

The effects of initial gas composition and pressure on the growth behavior of CVD SiC films

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The effects of pressure from 5 torr to 40 torr and the alteration of diluent gas species on the growth rate and structure of deposits have been studied. The experimental results showed that the deposition rate increased with increasing total pressure for a H₂ diluent system and decreased for N₂. The reactant depletion effect increased especially with an ambient H₂ diluent gas. As the diluent gas was added, the deposition rate decreased parabolically, especially for H₂ ambient. The theoretical relation between deposition rate and partial pressures of methyltrichlorosilane (MTS) and H₂ was in a good accordance with experimental results.

Key words: CVD, Silicon Carbide, reactant depletion, boundary layer, deposition rate.

Introduction

Silicon Carbide (SiC) made by chemical vapor deposition (CVD) has good properties such as excellent hardness and chemical resistance at high temperatures. The properties of SiC coatings are affected by the many kinds of deposition parameters such as temperature, pressure, diluent gases and system geometry [1-2]. Temperature has been widely investigated as a parameter which affects the kinetics of deposition and morphology of SiC deposits. At high temperatures, the deposition kinetics is controlled by a mass transfer reaction and at low temperatures, the kinetics are controlled by a surface reaction. The effect of diluent gas input ratio on growth behavior also had been studied widely.

Many investigators have studied the relationships between deposition rate and growth kinetics of CVD β -SiC using MTS (methyltrichlorosilane CH₃SiCl₃) [3-9]. Most of the previously reported studies have used hydrogen (H₂) as a carrier and diluent gas. The use of a MTS-H₂ mixture system has given many different results according to deposition parameters. On the basis of these studies, several researches have been performed concerning the variation of the characteristics of CVD-SiC films when argon (Ar) was used as a diluent gas precursor and about the comparison of CVD-SiC films using H₂ as the diluent gas system with the films using the Ar precursor system. Kobayashi *et al.* [4] showed the H₂, H₂+Ar and Ar diluent gas effect. For all temperature ranges (i.e. 1000 ≤ T ≤ 1500°C), they

noticed the growth rate of SiC was higher in H₂ than in the presence of Ar. By contrast, Nordell *et al.* [10] reported that the growth rate with pure Ar carrier gas was higher than that for the Ar/H₂ mixture. Kim and Choi [5] reported that below 1150°C, the deposition rate of SiC films using H₂ as a diluent gas was higher than that of films using Ar, but above 1200°C, the opposite result was observed. However, the effects of other gas species such as N₂ as diluent or carrier gas for preparing CVD SiC films have not been reported.

The aim of the present study is to compare the effect of diluent gases H₂ and N₂ on the growth of CVD-SiC films. According to deposition position, we determined the growth rate change with pressure and input gas composition. We also investigated the partial pressure effects of hydrogen and MTS on the deposition rate theoretically and experimentally.

Experimental Details

The deposition experiments were performed in a horizontal hot wall low pressure chemical vapor deposition (LPCVD) reactor as previously described [6]. Three deposition positions in the same batch, each separated by 3.54 cm, were chosen in the gas flow direction, and denoted as D1, D2, and D3. (Hereafter, we refer to each deposition position as D1, D2, and D3 in this report.) D2 had the maximum temperature in the reactor, but the difference of temperature between D1 and D2 or D2 and D3, was within 10°C for the whole range of deposition temperatures. The graphite susceptor was tilted at about 10° for the diminution of reactant depletion. Silicon carbide was deposited onto isotropic graphite that had similar thermal expansion coefficient to that of SiC using MTS, and a hydrogen or nitrogen gaseous mixture. MTS was chosen because it has the

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equivalent ratio of Si to C and gives a relatively low thermal decomposition temperature. Hydrogen was used as the carrier gas, this transfers source precursor through the bubbler to the main reactor. Hydrogen or nitrogen was used as the diluent gas, this regulates the concentration of the mixture involving the MTS vapor and carrier gas. Diluent gas and carrier gas containing MTS vapor were mixed with each other before being introduced into the reactor. The flow rate of MTS vapor was fixed at 100 sccm by adjusting the bubbler pressure and the flow rate of the carrier gas (H_2) was adjusted so that the temperature of the bubbler containing liquid MTS was maintained at $0^\circ C$. The pressure in the reactor was monitored with a capacitance manometer and controlled with a throttle valve located between the reactor and the mechanical pump. The deposition pressure ranged from 5 torr to 40 torr and the deposition temperature was fixed at $1300^\circ C$. The input gas ratio of diluent plus carrier gas to MTS, $\alpha = P_{(diluent+carrier)}/P_{MTS}$ was varied from 1 to 10 and the total pressure was fixed at 10 torr.

The deposition rates were obtained by the weight gain of as-deposited films divided by the substrate area and time.

Results and Discussion

The reactant depletion effects on the growth rate of SiC as a function of pressure have been investigated for two different diluent gases H_2 and N_2 are shown in Fig. 1 and 2 respectively, whose slopes from D1 to D3 indicate the degree of the depletion effect. In the pure H_2 atmosphere, the reactant depletion effect occurred,

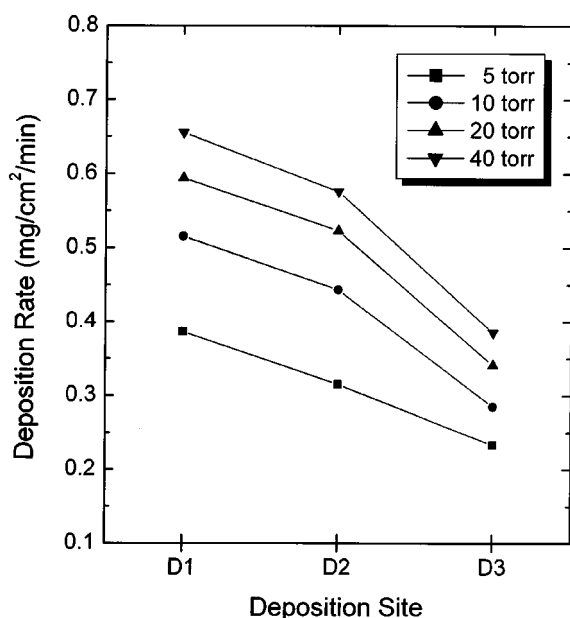


Fig. 1. The variation of deposition rate of SiC films with deposition pressure and deposition site. ($T_{dep}=1300^\circ C$, MTS(source): H_2 (carrier): H_2 (dilute)=1:1:3).

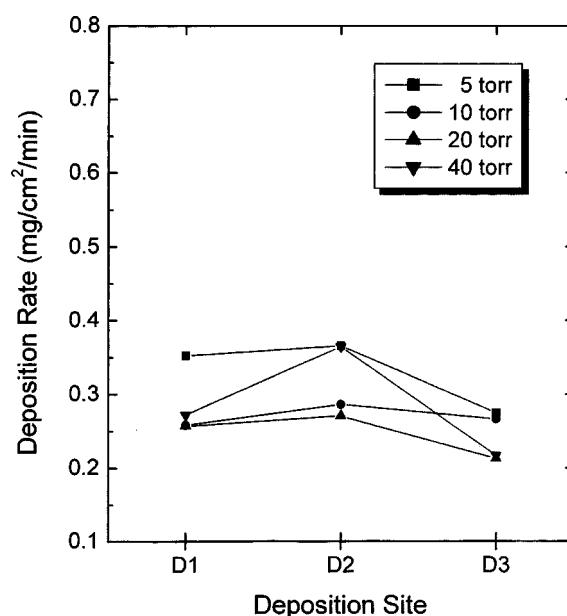


Fig. 2. The variation of deposition rate of SiC films with deposition pressure and deposition site. ($T_{dep}=1300^\circ C$, MTS(source): H_2 (carrier): N_2 (dilute)=1:1:3)

while there is no dependence of the depletion effect on the pressure because of the same slopes of the growth rate. For the N_2 diluent system, the reactant depletion effect has been lessened. This is especially true in the case of a pressure of 40 torr, where the growth rate increase occurred at D2 position that is in the relatively hot-zone of the horizontal system.

The growth rates that are sum of each position, D1, D2 and D3 are plotted as a function of total pressure, in Fig. 3, for two the different diluent gases. The growth rate increased with pressure for the H_2 diluent system,

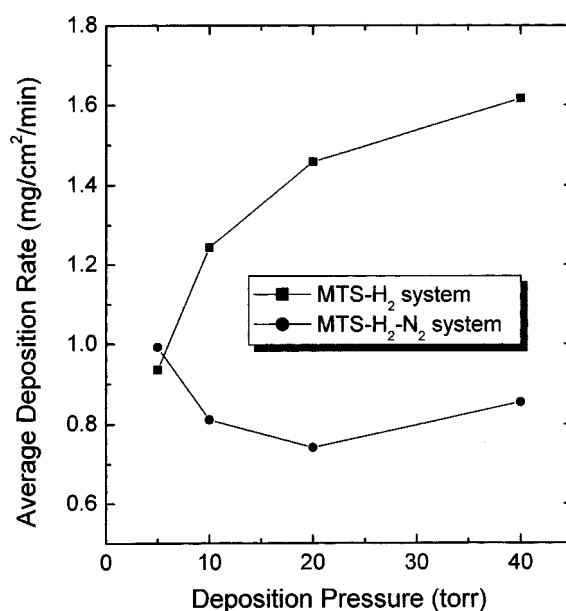


Fig. 3. Growth rate comparison with different diluent gases and deposition pressure. ($T_{dep}=1300^\circ C$, 1 hr, source:dilute=1:4).

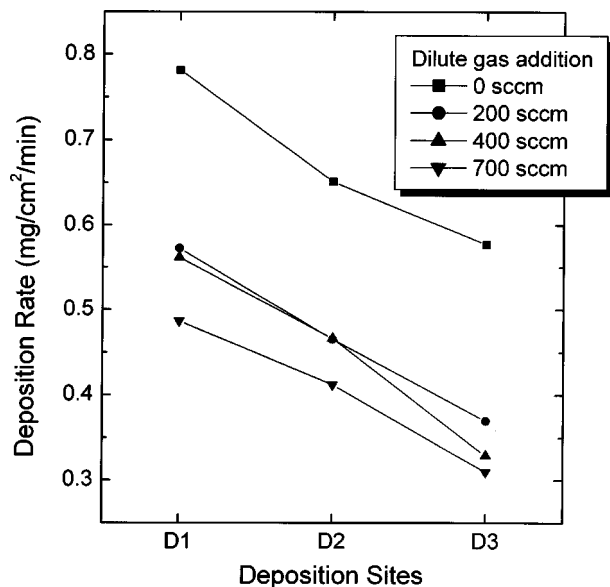


Fig. 4. The variation of deposition rate of CVD SiC with diluent gas addition and deposition sites ($T_{\text{dep}}=1300^{\circ}\text{C}$, $P_{\text{tot}}=10$ torr, H_2 diluent system).

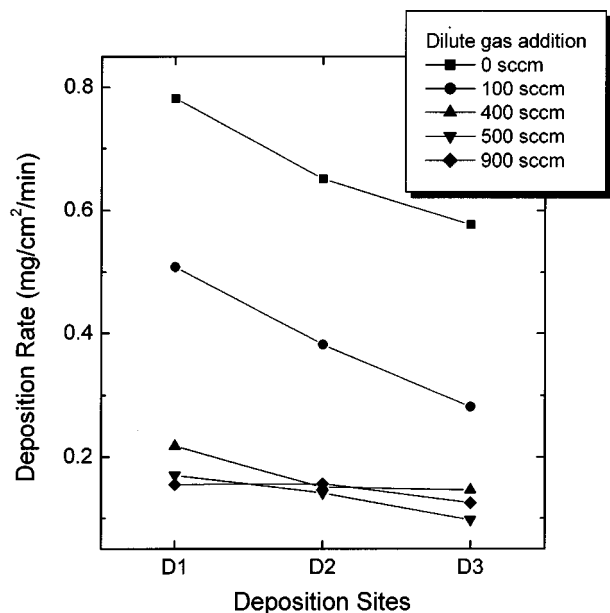


Fig. 5. The variation of deposition rate of CVD SiC with diluent gas addition and deposition sites ($T_{\text{dep}}=1300^{\circ}\text{C}$, $P_{\text{tot}}=10$ torr, N_2 diluent gas system).

otherwise for N_2 diluent system the growth rate decreased with pressure.

The reactant depletion effects on the growth rate of SiC as a function of diluent gas addition have been investigated for two different diluent gases H_2 and N_2 and are shown in Fig. 4 and 5 respectively. For both cases, the depletion effect occurred. For the N_2 diluent system, the depletion effect decreased with an increment of diluent gas addition. The reactant depletion is not only related to the pre-deposition on the wall of the tube and the front side of susceptor but also to the

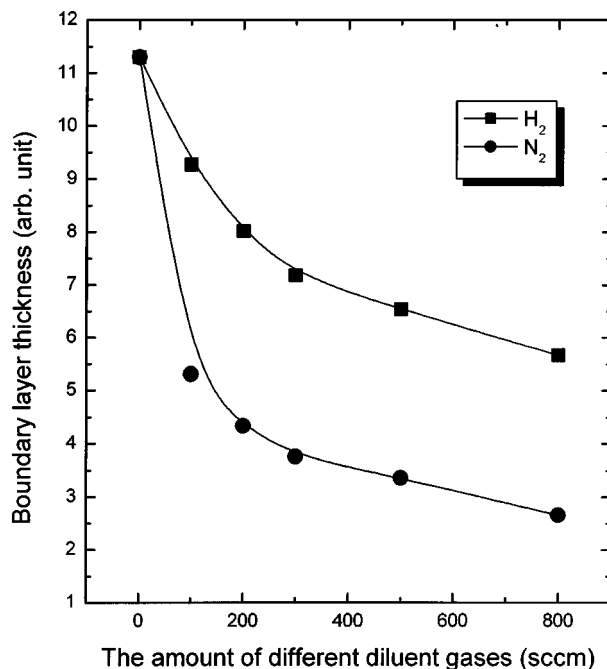


Fig. 6. Growth rate comparison with different diluent gases and diluent gas additions: ($T_{\text{dep}}=1300^{\circ}\text{C}$, $P_{\text{tot}}=10$ torr).

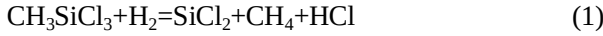
deposition kinetics that was established in a previous report [9]. For the H_2 diluent system, we showed the deposition condition at 1300°C was a mass transfer governed region and the N_2 diluent system, was a surface reaction controlled region. When the surface reaction governs the deposition kinetics the deposition rate is controlled by the degree of surface activation. Since the D2 position is relatively hot compared with D1 and D3, so the growth rate is higher at the D2 position.

The sum of the growth rates of each position with the different diluent systems are compared in Fig. 6 as a function of the initial gas composition. The H_2 diluent system showed a lower degree of decrement in growth rate compared to the N_2 diluent system. For the H_2 diluent system, the growth rates decreased from 0 to 200 sccm and remained nearly constant up to 800 sccm. For the N_2 diluent system, the growth rate drastically decreased from 0 to 400 sccm.

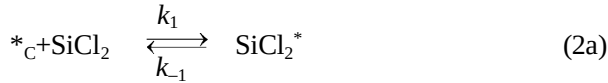
A total pressure increment makes the gas mixtures reside longer in the reaction tube and this causes the same effect of total flow increase by addition of diluent gases. According to the boundary layer theory [11], the thickness of the boundary layer decreases with increasing total pressure. This is the reason why surface reaction kinetics overwhelmed the process at elevated pressures. Accordingly, for both diluent gas systems, growth kinetics can be governed by a surface reaction at higher pressures.

From a comparison of the effects of different types of diluent gases on growth rates, hydrogen may participate in the MTS decomposition and SiC formation.

CVD SiCs are formed by intermediate gases that are made from decomposed MTS. Two major intermediate gas species are carbon-bearing species and silicon-bearing species [4, 12-14]. Carbon-bearing intermediates are known to be CH_4 , C_2H_2 . Silicon-bearing intermediates are known to be SiCl_2 , SiCl_3 , SiCl_4 . Here, we assumed that the main gas species were CH_4 and SiCl_2 for SiC deposition from MTS. Also we assumed steady state, the adsorbed intermediate gases are in a steady state and thus the overall reaction is:



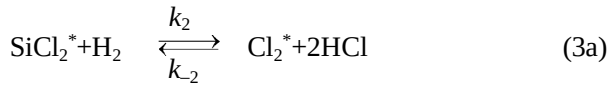
Each intermediate species adsorbs on surface free sites.



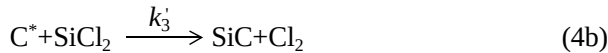
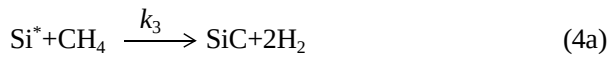
where, * : free surface site

k_1, k_{-1} : reaction constant for adsorption and desorption
 $\text{SiCl}_2^*, \text{CH}_4^*$: adsorbed species

adsorbed SiCl_2 and CH_4 react with hydrogen and chlorine gases.



adsorbed Si^* and C^* react with CH_4 and SiCl_2 , respectively and form silicon carbide.



From the equations (4a) and (4b), the equation of the growth rate is

$$R_1 = k_3 \theta_{\text{Si}} P_{\text{CH}_4} \quad (5a)$$

$$R_2 = k_3' \theta_{\text{C}} P_{\text{SiCl}_2} \quad (5b)$$

where R_1, R_2 : growth rate

$\theta_{\text{Si}}, \theta_{\text{C}}$: the fraction of Si and C free surface sites
 $P_{\text{CH}_4}, P_{\text{SiCl}_2}$: partial pressure of CH_4 and SiCl_2

From the steady state assumption, if the concentrations of Si, C, SiCl_2 and CH_4 are not changed with time, the expression will be

$$\frac{d\theta_{\text{Si}}}{dt} = k_2 \theta_{\text{SiCl}_2} P_{\text{H}_2} - k_{-2} \theta_{\text{Si}} P_{\text{HCl}}^2 - k_3 P_{\text{CH}_4} = 0 \quad (6a)$$

$$\frac{d\theta_{\text{C}}}{dt} = k_2' \theta_{\text{CH}_4} P_{\text{Cl}_2} - k_{-2}' \theta_{\text{C}} P_{\text{HCl}}^2 - k_3' P_{\text{SiCl}_2} = 0 \quad (6b)$$

$$\begin{aligned} \frac{d\theta_{\text{SiCl}_2}}{dt} &= k_1 [*_\text{C}] P_{\text{SiCl}_2} - k_{-1} \theta_{\text{SiCl}_2} - k_2 \theta_{\text{SiCl}_2} P_{\text{H}_2} \\ &\quad + k_{-2} \theta_{\text{Si}} P_{\text{HCl}}^2 = 0 \end{aligned} \quad (7a)$$

$$\begin{aligned} \frac{d\theta_{\text{CH}_4}}{dt} &= k_1' [*_\text{Si}] P_{\text{CH}_4} - k_{-1}' \theta_{\text{CH}_4} - k_2' \theta_{\text{CH}_4} P_{\text{Cl}_2} \\ &\quad + k_{-2}' \theta_{\text{C}} P_{\text{HCl}}^2 = 0 \end{aligned} \quad (7b)$$

where $[*_\text{Si}], [*_\text{C}]$: the density of free surface site in equation (3), the terms of k_{-2} and k_{-2}' can be neglected since the forward reaction is dominant. Equations (6) and (7) become

$$\theta_{\text{Si}} = \frac{k_2 \theta_{\text{SiCl}_2} P_{\text{H}_2}}{k_3 P_{\text{CH}_4}} \quad (8a)$$

$$\theta_{\text{C}} = \frac{k_2' \theta_{\text{CH}_4} P_{\text{Cl}_2}}{k_3' P_{\text{SiCl}_2}} \quad (8b)$$

$$\theta_{\text{SiCl}_2} = \frac{k_1 [*_\text{C}] P_{\text{SiCl}_2}}{k_{-1} + k_2 P_{\text{H}_2}} \quad (9a)$$

$$\theta_{\text{SiCl}_2} = \frac{k_1' [*_\text{Si}] P_{\text{CH}_4}}{k_{-1}' + k_2' P_{\text{Cl}_2}} \quad (9b)$$

$[*_\text{Si}]$ and $[*_\text{C}]$ can be written

$$[*_\text{C}] = n_0 - \theta_{\text{SiCl}_2} - \theta_{\text{Si}} \quad (10a)$$

$$[*_\text{Si}] = n_0 - \theta_{\text{CH}_4} - \theta_{\text{C}} \quad (10b)$$

where n_0 : total number of sites

Here, since $\theta_{\text{SiCl}_2} \gg \theta_{\text{Si}}$ and $\theta_{\text{CH}_4} \gg \theta_{\text{C}}$, equation (10) be rewritten as

$$[*_\text{C}] \cong n_0 - \theta_{\text{SiCl}_2} \quad (11a)$$

$$[*_\text{Si}] \cong n_0 - \theta_{\text{CH}_4} \quad (11b)$$

K is equilibrium reaction constant in equation (2)

$$\frac{k}{k_{-1}} = \frac{\theta_{\text{SiCl}_2}}{[*_\text{C}] \cdot P_{\text{SiCl}_2}} = K_1 \quad (12a)$$

$$\frac{k}{k_{-1}'} = \frac{\theta_{\text{CH}_4}}{[*_\text{Si}] \cdot P_{\text{CH}_4}} = K_1' \quad (12b)$$

equation (12) is added to (11) and the following relation is obtained:

$$[*_\text{C}] = \frac{n_0}{1 + K_1 \cdot P_{\text{SiCl}_2}} \quad (13a)$$

$$[*_\text{Si}] = \frac{n_0}{1 + K_1' \cdot P_{\text{CH}_4}} \quad (13b)$$

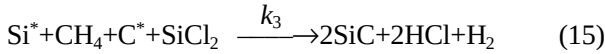
$$\theta_{\text{Si}} = \frac{K_1 k_2 P_{\text{SiCl}_2} \left(\frac{P_{\text{H}_2}}{k_{-1} + k_2 P_{\text{H}_2}} \right) [*_\text{C}]}{k_3 P_{\text{CH}_4}}$$

$$= \frac{n_0 k_1 k_2}{k_3 P_{CH_4}} \left(\frac{P_{H_2}}{k_{-1} + k_2 P_{H_2}} \right) \left(\frac{K_1 P_{SiCl_2}}{1 + K_1 P_{SiCl_2}} \right) \quad (14a)$$

$$\theta_C = \frac{K_1' k_2' P_{CH_4}}{k_3' P_{SiCl_2}} \left(\frac{P_{Cl_2}}{k_{-1}' + k_2' P_{Cl_2}} \right) [^*Si]$$

$$= \frac{n_0 k_1' k_2'}{k_3 P_{SiCl_2}} \left(\frac{P_{Cl_2}}{k_{-1}' + k_2' P_{Cl_2}} \right) \left(\frac{K_1' P_{CH_4}}{1 + K_1' P_{CH_4}} \right) \quad (14b)$$

Overall SiC deposition reaction can be obtained by the sum of reactions (4a) and (4b)



The overall deposition rate thus becomes

$$R = k_3'' \sqrt{\theta_{Si} \theta_C} P_{CH_4}^{1/2} P_{SiCl_2}^{1/2} \quad (16)$$

The relation of the overall deposition rate (16) can be rewritten by adding (14)

$$R = n_0 (k_2 k_2')^{1/2} \sqrt{\frac{P_{H_2}}{1 + a P_{H_2}}} \left(\frac{K_1 P_{SiCl_2}^{1/2}}{1 + K_1 P_{SiCl_2}} \right)$$

$$\sqrt{\frac{P_{Cl_2}}{1 + b P_{Cl_2}}} \left(\frac{K_1 P_{CH_4}^{1/2}}{1 + K_1 P_{CH_4}} \right) \quad (17)$$

where a: k_2/k_{-1}
b: k_2'/k_{-1}'

If intermediate species of $SiCl_2$ and CH_4 are not easily adsorbed, that is to say, if the reaction constant k_1 and k_1' is too small, the relations of $K_1 P_{SiCl_2}^{1/2} \ll 1$ and $K_1' P_{CH_4}^{1/2} \ll 1$ are established. The content of Cl_2 is smaller than H_2 since Cl_2 is produced only by decomposition of the source. The simplified growth rate relation becomes

$$R = k_{OV} P_{SiCl_2}^{1/2} P_{CH_4}^{1/2} \sqrt{\frac{P_{H_2}}{1 + a P_{H_2}}} \quad (18)$$

$$\text{where } k_{OV} = n_0 (k_2 k_2')^{1/2} \left(\frac{P_{Cl_2}}{1 + b P_{Cl_2}} \right)$$

Since P_{SiCl_2} and P_{CH_4} are proportional to the partial pressure of MTS, the above relation becomes

$$R = k_{OV} k k' P_{MTS} \sqrt{\frac{P_{H_2}}{1 + a P_{H_2}}} \quad (19)$$

where k and k' : MTS decomposition rate

Relation (19) is the theoretical growth rate equation that shows the effects of source and diluent gas on deposition. Fig. 7 shows the relation of the growth rate to the partial pressure of MTS. The growth rate is linearly proportional to the partial pressure of MTS irrespective of diluent gas species. Fig. 8 shows the

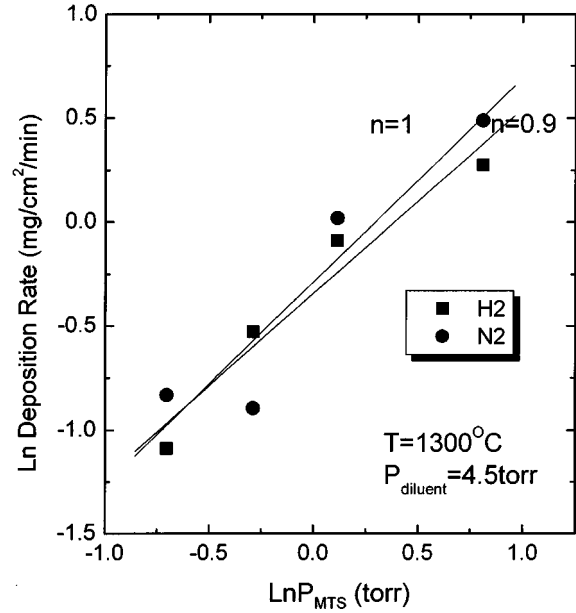


Fig. 7. Growth rate variation with initial MTS partial pressure (P_{MTS}). ($T=1300^\circ\text{C}$, $P_{\text{diluent}}=4.5$ torr).

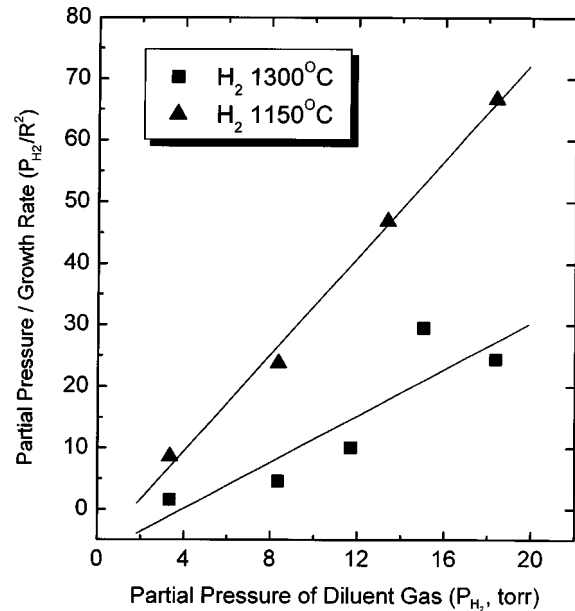


Fig. 8. Effect of partial pressure of H_2 on P_{H_2}/R^2 ($T_{\text{dep}}=1300, 1150^\circ\text{C}$, $P_{MTS}=1.67$ torr).

relation of the growth rate to the partial pressure of H_2 at 1300°C and 1150°C . For easy comparison, equation (19) can be rewritten as:

$$\frac{P_{H_2}}{R^2} = A + B P_{H_2} \quad (20)$$

where A : $1/k_{OV} k k' P_{MTS}$

B : $a/k_{OV} k k' P_{MTS}$

Therefore P_{H_2}/R^2 is linearly proportional to P_{H_2} . For the relatively low temperature of 1150°C, the experimental result is well adopted to the theoretical result. Since the theoretical approach is only based on the surface reaction of the SiC film, and at high temperature, the deposition kinetics are governed by mass transfer reaction, the experimental result for 1300°C shows some deviation from linearity.

Conclusions

The reactant depletion that is encountered in a horizontal hot-wall CVD reactor has a large impact on the deposition rate of deposited films. For the H_2 diluent gas system, the effect of the reactant depletion occurred at all pressure ranges. However, by substitution N_2 for H_2 , the depletion effect can be diminished. From these results of composition variables, a N_2 diluent gas ambient makes the system at constant pressure to be governed by a surface reaction. Oppositely for H_2 , at elevated temperature, the deposition kinetics of mass transfer governed with all composition ranges. Consequently the various diluent gas additions do not change the deposition kinetics of MTS- H_2 and MTS- H_2 - N_2 systems. A remarkable phenomenon was the different degree of deposition rate decrease with different diluent gas systems. This can be explained by the participation of H_2 diluent gas on the deposition reaction.

The simplified model of growth rate with R_{H_2} and P_{MTS} was in a good accordance with the experimental results. The partial pressure changes of MTS have a linear effect on the growth rate of CVD SiC. Hydrogen also affected the growth rate of CVD SiC.

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