JOURNAL OF MATERIALS SCIENCE 35 (2000) 4519–4526

The effect of diluent gases on the growth behavior of CVD SiC films with temperature

YOUNG-JIN LEE, DOO-JIN CHOI[*‡]
Department of Ceramic Engineering, Yonsei University, 134 Shinchon, Sudaemun-Ku, Seoul, South Korea
E-mail: drchoidj@bubble.yonsei.ac.kr

JI-YEON PARK, GYE-WON HONG
Korea Atomic Energy Research Institute, 150 Tuckjin, Yusong, Taejon, South Korea

Silicon carbide films have been grown onto graphite substrates by low pressure chemical vapor deposition using MTS (CH_3SiCl_3) as a source precursor and H_2 or N_2 as a diluent gas. The experiments were performed at fixed conditions of a flow rate of 100 sccm for each MTS and carrier gas, a flow rate of 300 sccm for diluent gas addition, and a total pressure of 5 torr. The effect of temperature from 900°C to 1350°C 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 deposition temperature irrespective of diluent gases and reactant depletion effect increased especially at H_2 diluent gas ambient. At MTS-H_2 system, the deposition mechanism changed from chemical reaction to mass transfer controlled reaction with temperature. Otherwise, For MTS-H_2-N_2 system, surface chemical reaction controlled the growth process at whole deposition temperature ranges. For N_2 addition, surface morphology of leaf-like structure appeared, and for H_2, faceted structure at 1350°C. The observed features were involved by crystalline phase of β-SiC and surface composition with different gas ambient. © *2000 Kluwer Academic Publishers*

1. Introduction

Silicon Carbide (SiC) by chemical vapor deposition (CVD) has prominent properties such as excellent hardness and chemical resistance at high temperatures. SiC also has wide band gap, high electric mobility and high thermal conductivity. Therefore its application includes from structural material to electric devices at elevated temperature [1–3]. The CVD silicon carbide coating on graphite substrate is an interesting field that has been widely studied for industrial applications such as oxidation protector and diffusion barrier at high temperature. Many investigators have studied the relationships between deposition rate and growth kinetics of CVD β-SiC using methyltrichlorosilane (MTS; CH_3SiCl_3) [4–9]. Besides MTS, diethyl silane (DES) [10], hexamethyldisilane (HMDS) [11, 12], ditertiarybutylsilane (DTBS) [13], and silane have been used as the CVD source precursors. Contrary to the variety of source precursors, most of previously reported studies had used hydrogen (H_2) as a carrier and diluent gas which delivers the source to the inlet of reaction tube and which regulates the concentration of mixed gas precursors. The use of MTS-H_2 mixture system has showed many different results according to deposition parameters like deposition temperature, total pressure and input gas fraction. On the basis of these studies, several researches have been performed about the variation of characteristics of CVD-SiC films when argon (Ar) was used as a diluent gas precursor and about the comparison of CVD-SiC films using H_2 diluent gas system with the films using Ar precursor system. Kobayashi *et al.* [4] showed the H_2, $H_2 + Ar$ and Ar diluent gas effect. For all temperature ranges (i.e. $1000 \leq T \leq 1500$°C), they noticed the growth rate of SiC was higher in H_2 than in the presence of Ar. On the contrary, Nordell *et al.* [11] reported that the growth rate with pure Ar carrier gas was higher than that for the Ar/H_2 mixture. Kim *et al.* [6] reported that below 1150°C, the deposition rate of SiC films using H_2 as a diluent gas was higher than that of films using Ar, but above 1200 °C, the opposite result was observed. There were also the compositional and morphological changes under different diluent gas addition. However the effects of the other gas species like N_2 as diluent or carrier gas for preparing CVD SiC films have not been reported.

The aim of this work is to compare the effect of diluent gases of H_2 and N_2 on the growth of CVD-SiC films and their microstructures. According to deposition position change, we determined the growth rate change with temperature. We also investigated the temperature

[*] Author to whom all correspondence should be addressed.
[‡] *Present Address*: Department of Ceramic Engineering 134, Shinchon-dong, Sudaemoon-ku, Seoul, 120-749, Korea.

and diluent gas effects on morphological and orientational changes related to the ambient gas.

2. Experimental details

The deposition experiments were performed in a horizontal hot wall LPCVD reactor as previously described [7]. Three deposition positions in a same batch, each separated by 3.54 cm, were chosen in a gas flow direction, or denoted as D1, D2, D3. (Hereafter, we refer to each deposition position as D1, D2, D3 in this report.) D2 has 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 deposition temperatures. The graphite susceptor was tilted at about 10° for the diminution of reactant depletion. Silicon carbide was deposited onto isotropic graphite which has similar thermal expansion coefficient to that of SiC, using MTS and hydrogen or nitrogen gaseous mixture. MTS was chosen because it has equivalent ratio of Si to C and shows relatively low thermal decomposition temperature. Hydrogen was used as a carrier gas, which transfers source precursor through the bubbler to the main reactor. Hydrogen or nitrogen was used as a diluent gas, which regulates the concentration of the mixture involving MTS vapor and carrier gas. Diluent gas and carrier gas containing MTS vapor were mixed each other before introducing to the reactor. The flow rate of MTS vapor was controlled by adjusting the bubbler pressure and the flow rate of the carrier gas (H_2) in the condition that the temperature of the bubbler containing liquid MTS was maintained at 0°C. The pressure in the reactor was monitored with capacitance manometer and controlled with throttle valve located at between the reactor and a mechanical pump. Deposition temperature ranged from 900 to 1350°C and total pressure was 5 torr. The input gas ratio of diluent plus carrier gas to MTS, $\alpha = P_{(\text{diluent+carrier})}/P_{\text{MTS}}$ was fixed at 4 and total flow rate was fixed at 500 sccm. More details for deposition conditions are shown in Table I.

The crystalline phase and the preferred orientation were characterized by means of an X-ray diffraction (XRD) technique. In order to analyze the surface microstructure of as-deposited films, we used the scanning electron microscopy (SEM). The stoichiometry of the film is examined by a X-ray photoelectron spectroscopy (XPS). The deposition rates were obtained by the weight gain of as-deposited films divided by substrate area and time.

TABLE I Deposition conditions of CVD–SiC film

Deposition temperature	900–1350 °C
Deposition time	1 hr
Total pressure	5 torr
Dilute Gas/MTS ratio ((H_2, N_2) : H_2(carrier) : MTS)	4 (3 : 1 : 1)
Total flow rate	500 sccm
Deposition site	D1–D3 (each site distance : 3.54 cm)
Each Distance from D_1, D_2 and D_3 to mulite tube inlet	D1 : 14.8 cm D2 : 18.3 cm D3 : 21.8 cm

3. Results and discussion

The reactant depletion effects on growth rate of SiC as a function of temperature have been investigated for two different diluent gases of H_2 and N_2 in Fig. 1a and b respectively, whose slopes from D1 to D3 indicate the degree of depletion effect. For H_2 diluent system (Fig. 1a, the reactant depletion occurred above 1200°C and became larger with temperature increase. For MTS-H_2-N_2 system (Fig. 1b), the reactant depletion effect occurs only between D2 and D3. The growth rate of D2 is nearly equal to that of D1, which indicate the reduced depletion effect of N_2 diluent gas ambient. When the

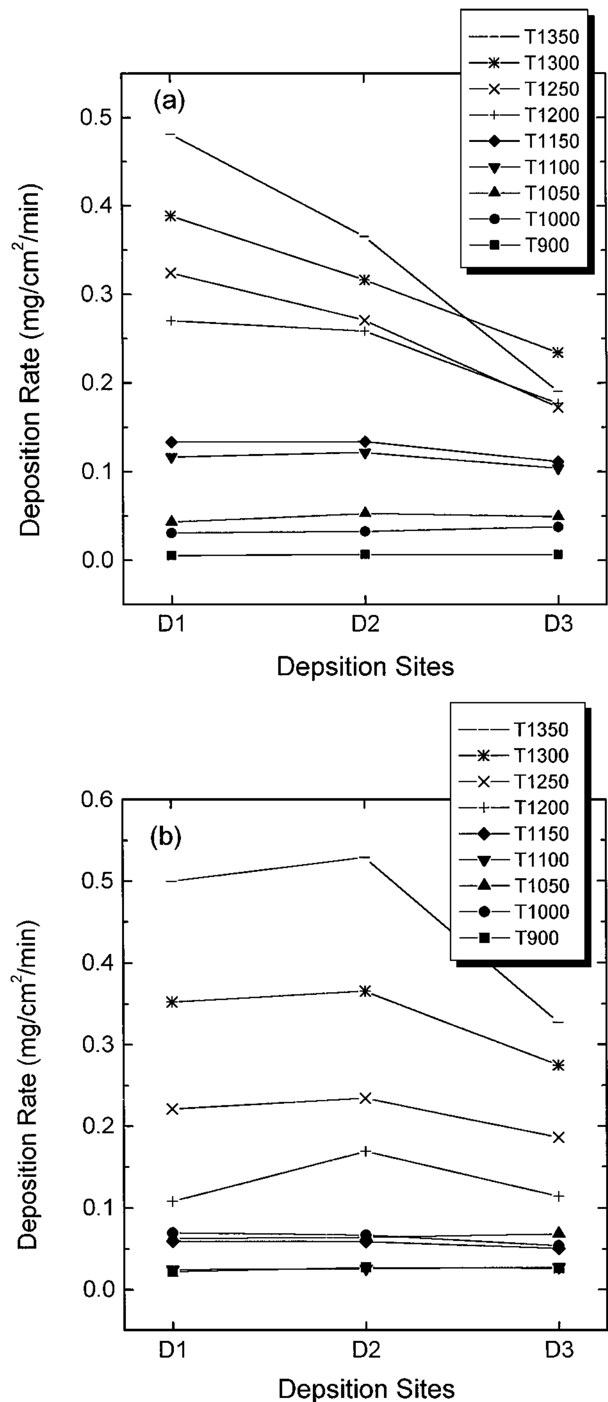


Figure 1 Variation of deposition rate with deposition temperature and deposition site showing depletion effects. (a) MTS-H_2 system ($P_{\text{tot.}} = 5$ torr, MTS : H_2 = 1 : 4) (b) MTS-H_2-N_2 system ($P_{\text{tot.}} = 5$ torr, MTS : H_2 : N_2 = 1 : 1 : 3).

source gas mixture is injected to the reaction tube, the chemical decomposition of MTS occurs and reactant is depleted to the direction of gas flow. The degree of depletion effect along the axis of flow decreases with gas velocity increase [14]. According to the Bernoulli equation, the velocity of a gas increases with the density at constant pressure. With the addition of N_2 gas that is more dense than H_2 (Table II) [15], the velocity of reactant mixture will increase and the reduced depletion effect might occur.

The growth rates at each position, D1, D2 and D3 are plotted as a function of the reciprocal temperature, in Fig. 2, for two different diluent gases. For H_2 diluent system (Fig. 2a), up to 1100°C, the growth rate of SiC changed rapidly with the deposition temperatures.

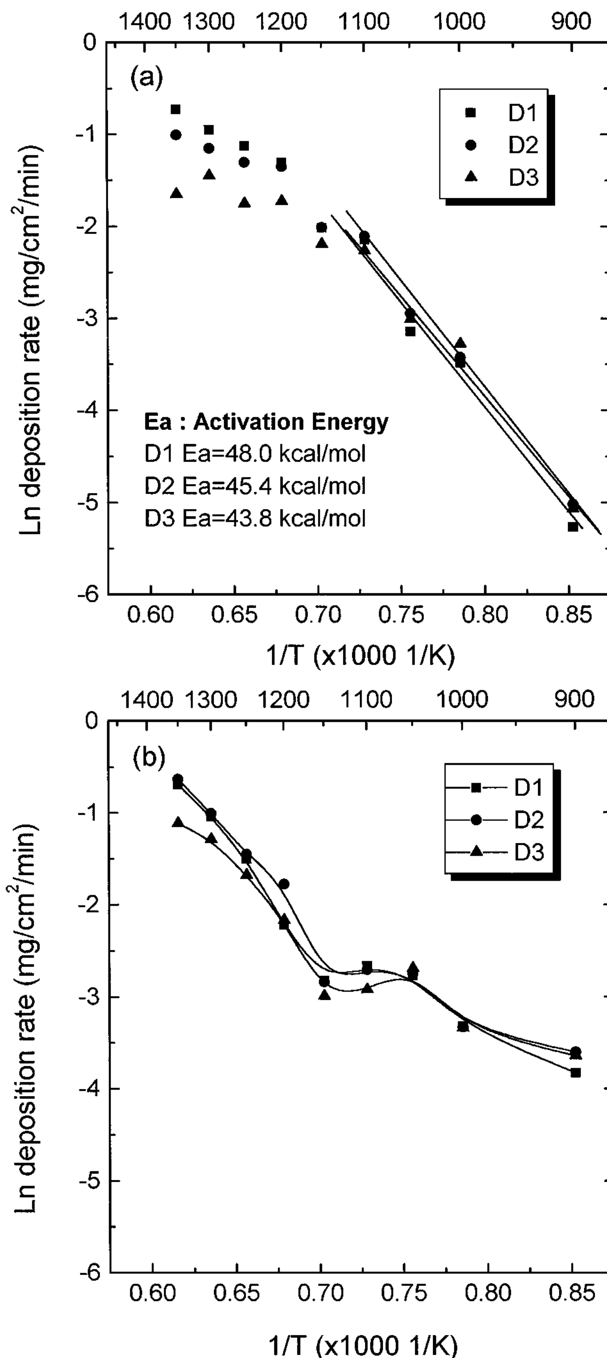


Figure 2 Arrhenius plots of the deposition rate of SiC at various deposition sites. (a) MTS-H_2 system ($P_{tot.} = 5$ torr, MTS : H_2 = 1 : 4) (b) MTS-H_2-N_2 system ($P_{tot.} = 5$ torr, MTS : H_2 : N_2 = 1 : 1 : 3).

TABLE II Typical values for various properties of different gases (conditions: Temp. = 1000 K, Press. = 1 atm)

properties \ gases	H_2	N_2
C_p (J/Kg · K)	14990	1168
k (W/m · K)	0.428	0.0631
ρ (kg/m^3)	0.0246	0.342
η (kg/m · s)	2.07×10^{-5}	4.04×10^{-5}

At low temperature region, the apparent activation energies are about 45 kcal/mol, which indicate surface reaction controlled region. The apparent activation energy is well agreed with other researcher's results [6, 7, 9–13] although it slightly changes with deposition parameters. On the other hand, above 1150°C, it changes slowly with temperatures indicating mass transfer controls the deposition process. For N_2 diluent system (Fig. 2b), the growth rate sharply increases above 1150°C. This means that there is no mass transfer controlled kinetics at the elevated temperature above 1150°C under MTS-H_2-N_2 atmosphere. Though the deposition temperature increases, the growth rate chases surface reaction process because the boundary layer thickness is not thick enough when N_2 is added in substitution with H_2.

The different growth rates and activation energies are thought to be due to thickness variation of stagnant boundary layer through which decomposed gas species diffuse. As the thickness of boundary layer increases, the growth kinetics will be governed by mass transport. Assuming non-tilted susceptor, the theoretical stagnant boundary layer thickness, δ, with temperature is as follows [16]:

$$\delta = a\left[\frac{\eta \cdot x}{\rho \cdot v}\right]^{1/2} \quad (1)$$

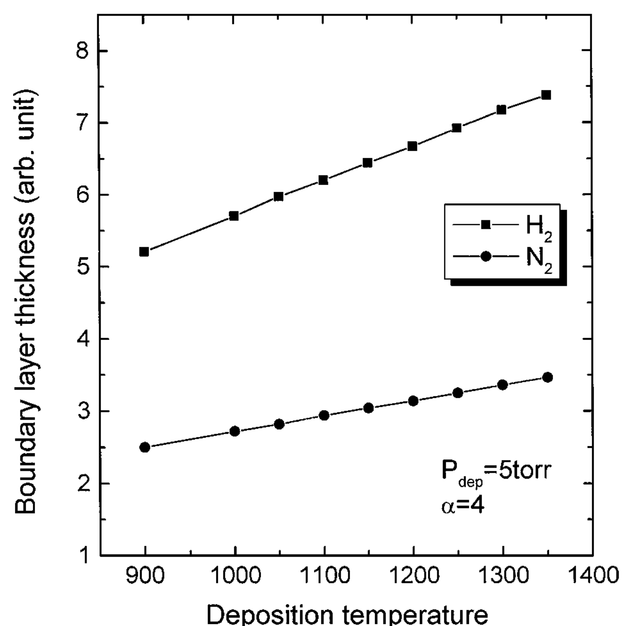


Figure 3 The variation of stagnant boundary layer thickness with temperature and ambient gases.

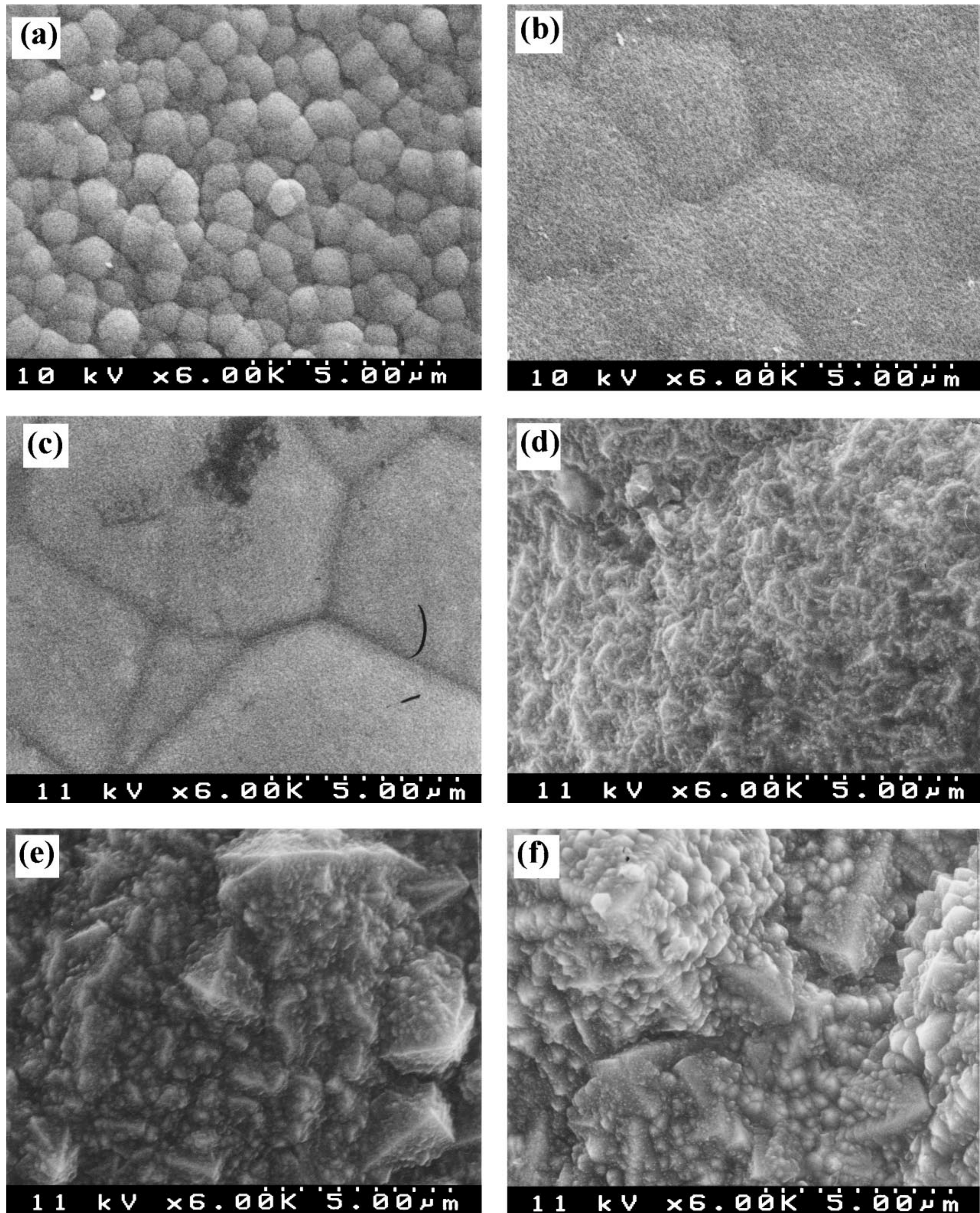


Figure 4 Surface morphology of SiC films with deposition temperature when H_2 is used as diluent gas: (a) 1000°C, (b) 1100°C, (c) 1150°C, (d) 1250°C, (e) 1300°C and (f) 1350°C.

where, a and x are proportional constant and distance, respectively; η, the viscosity of the gas; ρ, the density of the gas; v, the linear velocity of the gas. The typical values and conditions for calculation are shown at Table II. As densities and viscosities of gases are function of temperature, we estimated the density of the gas by the ideal gas law and viscosity at elsewhere [17]. Fig. 3 represents the theoretical result of calculated boundary layer thickness with temperature. In all temperature ranges, boundary layer thickness of H_2 diluent system is greater than that of N_2 diluent system. Similarly, the layer thickness increases with temperature for the both diluent systems. From these results, H_2 diluent system is likely to be controlled by mass transport reaction mechanism especially at high temperature. The deposition kinetics of N_2 diluent system is governed by surface chemical reaction for all temperature regions. Consequently, owing to the difference of gaseous velocity and stagnant layer thickness, the reactant depletion effect of the MTS-H_2-N_2 system might be decreased and the growth process governed by the surface reaction.

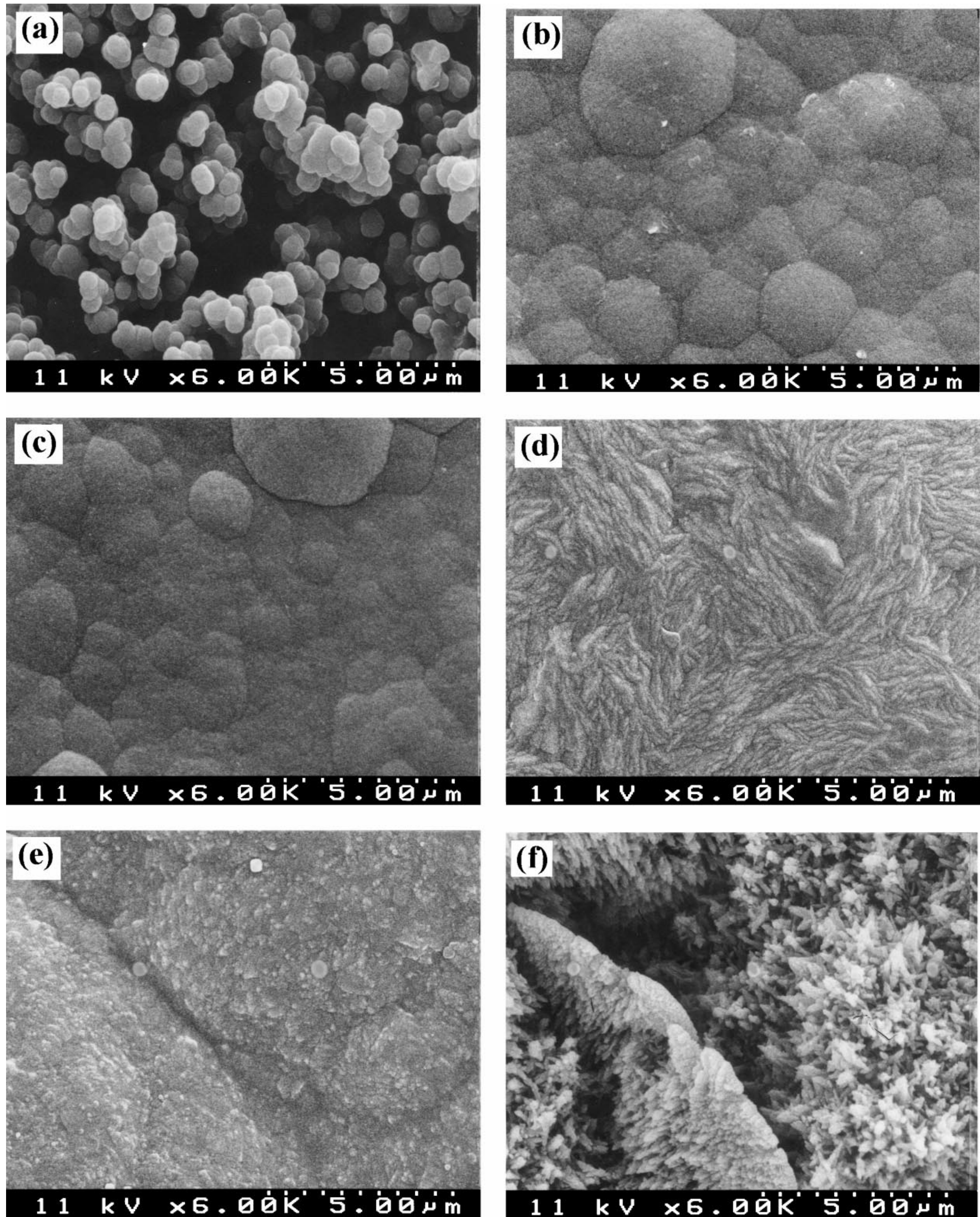


Figure 5 Surface morphology of SiC films with deposition temperature when N_2 is used as diluent gas: (a) 1000°C, (b) 1100°C, (c) 1150°C, (d) 1250°C, (e) 1300°C and (f) 1350°C.

For N_2 diluent system in near by $T = 1150°C$, Arrhenius plot exhibits the change of slop which has a relative minimum of the growth rate. Loumagne *et al.* [10] reported the same phenomenon for MTS-H_2 system, under conditions of $T_{dep} = 1100°C$ and 1120°C. They explained the growth rate decreased with inhibition effect of HCl that was produced by MTS decomposition in the gas phase. The inhibition effect of HCl is caused by the chemical adsorption of chlorine bearing gas species. This is the reason why the Arrhenius plot shows the negative slope.

As the deposition temperature increases, for the H_2 diluent system, surface morphologies changed from hemispherical angular structure to facet structure. However for the N_2 diluent system, it changed to leaf-like structure. Kuo *et al.* [18], reporting the correlation between the surface morphologies and the texture of deposits, showed the change of surface morphologies from laminar crystals to leaf-like structures by adding CH_4 to MTS-H_2 system. Lin *et al.* [19] also reported that the increase of C_3H_8 flow rate gave rise to the leaf-like structure. These mean that carbon bearing

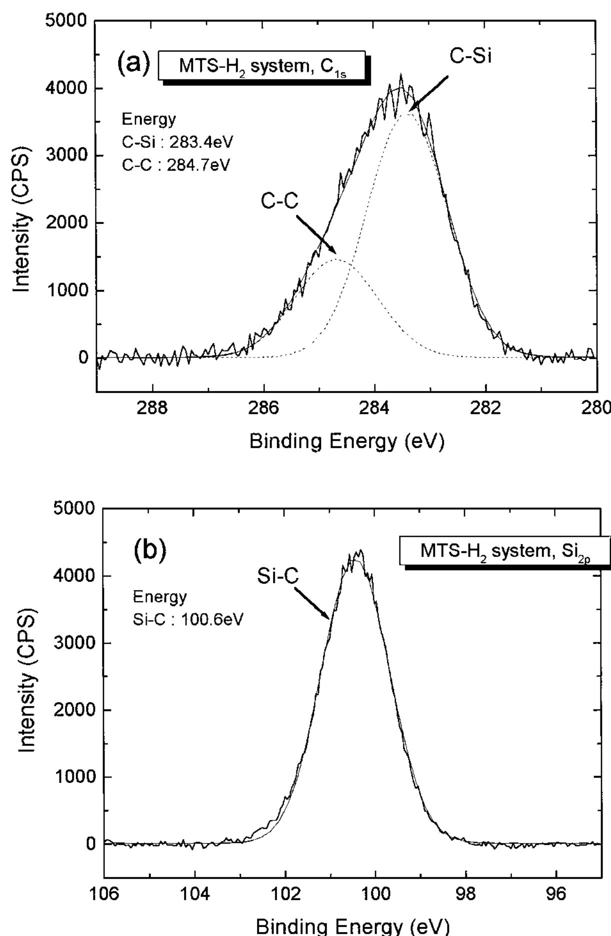


Figure 6 Deconvolution of narrow scan spectra of CVD SiC film for H_2 diluent. (a) C1s and (b) Si2p.

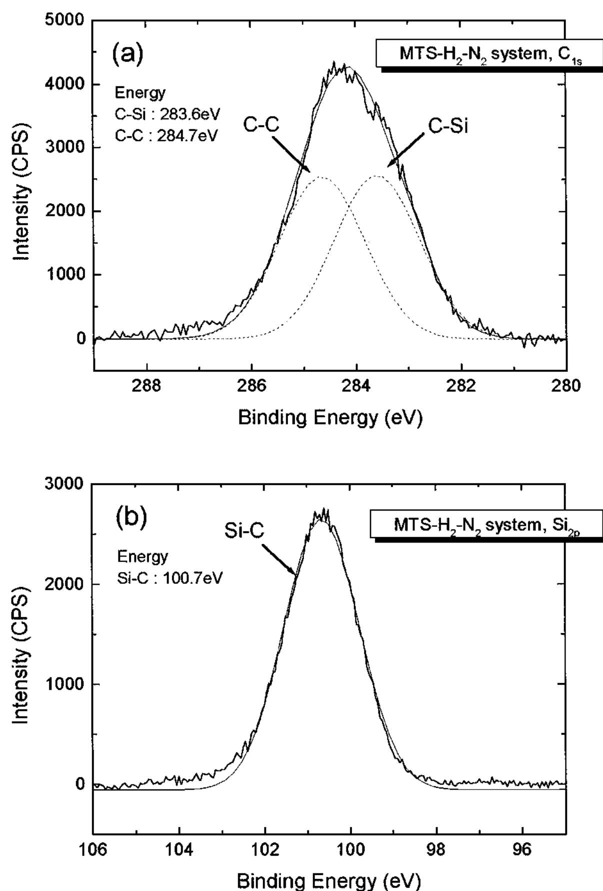


Figure 7 Deconvolution of narrow scan spectra of CVD SiC film for N_2 diluent. (a) C1s and (b) Si2p.

intermolecular species affect the structural growth direction i.e., leaf-like structure. And in both cases, the deposition rates are increased with CH_4 and C_3H_8 flow rate. According to Lespiaux *et al.*'s chemisorption model [20], carbon species, mainly C_2H_2, is favored at low α values and they predicted carbon rich SiC deposition at low α ratios, low total pressure and high temperature. In case of no condensed phase present, Chiu *et al.* [21] had calculated the excess graphite co-deposition content under small H_2/MTS ratios. Therefore, when N_2 is substituted for H_2 at high temperature, the relative value of α is low and then there may be abundant in carbon bearing gas species and excess carbon deposition, which results in leaf-like structure and the growth rate increase compared to that of H_2 ambient.

To compare the quantity of excess carbon for different diluent system, the chemical compositions of deposits were examined by XPS. Fig. 6 and 7 show the deconvolution of C and Si peaks with different diluent gases. At 1350°C and D2 position, the ratio of C/Si was 2.1 for N_2 diluent system, 1.2 for H_2. These results reveal that carbon rich deposits are present on the film at N_2 diluent system. For H_2 diluent system, approximately stoichiometric deposits were obtained.

Table III shows the thermodynamic yield of condensed phases that were calculated by SOLGASMIX-PV thermodynamic computer program [22]. For the deposition conditions of 5 torr and $\alpha = 4$, an excess carbon content is up to 50% with N_2 diluent gas ambient, whereas SiC content is above 90% with H_2 diluent gas ambient. According to our calculations of thermodynamic yields, no condensed Si_3N_4 phase observed above 1080°C. From these results, we can deduce the N_2 inhibits the Si deposition and Si and C bearing intermediate gas species adsorb on the surface respectively. It has been said that $SiCl_2$ and CH_4 are the important gas species for CVD SiC film deposition [5, 9, 23]. Adsorbed $SiCl_2$ and CH_4 would react with H_2 and Cl_2

TABLE III Thermodynamic yield of SiC and C at various temperatures by SOLGASMIX–PV program ($P_{tot} = 5$ torr, α, $\alpha' = 4$)

			Temperature(°C)					
	Diluent gas species	Condensed phase	1100	1150	1200	1250	1300	1350
Thermodynamic Yield (%)	H_2	SiC	93	93	92	91	89	88
		C	7	7	8	9	11	12
	N_2	Sic	55	53	49	45	41	37
		C	45	47	51	55	59	63

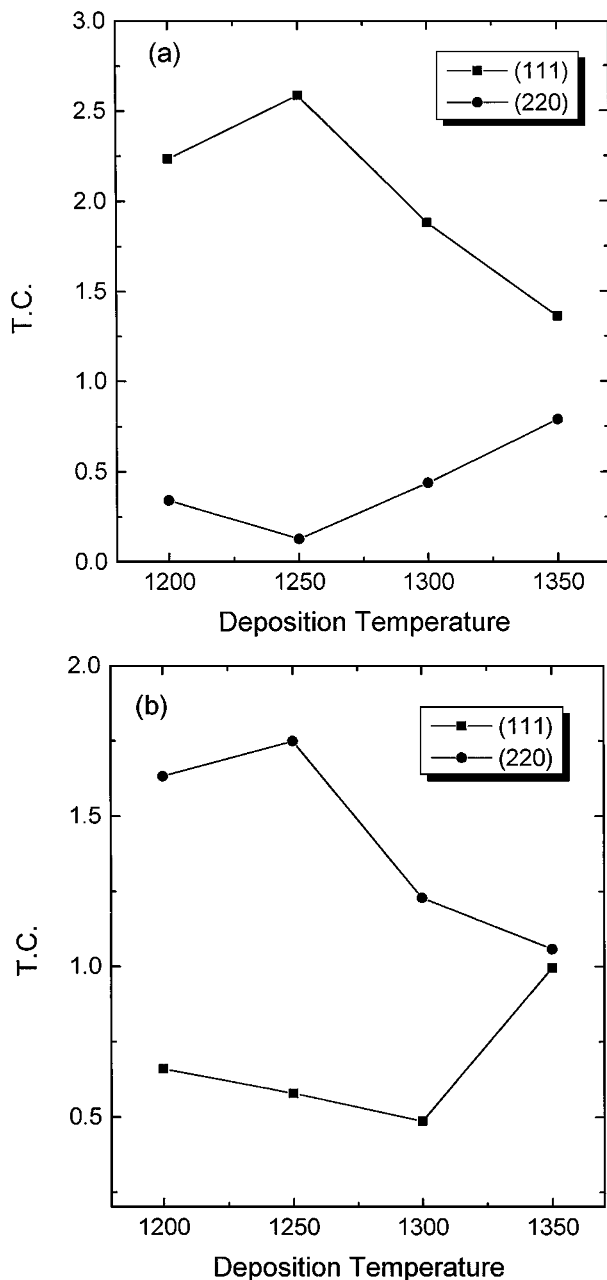
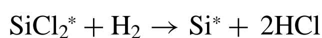
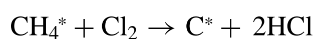


Figure 8 The variation of texture coefficient with deposition temperature at different diluent gases: (a) H_2 diluent ambient (b) N_2 diluent ambient.

independently and could form the free surface of Si and C.



$$SiCl_2^* + H_2 \rightarrow Si^* + 2HCl$$



$$CH_4^* + Cl_2 \rightarrow C^* + 2HCl$$

Reduced H_2 content may result in the increase of relative amount of Cl_2 in the gas phase. Consequently, N_2 addition could lead to the lack of reactive H_2 gas and to the excess carbon deposition.

Fig. 8 represents the variation of a texture coefficient (T.C.) with different diluent gas species and deposition temperature. The T.C. that is obtained by Harris method [24] for observing the relative degree of preferred orientation among planes is as follows;

$$\mathrm{TC}(hkl) = \frac{I_{(hkl)}/I_{\mathrm{O}(hkl)}}{\frac{1}{N}\sum[I_{(hkl)}/I_{\mathrm{O}(hkl)}]} \quad (2)$$

where, $I_{(hkl)}$, $I_{\mathrm{O}(hkl)}$, and N are the measured intensities of the film, the standard integrated intensities (from JCPDS file) of powdered SiC, and the number of reflections, respectively. As evidenced from Fig. 8a, for H_2 diluent gas, the preferred orientation in the whole temperature ranges is (111) plane. While the preferred orientation under N_2 diluent gas ambient which is shown in Fig. 8b is (220) plane. By Lee [25], he proposes that for FCC crystals, lower atom ion concentration results in the development of {111} plane. In the same way, higher atom ion concentration results in the development of {110} plane. As mentioned above, for N_2 diluent ambient system, stagnant boundary layer thickness is smaller and deposition rate governed by surface reaction, which means that there is high atom concentration adjacent to the deposits and SiC grows more easily on the activated surface. This is why the (220) plane is more dominant at N_2 diluent ambient than H_2. Whereas atom concentration is high at the higher temperature, the (220) texture grows a little bit with temperature in the pure H_2 atmosphere. Otherwise, for N_2 diluent system, (111) plane somewhat increases at 1350°C. This result can be explained by the influence of carbon species. When the leaf-like structure of SiC is deposited, its crystalline phase has (111) plane. [18, 19]. Consequently, the addition of N_2 diluent gases results in carbon rich gas phase and decreases (220) texture to a little extent.

4. Conclusion

The reactant depletion that is encountered in a horizontal hot-wall CVD reactor has a large impact on deposition rate of SiC films. For H_2 diluent gas system, the effect of the reactant depletion becomes larger with increasing deposition temperature. However, by substitution N_2 for H_2, depletion effect can be diminished. For the condition of MTS-H_2-N_2 system, we have calculated the decrease of stagnant boundary layer thickness, which results in high growth rate and less depletion effect. Remarkable phenomenon for N_2 diluent system is that CVD SiC is not governed by mass transfer kinetics but by surface reaction mechanism. For N_2 diluent gas ambient, excess carbon deposits were obtained at 1350°C. Carbon bearing gas depresses the (220) texture of CVD SiC and stimulates the growth rate and its surface morphology changed to leaf like structure. For MTS-H_2 system, we noticed that the (111) texture is dominant and (220) for N_2 diluent system. We concluded from this study that the deposition temperature and diluent gas species of H_2 or N_2 are the major factor affecting the growth behavior of CVD SiC.

Acknowledgements

Authors acknowledge the support of Korea Atomic Energy Research Institute.

References

1. D. P. STINTON, T. M. BESMANN and R. A. LOWDEN, *Ceram. Bull.* **67** (1988) 350.

2. W. R. HAIGIS and M. A. PICKERING, *Materials & Design* **14** (1993) 130.
3. S. SOMIYA and Y. INOMATA, "Silicon Carbide Ceramics-1 Fundamentals and Solid Reaction" (Elsevier Science Publishers Ltd., 1991).
4. F. KOBAYASHI, K. IKAWA and K. IWAMOTO, *J. Crystal Growth* **28** (1975) 395.
5. D. LESPIAUX, F. LANGLAIS, R. NASLAIN, S. SCHAMM and J. SEVELY, *J. Mater. Sci.* **30** (1995) 1500.
6. H. S. KIM and D. J. CHOI, *J. Amer. Ceram. Soc.* **82**(2) (1999) 331.
7. D. J. KIM, D. J. CHOI and Y. W. KIM, *Thin Solid Films* **266** (1995) 192.
8. S. MOTOJIMA and M. HASEGAWA, *J. Vac. Sci. Technol. A* **8**(5) (1990) 3763.
9. F. LOUMAGNE, F. LANGLAIS and R. NASLAIN, *J. Crytal Growth* **155** (1995) 198.
10. J. M. GROW, R. A. LEVY, Y. T. SHI and R. L. PFEFFER, *J. Electrochem. Soc.* **140**(3) (1993) 851.
11. N. NORDELL, S. NISHINO, J. W. YANG, C. JACOB and P. PIROUZ, *ibid.* **142**(2) (1995) 565.
12. C. H. WU, C. JACOB, X. J. NING, S. NISHINO and P. PIROUZ, *J. Crystal Growth* **158** (1996) 480.
13. J. M. GROW, R. A. LEVY and M. BHASKARAN, *J. Electrochem. Soc.* **140**(10) (1993) 3001.
14. F. C. EVERSTEYN, P. J. W. SEVERIN, C. H. J. V. D. BREKEL and H. L. PEEK, *ibid.* **117**(7) (1970) 925.
15. GASKELL, "An Introduction to Transport Phenomena in Materials Engineering" (Macmillan Publishing Co., 1992) p. 613.
16. A. S. GROVE, "Physics and Technology of Semiconductor Devices" (John Wiley and Sons, Inc., 1967).
17. R. C. REID, J. M. PRAUSNITZ and T. K. SHERWOOD, 'The Properties of Gases and Liquids' (McGraw-Hill Book Co., 1977).
18. D. H. KUO, D. J. CHENG and W. J. SHYY, *J. Electrochem. Soc.* **137**(11) (1990) 3688.
19. T. T. LIN and M. H. HON, *J. Mater. Sci*. **30** (1995) 2675.
20. D. LESPIAUX and F. LANGLAIS, *Thin Solid Films* **265** (1995) 40.
21. C. C. CHIU, S. B. DESU and G. CHEN, *J. Mater. Sci*. **10**(5) (1995) 1099.
22. B. W. SHELDON, Solgasmix-PV for the PC, Oak Ridge National Laboratory, October 1989.
23. G. S. FISCHMAN and W. T. PETUSKEY, *J. Am. Ceram. Soc.* **68**(4) (1985) 185.
24. C. S. BARRETT and T. B. MASSALSKI, 'Structure of Metals' (Pergamon Press, Oxford, 1980) p. 204.
25. D. N. LEE, *J. Mater. Sci.* **24** (1989) 4375.

Received 25 October 1999
and accepted 18 February 2000