gas flow rate were 50700 Pa and 2 SLM (Standard Liter per Minute), respectively. The setting temperature at the reactor wall Tₛ was changed from 1323 K to 1473 K. The mole fraction of oxygen was 0.05 or 0.85. The mole fraction of HMDSO was about 0.0004 and the experimental time was 20 min.

3. Numerical Simulation

Two-dimensional numerical simulation in the horizontal reactor in O[Si(CH₃)₂]-O₂-N₂ system was conducted. Table 1 shows the governing equations for the numerical simulation. Fig. 2 shows the calculation domain and boundary conditions. These governing equations and boundary conditions were discretized by the control volume method and solved by the THOMAS method. The velocity and pressure profiles were solved by the SIMPLE method.
Table 1 Continuity, Navier-Stokes equation, Energy balance and Mass balance of HMDSO during SiO2 thermal CVD

| Source of Mass | Equation |
|----------------|----------|
| Continuity     | \[ \frac{1}{r} \frac{\partial}{\partial r} (r \rho u) + \frac{\partial \rho w}{\partial z} = 0 \] |
| Navier-Stokes (r direction) | \[ \frac{1}{r} \frac{\partial}{\partial r} (r \rho u u) + \frac{\partial \rho w v}{\partial z} = - \frac{\partial p}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rr}) - \frac{\partial \tau_{rz}}{\partial z} \] |
| Navier-Stokes (z direction) | \[ \frac{1}{r} \frac{\partial}{\partial r} (r \rho w u) + \frac{\partial \rho w^2}{\partial z} = - \frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) - \frac{\partial \tau_{rr}}{\partial z} \] |
| Energy balance | \[ \frac{1}{r} \frac{\partial}{\partial r} (r \rho C_p u T) + \frac{\partial \rho C_p w T}{\partial z} = \frac{\partial}{\partial r} \left( r \lambda \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( r \lambda \frac{\partial T}{\partial z} \right) \] |
| Mass balance for HMDSO | \[ \frac{1}{r} \frac{\partial}{\partial r} (r \rho_y HMDSO u) + \frac{\partial \rho_y HMDSO w}{\partial z} = r \rho_D + \rho_D \left( \frac{\partial \rho_y HMDSO}{\partial r} \right) \] |

4. Results and Discussion

4.1 Growth rate distribution of SiO2 film

Fig. 3 shows both the semi-log plot of the growth rate distribution of the SiO2 film and normal plot of temperature distribution along the flow axis. In Fig. 3 (a) for \( x_{O_2, \text{init}} = 0.05 \) and \( T_S = 1323 \) K, the film coating was started at \( z = 0.09 \) m. The growth rate and the temperature increased with the position at \( 0.1 < z < 0.2 \) m. Mass transfer in CVD has been reported to consist of three rate-limiting processes: (i) diffusion of raw material, (ii) gas phase reaction, and (iii) surface reaction. In this study, as the gas phase reaction will be assumed to be very fast among these three, and
mass transfer is considered to be composed of (i) diffusion of raw material and (ii) surface reaction. In the region before the maximum growth rate, as the growth rate increased with the temperature, the film formation process could be surface reaction rate limited. Here, surface reaction refers to the reaction in which the film forming precursor is converted to a solid film on the surface of the substrate. At \( z = 0.2 \) m, the growth rate decreased exponentially with the position because in the second section mass transfer was controlled by the diffusion \(^5\). The gradient of the growth rate was utilized to estimate the diffusion coefficient. The growth rate distribution for \( T_S = 1473 \) K did not differ much from that for \( T_S = 1323 \) K. However, the maximum growth rate at \( T_S = 1473 \) K was shifted to more upstream side than that at \( T_S = 1323 \) K because the surface reaction could be promoted. The higher the wall temperature made the greater the gradient of the growth rate. In Fig. 3 (b) for \( x_{O2,init} = 0.85 \) and \( T_S = 1323 \) K, the film coating was started faster than that for \( x_{O2,init} = 0.05 \) and \( T_S = 1323 \) K because the surface reaction was dependent on the oxygen concentration. Although there was some variation at \( 0.2 < z < 0.3 \) m, the gradient of the growth rate along the flow axis at the diffusion controlled region was also greater than that for \( x_{O2,init} = 0.05 \) and \( T_S = 1323 \) K. The higher the concentration of oxygen made the greater the gradient of the growth rate.

### 4.2 Surface reaction rate constant

As shown in Fig. 4, the HMDSO mass flow rate of the \( i \) th quartz short pipe was calculated by the mass balance in the region considered to be the surface reaction rate limit using the differential reactor model \(^6\).

\[
G_{\text{HMDSO}} - G_{\text{HMDSO},i+1} = \frac{1}{2} G_{\text{SiO}_2} \cdot \frac{M_{\text{SiO}_2}}{M_{\text{HMDSO}}}
\]

Where \( G_{\text{HMDSO}} \) [kg/s], \( G_{\text{SiO}_2} \) [kg/s], \( M_{\text{HMDSO}} \) [kg/mol] and \( M_{\text{SiO}_2} \) [kg/mol] show the mass flow rate of HMDSO, the film formation rate of \( \text{SiO}_2 \), molecular weight of HMDSO and molecular weight of \( \text{SiO}_2 \), respectively.

By the same process, the mass flow rates of \( \text{O}_2, \text{CO}_2 \) and \( \text{H}_2\text{O} \) would be obtained. The mole fraction of HMDSO \( x_{\text{HMDSO}} \) is given by the following equation.

\[
x_{\text{HMDSO}} = \frac{G_{\text{HMDSO},i} M_{\text{HMDSO}}}{G_{\text{O2},i} M_{\text{O2}} + G_{\text{CO2},i} M_{\text{CO2}} + G_{\text{H2O},i} M_{\text{H2O}} + G_{\text{N2},i} M_{\text{N2}}}
\]

Where \( G_{\text{i,j}} \) [kg/s] and \( M_{\text{i}} \) [kg/mol] show the mass flow rates of component \( i \) and molecular weight of component \( j \), respectively.

The molar concentration of HMDSO \( C_{\text{HMDSO}} \) is expressed by Eq. (4).

\[
C_{\text{HMDSO}} = \frac{P}{R T_{wall} x_{\text{HMDSO}}}
\]

Where \( P \) [Pa], \( R \) [J/(K mol)] and \( T_{wall} \) [K] show the operating pressure, the universal gas constant and the wall temperature, respectively.

If the chemical reaction during \( \text{SiO}_2 \) film coating is assumed by the first order reaction of HMDSO, the deposition rate \( N_{\text{SiO}_2} \) [mol/m\(^2\)/s] is expressed by.

\[
N_{\text{SiO}_2} = G_{\text{HMDSO}} \cdot \frac{M_{\text{SiO}_2}}{M_{\text{HMDSO}}} \frac{k_{\text{S}}}{S} C_{\text{HMDSO}} = G_{\text{HMDSO}} \cdot \frac{M_{\text{SiO}_2}}{M_{\text{HMDSO}}} \frac{k_{\text{S}}}{S} \frac{C_{\text{HMDSO}}}{2}
\]

Accordingly,

\[
k_{\text{S}} = \frac{G_{\text{SiO}_2}}{M_{\text{SiO}_2} C_{\text{HMDSO}}} \cdot \frac{1}{S}
\]

Where \( k_{\text{S}} \) [m/s] and \( S \) [m\(^2\)] show the surface reaction rate constant and the surface area of the quartz short tube, respectively.

As shown in Fig. 5 (a), the surface reaction rate constant during chemical vapor deposition of the \( \text{SiO}_2 \) film for \( x_{O2,init} = 0.05 \) was different from that for \( x_{O2,init} = 0.85 \).

\[
k_{\text{S}} x_{O2,init} = 20020 \exp \left( \frac{-117000}{R T_{wall}} \right)
\]

\[
k_{\text{S}} x_{O2,init} = 7580 \exp \left( \frac{-144000}{R T_{wall}} \right)
\]

As shown in Eq. (1), if the chemical reaction rate during the CVD depended not only on the first order of the concentration of HMDSO but also the power \( n \) of the concentration of oxygen, the growth rate could be expressed by Eq. (9).

\[
N_{\text{SiO}_2} = G_{\text{HMDSO}} \cdot \frac{M_{\text{SiO}_2}}{M_{\text{HMDSO}}} C_{\text{O2}}^n
\]

The power \( n \) was about 0.55 from the curve fitting. Fig. 5 (b) shows the Arrhenius plot of the modified surface reaction rate constant during CVD. From this Arrhenius plot, both of the rate constants for \( x_{O2,init} = 0.05 \) and for \( x_{O2,init} = 0.85 \) can be represented by one approximate straight line.
Since the frequency factor indicated by the intercept of this approximate straight line was 8940 and the gradient indicates the ratio $\Delta E/R_0$ of the activation energy to the general gas constant, which indicated that the activation energy $\Delta E$ was 127 kJ/mol. With these facts, both of the rate constants for $x_{O_2,\text{init}} = 0.05$ and for $x_{O_2,\text{init}} = 0.85$ could be expressed by Eq. (10).

$$k' = 8940 \exp \left( \frac{127,000}{R_0 T_W} \right)$$  \hspace{1cm} (10)

### 4.3 Diffusion coefficient

The diffusion coefficient $D$ [m$^2$/s] in CVD was reported by Y. Akiyama$^3$ and given by,

$$D = -\frac{d(\ln N_{\text{SiO}_2})}{dz} \frac{1}{r u S_h}.$$  \hspace{1cm} (11)

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

As shown in Fig. 3, the higher the wall temperature and the higher the concentration of oxygen made the higher the gradient of the growth rate along the flow axis. Fig. 6 shows the dependence of the diffusion coefficient on the average temperature in the section of the diffusion controlled region for $x_{O_2,\text{init}} = 0.05$ and for $x_{O_2,\text{init}} = 0.85$. The keys and lines show the experimental data and the curve fitting lines of $T_w^{1.75}$, respectively. The power 1.75 of temperature was reported by E. N. Fuller et al. for the polyatomic gas$^7$. The diffusion coefficient could be explained by $T_w^{1.75}$ with some variation. The diffusion coefficient for $x_{O_2,\text{init}} = 0.85$ was higher than that for $x_{O_2,\text{init}} = 0.05$. Although the growth rate distribution may correlate with the particle formation as described in a later section, the reason is unknown. In order to understand this mechanism, the diffusion coefficient will be investigated under no particle formation in future work. As a specific countermeasure, in order to prevent the formation of particles, it is necessary to form a film in an experimental apparatus under reduced pressure conditions. In addition, when powder is generated even under reduced pressure conditions, it is considered necessary to observe the appearance of particles by SEM and measure the particle diameter.

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

Fig. 7 shows the normal plot of the growth rate distribution of SiO$_2$ film along the route from heater inlet, $z$. Plots and lines show the experimental and calculated results, respectively. The calculated results agreed partly with the experimental results before the peak of the growth rate except for $x = 0.05$ and $T = 1323$ K. However, the calculated growth rate of SiO$_2$ decreased more slowly
along the axial position than that of the experimental results after the peak. If excessive nucleation had occurred in the gas phase, the particles rather than the film coating would be formed on the substrate under these atmospheric conditions at 50663 Pa. In order to investigate the effect of the particle formation, a membrane filter was set at the outlet of the heater and the thermal CVD experiment was conducted. As Fig. 8 shows, on the membrane filter some particles were formed in the heater and exhausted from the outlet of the heater. In Table 2, the mass of particles was about twice that of the film mass. Therefore, the calculation growth rate after the peak without particle formation was higher than that for the experimental growth rate.

In future work, film coating experiments under a low pressure condition will be conducted without particles.

5. Conclusion

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

1) The control steps of mass transfer were changed from the surface reaction to the diffusion of raw material.
2) By using the differential reactor model, the surface reaction rate was dependent on not only the first order of the hexamethyldisiloxane concentration, but also the power 0.55 of the oxygen concentration. The activation
energy of the reaction rate constant was 127 kJ/mol.

3) In the diffusion control step, the apparent diffusion coefficient was obtained by Akiyama’s model and was dependent on the power 1.75 of the temperature.

4) Except for the diffusion control step, the growth rate distribution was partly reproduced by the numerical simulation of heat and mass transfer using the chemical reaction.

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