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GAS PHASE REACTION IN SYNTHESIS OF SiC FILMS BY LOW PRESSURE CHEMICAL VAPOR DEPOSITION FROM Si₂H₆ AND C₂H₂ AT 873 K

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Abstract-Silicon carbide (SiC) films were synthesized by the low pressure chemical vapor deposition (LPCVD) method, using Si₂H₆ and C₂H₂ as reactant gases at 873 K in a horizontal tubular reactor. Kinetic studies using gas chromatography were used to understand the gas-phase and surface chemistry of Si₂H₆ in the presence of C₂H₂. The results showed that the direct reaction of Si₂H₆ on substrate surface was strongly retarded by C₂H₂ and that the film formation species was either SiH₂ or a gas-phase intermediate derived from Si₂H₆ and C₂H₂, having a sticking probability of 0.1.

1.-Introduction

The unique physical and electronic properties of silicon carbide (SiC) make it an attractive material for both structural and electronic applications. Extensive effort has been devoted to depositing SiC films by CVD methods. Generally, high process temperature, usually exceeding 1500 K, was a necessity due to the chemical stability of the carbon source gases. Recently, the authors showed a possibility to synthesize SiC films at quite low temperature using the reaction of SiH₄ and C₂H₂. In this study, disilane (Si₂H₆), which is more reactive than SiH₄, was used to react with C₂H₂ to form SiC films. Emphasis was placed on the gas-phase and surface chemistry of Si₂H₆ in the presence of C₂H₂. The sticking probabilities of the chemical species involved in the film formation were also measured to provide a clear understanding of the film formation mechanism.

2.-Experimental

The deposition experiments were performed in a LPCVD system configured as shown in Fig. 1. The reactor was a fused quartz tube heated by an electric heater. Temperature was controlled by a thermal controller with a thermocouple inserted on the inner surface of the heater at the center. The uniform temperature zone in the reactor was 20 cm in length. Quartz tubes, with diameters ranging from 4.3-15.6 mm, were used to change surface-to-volume ratio (S/V). Si₂H₆ and C₂H₂ were premixed with Ar and then introduced into the reactor. Mass flow controllers were used to regulate the flow of gases to obtain the desired gas concentration. The reactor pressure was maintained at an average value of 3.3 torr at the reactor center by adjusting a plug valve placed between the reactor...
outlet and vacuum pump. Residence time in the reactor, which was defined as the ratio of the volume of the tube reactor to the volumetric gas flow rate, was maintained at 22 ms by adjusting the total volumetric flow rate depending on reactor diameter and reaction temperature. The deposition experiments were performed under a condition of partial pressure of $\text{S}_2\text{H}_6$ 0.15 torr and $\text{C}_2\text{H}_2$ 0.9 torr in a reactor of 15.6 mm in diameter and 873 K. The conversion of $\text{S}_2\text{H}_6$, which is defined as the fraction of $\text{S}_2\text{H}_6$ molecules converted in the reactor, was determined using gas chromatography, measuring the composition of the gas mixture before and after reaction. The crystalline structure of the film was analyzed by X-ray diffraction (XRD). The chemical composition of the deposited film was measured by X-ray photoelectron spectroscopy (XPS). Film growth rate was determined by dividing film thickness, which was measured by scanning electron microscopy (SEM), by deposition time.

![Fig. 1 Schematic diagram of experimental apparatus. P, G.C., V, and RP represent a pressure gauge, a gas chromatographer, a plug valve, and a rotary pump, respectively.](image1)

![Fig. 2 SiH₄ conversion as a function of C₂H₂ concentration at various reactor diameters. Reaction was performed at Pₜₚ₅H₆ = 0.15 torr and 873 K.](image2)

### 3.-Results and discussion

The deposited film, taken at the position 6 cm from the reactor inlet, was amorphous according to the XRD measurement. The XPS analysis showed a stoichiometric composition of silicon carbide ($\text{SiC}_x\cdot x=1$).

Figure 2 shows the conversion of $\text{S}_2\text{H}_6$ as a function of $\text{C}_2\text{H}_2$ partial pressure at various reactor diameters. This figure shows two important features. First, the conversion of $\text{S}_2\text{H}_6$ decreased with increasing $\text{C}_2\text{H}_2$ partial pressure, which means that the reaction of $\text{S}_2\text{H}_6$ is retarded by adding $\text{C}_2\text{H}_2$ into the system. Second, for the reaction of $\text{S}_2\text{H}_6$ only ($\text{PC}_2\text{H}_2 = 0$), the conversion of $\text{S}_2\text{H}_6$ increased with decreasing reactor diameter. Since the surface-to-volume ratio increases with decreasing reactor size, the increase of conversion when reactor diameter was reduced is caused by the surface reaction of $\text{S}_2\text{H}_6$. On the other hand, in high $\text{C}_2\text{H}_2$ concentration region, the conversion of $\text{S}_2\text{H}_6$ showed no dependence on reactor diameter and was a constant of about 45%. This indicates that a homogeneous reaction, probably the gas-phase decomposition of $\text{S}_2\text{H}_6$ into $\text{SiH}_2$ and $\text{SiH}_4$, is rate-controlling. In conclusion, the reaction of $\text{S}_2\text{H}_6$ includes surface reaction and gas-phase reaction paths, in parallel. The surface reaction route is reduced gradually by adding $\text{C}_2\text{H}_2$ into the reaction system and only the gas-phase reaction route is left in high $\text{C}_2\text{H}_2$ concentration region. For this reason, the overall reaction rate constant of $\text{S}_2\text{H}_6$, $k_a$ (1/s), which was calculated from the reaction conversion of $\text{S}_2\text{H}_6$ by assuming a first order dependency of the reaction rate, can be expressed as follows:
\[ k_a = k_d + (S/V)k_s \]  

where \( k_a \) (1/s) is the gas phase reaction rate constant, \( k_s \) (m/s) is the surface reaction rate constant, and \( S/V \) is the surface-to-volume ratio which equals to \( 4/d \) (d, reactor diameter) in a tubular reactor. Figure 3 shows the relation of \( k_a \) versus \( S/V \) for reaction of \( \text{Si}_2\text{H}_6 \) in the absence of \( \text{C}_2\text{H}_2 \). A good linearity exists. The slope of the line is \( 1.95 \times 10^{-2} \text{ m/s} \) and the intercept of the y axis is \( 28.5 \text{ s}^{-1} \), which correspond to \( k_d \) and \( k_s \), respectively. The value of \( k_d \) (28.5 s\(^{-1}\)) was used to calculate backwards to give a reaction conversion of 46.6\%, agreeing well with that observed in the high \( \text{C}_2\text{H}_2 \) concentration region as shown in Fig. 2.

Figure 3 shows the dependence of the overall reaction rate constant of \( \text{Si}_2\text{H}_6 \) on the surface-to-volume ratio of the tubular reactor (4/d, where d is the inner diameter of the reactor). Reaction was performed at \( P\text{Si}_2\text{H}_6 = 0.15 \text{ torr} \), \( P\text{C}_2\text{H}_2 = 0 \text{ torr} \), and \( 873 \text{ K} \).

![Graph showing the relation of \( k_a \) versus \( S/V \) for reaction of \( \text{Si}_2\text{H}_6 \) in the absence of \( \text{C}_2\text{H}_2 \).](image)

**Fig. 3** Dependence of the overall reaction rate constant of \( \text{Si}_2\text{H}_6 \) on the surface-to-volume ratio of the tubular reactor (4/d, where d is the inner diameter of the reactor). Reaction was performed at \( P\text{Si}_2\text{H}_6 = 0.15 \text{ torr} \), \( P\text{C}_2\text{H}_2 = 0 \text{ torr} \), and \( 873 \text{ K} \).

![Graph showing \( k_a \) versus \( C_2H_2 \) concentration at various temperatures.](image)

**Fig. 4** \( \text{Si}_2\text{H}_6 \) conversion as a function of \( \text{C}_2\text{H}_2 \) concentration at various temperatures. Reaction was performed at \( P\text{Si}_2\text{H}_6 = 0.15 \text{ torr} \) and reactor diameter of 15.6 mm.

Figure 4 shows the conversion of \( \text{Si}_2\text{H}_6 \) as a function of \( \text{C}_2\text{H}_2 \) concentration at various temperatures. Equation (1) was used to separate the contribution of the surface reaction \( k_s(S/V) \) from the overall reaction \( (k_a) \), assuming that all the surface reaction was suppressed in the presence of an abundance of \( \text{C}_2\text{H}_2 \). The result is shown in Table I. Both \( k_s \) and \( k_s \) increased when the temperature was raised. Figure 5 shows the Arrhenius plot of \( \ln k_g \) versus \( 1/T \), which is linear and gives an activation energy of 39.2 kcal/mol. In Fig. 6, the sticking probability of \( \text{Si}_2\text{H}_6 \) \( \eta \), which is calculated from \( k_s \) using the relation \( k_s = 1/4 \eta v \) (\( v \) is the average speed of \( \text{Si}_2\text{H}_6 \) gas), also shows an Arrhenius behavior with respect to temperature. The slope under the present conditions corresponds to an activation energy of 21.8 kcal/mol.

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<td>42.2</td>
<td>21.9</td>
<td>6.1 \times 10^{-4}</td>
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</tbody>
</table>

**Table I.** Contribution of the gas-phase reaction and surface reaction of \( \text{Si}_2\text{H}_6 \) at various temperatures.

![Graph showing \( k_a \) versus \( 1000/T \) (1/K).](image)

**Fig. 5** Dependence of the gas-phase reaction rate \( (k_a) \) on temperature.
Figure 7 shows the conversion of SiH$_6$ as a function of C$_2$H$_2$ concentration at various SiH$_6$ initial concentrations. In the high C$_2$H$_2$ concentration region, the SiH$_6$ conversions (about 45%) were independent of the concentration of SiH$_6$ at SiH$_6$ partial pressures of 0.075 torr and 0.15 torr while the conversion increased when SiH$_6$ partial pressure was raised to 0.3 torr and 0.6 torr. This result indicates a first order reaction with respect to SiH$_6$ when SiH$_6$ partial pressure is lower than 0.15 torr, and a higher reaction order when SiH$_6$ partial pressure is larger than 0.15 torr. This nonlinear kinetics is attributable to a reaction of the reactant SiH$_6$ with its initial gas-phase product, SiH$_2$, to form Si$_2$H$_6$ or other high order silanes (Si$_n$H$_{2n+2}$, n>3).

The pyrolysis of Si$_2$H$_6$ has been extensively studied. The primary step of the homogeneous reaction, most favored, is proposed to be the decomposition of Si$_2$H$_6$ into SiH$_2$ and SiH$_4$. Buss et al. have studied the surface chemistry of SiH$_6$. They showed that the reactive sticking probability of SiH$_6$ on a silicon surface was a function of both temperature and SiH$_6$ gas flux. Though different experimental conditions were used, the reactive sticking probability extrapolated at 873 K and SiH$_6$ partial pressure of 0.15 torr was about $10^{-4}$, coinciding well with the present data as shown in Table I.

Based on the above information, a film formation mechanism, schematically shown in Fig. 8, can be proposed as follows:

1. The adsorbed SiH$_6$ reacts with the adsorbed C$_2$H$_2$ on the substrate surface to form SiC films.

   \[
   \text{SiH}_6 \rightarrow \text{SiH}_6\text{(ad)} \quad (2)
   \]

   \[
   \text{SiH}_6\text{(ad)} + \text{C}_2\text{H}_2\text{(ad)} \rightarrow 2\text{SiC} \quad (3)
   \]

2. Si$_2$H$_6$ decomposes in the gas phase to generate SiH$_2$ and SiH$_4$. The intermediate species SiH$_2$, with two free radicals, is quite reactive and is expected to react with Si$_2$H$_6$ and C$_2$H$_2$ as follows:

   \[
   \text{Si}_2\text{H}_6 \underset{k_4}{\rightarrow} \text{SiH}_2 + \text{SiH}_4 \quad (4)
   \]

   \[
   \text{SiH}_2 + \text{SiH}_6 \rightarrow \text{Si}_3\text{H}_8 \quad (5)
   \]
The trapping reaction of SiH$_2$ and C$_2$H$_2$ may occur in the gas-phase or on the surface, i.e., SiH$_2$ may react with C$_2$H$_2$ in the gas phase or with the adsorbed C$_2$H$_2$.

SiH$_2$ + C$_2$H$_2$ $\rightarrow$ Intermediate $\rightarrow$ SiC  \hspace{1cm} (6)

The surface reaction of SiH$_6$ is almost suppressed in the presence of an abundance of C$_2$H$_2$, presumably due to the strong adsorption of C$_2$H$_2$ on the surface. The gas-phase reaction to form SiH$_2$ and SiH$_4$ should be the rate controlling step because of the large activation energy (39.2 kcal/mol). At high SiH$_6$ concentrations, the nonlinear reaction of SiH$_6$ and SiH$_2$ to form high order silanes may be the reason for the particle formation in the outlet of the reactor. When SiH$_6$ concentration is less than 0.15 torr, the gas-phase species SiH$_2$, with a negligible extent of reaction with SiH$_6$, mainly reacts with C$_2$H$_2$ to form SiC films.

Fig. 8 Schematic representation of the SiC film formation mechanism by SiH$_6$ + C$_2$H$_2$

![Fig. 8 Schematic representation of the SiC film formation mechanism by SiH$_6$ + C$_2$H$_2$](image)

Fig. 9 Scanning electron micrograph of the cross section of deposition film in a silicon trench (width = 2.1 μm, depth = 3.5 μm). Deposition was performed at PSiH$_6$ = 0.15 torr, PC$_2$H$_2$ = 0.9 torr, d = 15.6 mm, T = 873 K.

![Fig. 9 Scanning electron micrograph of the cross section of deposition film in a silicon trench](image)

Fig. 10 Film deposition profile in the macrocavity. The cavity spacing was 0.1 mm and the deposition time was 90 min.

![Fig. 10 Film deposition profile in the macrocavity](image)
An attempt to measure the reactive sticking probability of a film forming species was also made. A silicon wafer, with micron size of trenches (depth 3.5 µm, width 2.1 µm) constructed by the normal lithographic procedures, was used as a substrate. The film thickness profiles in the trench can be used to determine the reactive sticking probability of the film forming species. The profile as shown in Fig. 9 corresponds to a sticking probability of 0.1, indicating the film forming species is highly active. According to the above experimental results, the deposition experimental condition (PSiH₆ = 0.15 torr, PC₂H₂ = 0.90 torr, d = 15.6 mm, and T = 873 K) ensures that no nonlinear reaction respect to S₂H₆ occurs and that most of the surface reaction is retarded. For this reason, the film forming species was expected to be SiH₂ or a chemically active species produced from SiH₂ and C₂H₂.

Another approach named the Macro cavity Method was applied to support the proposed mechanism. In this work, two pieces of silicon wafer (13 × 15 mm²) were processed to form a macrocavity by putting spacers (0.1 mm in width) between them. The macrocavity was placed at 6 cm from the inlet of the reactor with its open mouth parallel to the gas flow and then subjected to a deposition experiment. Figure 10 shows the deposition profile in the macrocavity. The growth rate profile, which directly reflects the concentration profile of the film formation species, is characterized by a sharp decrease in the open mouth and a flat profile in the center. The sharp profile in the open mouth of the macrocavity indicates an active gas-phase intermediate does exist in this reaction system. The intermediate, accumulated in the gas-phase, diffuses into the macrocavity with its concentration decreasing sharply due to a large sticking probability of 0.1. The flat profile in the center suggests another species, most probably, Si₂H₆, diffusing deeply into the macrocavity because of its less reactivity, reacting to form an intermediate inside of the cavity (gas-phase reaction) and, perhaps, reacting on the surface (surface reaction) to constitute the film deposition. That is, the film growth rate (G.R.) in the center can be expressed by

\[ G.R. = k_s + \frac{V}{S}k_gC \rho \]  

where C is the Si₂H₆ concentration and ρ is the volume of solid product produced from a mole of Si₂H₆. Since kₔ, V/S (equals to W/2, W = cavity spacing), and G.R. are known and the Si₂H₆ concentration at the position where the macrocavity was placed can be estimated from kₖ, the surface reaction rate constant (kₖ) can be calculated. The result showed a value of kₖ = 4 × 10⁻⁴ m/s, under the condition of sufficient addition of C₂H₂. Compared with the reaction of Si₂H₆ in the absence of C₂H₂ (kₖ = 1.95 × 10⁻² m/s), the surface reaction rate constant is smaller by two orders, which suggests a complete retarding effect of C₂H₂ to the surface reaction of Si₂H₆.

4. Conclusion

In this study, SiC films were synthesized from Si₂H₆ and C₂H₂ by the LPCVD method at quite a low temperature of 873 K. The surface and gas-phase chemistry of Si₂H₆ in the presence of C₂H₂ was quantitatively investigated. Compared with the reaction of Si₂H₆ in the absence of C₂H₂, the surface reaction of Si₂H₆ was strongly retarded by C₂H₂ while the gas-phase reaction was unaffected. Addition of C₂H₂ allowed us to separate the surface reaction of Si₂H₆ from the overall reaction. In this way, the sticking coefficient of Si₂H₆ was, for the first time, measured without using a high vacuum reactor system. Also, we found that the gas-phase reaction of Si₂H₆ obeyed a nonlinear kinetics when Si₂H₆ concentration was larger than 0.15 torr, which was attributed to the insertion reaction of SiH₂ with reactant Si₂H₆ to form high order silanes (SiₙH₂n+2, n>2). Under the
condition of first order reaction with respect to SiH₂ and an abundance of C₂H₂, an intermediate, which may be SiH₂ or a compound produced from SiH₂ and C₂H₂, deposited on the substrate with a sticking probability of 0.1. A study of the detailed mechanism is now under way.

5.-References

/6/ H. Oyamada, Y. Shimogaki, and H. Komiyama, Kagaku Kougaku Ronbunsyu (an official publication of The Society of Chemical Engineering Japan), 16 (1990) 463
/7/ H. Komiyama, H. Oyamada, S. Tanaka, and Y. Shimogaki, Proceedings of the Eleventh International Conference on Chemical Vapor Deposition, Seattle (USA), (1990) 361