**GAS PHASE REACTION IN SYNTHESIS OF SiC FILMS BY LOW PRESSURE
CHEMICAL VAPOR DEPOSITION FROM Si_2H_6 AND C_2H_2 AT 873 K**

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Abstract-Silicon carbide (SiC) films were synthesized by the low pressure chemical vapor deposition (LPCVD) method, using Si_2H_6 and C_2H_2 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 Si_2H_6 in the presence of C_2H_2 . The results showed that the direct reaction of Si_2H_6 on substrate surface was strongly retarded by C_2H_2 and that the film formation species was either SiH_2 or a gas-phase intermediate derived from Si_2H_6 and C_2H_2 , 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 structural¹⁻³ and electronic⁴⁻⁵ 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 SiH_4 and C_2H_2 .⁶⁻⁷ In this study, disilane (Si_2H_6), which is more reactive than SiH_4 , was used to react with C_2H_2 to form SiC films. Emphasis was placed on the gas-phase and surface chemistry of Si_2H_6 in the presence of C_2H_2 . 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). Si_2H_6 and C_2H_2 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 Si_2H_6 0.15 torr and C_2H_2 0.9 torr in a reactor of 15.6 mm in diameter and 873 K. The conversion of Si_2H_6 , which is defined as the fraction of Si_2H_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.

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 (SiC_x , $x \approx 1$).

Figure 2 shows the conversion of Si_2H_6 as a function of C_2H_2 partial pressure at various reactor diameters. This figure shows two important features. First, the conversion of Si_2H_6 decreased with increasing C_2H_2 partial pressure, which means that the reaction of Si_2H_6 is retarded by adding C_2H_2 into the system. Second, for the reaction of Si_2H_6 only ($\text{PC}_2\text{H}_2 = 0$), the conversion of Si_2H_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 Si_2H_6 . On the other hand, in high C_2H_2 concentration region, the conversion of Si_2H_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 Si_2H_6 into SiH_2 and SiH_4 , is rate-controlling. In conclusion, the reaction of Si_2H_6 includes surface reaction and gas-phase reaction paths, in parallel. The surface reaction route is reduced gradually by adding C_2H_2 into the reaction system and only the gas-phase reaction route is left in high C_2H_2 concentration region. For this reason, the overall reaction rate constant of Si_2H_6 , k_a (1/s), which was calculated from the reaction conversion of Si_2H_6 by assuming a first order dependency of the reaction rate, can be expressed as follows:

Fig. 2 Si_2H_6 conversion as a function of C_2H_2 concentration at various reactor diameters. Reaction was performed at $\text{PSi}_2\text{H}_6 = 0.15$ torr and 873 K.

$$k_a = k_g + (S/V)k_s \quad (1)$$

where k_g (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 Si_2H_6 in the absence of C_2H_2 . A good linearity exists. The slope of the line is 1.95×10^{-2} m/s and the intercept of the y axis is 28.5 s^{-1} , which correspond to k_s and k_g , respectively. The value of k_g (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 C_2H_2 concentration region as shown in Fig. 2.

Fig. 3 Dependence of the overall reaction rate constant of Si_2H_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 $\text{PSi}_2\text{H}_6 = 0.15$ torr, $\text{PC}_2\text{H}_2 = 0$ torr, and 873 K.

Fig. 4 Si_2H_6 conversion as a function of C_2H_2 concentration at various temperatures. Reaction was performed at $\text{PSi}_2\text{H}_6 = 0.15$ torr and reactor diameter of 15.6 mm.

Figure 4 shows the conversion of Si_2H_6 as a function of C_2H_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 C_2H_2 . The result is shown in Table I. Both k_g 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 Si_2H_6 (η), which is calculated from k_s using the relation $k_s = 1/4 \eta v$ (v is the average speed of Si_2H_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.

Table I. Contribution of the gas-phase reaction and surface reaction of Si_2H_6 at various temperatures.

T (K)	k_a (1/s)	k_g (1/s)	$k_s(S/V)$ (1/s)	η
823	9.2	5.6	3.6	1.1×10^{-4}
873	32.7	25.2	7.5	2.1×10^{-4}
903	64.1	42.2	21.9	6.1×10^{-4}

Fig. 5 Dependence of the gas-phase reaction rate (k_g) on temperature.

Fig. 6 Dependence of the reactive sticking probability of Si_2H_6 (η) on temperature

Fig. 7 Si_2H_6 conversion as a function of C_2H_2 at various Si_2H_6 concentrations. Reaction was performed at 873 K and reactor diameter of 10.5 mm.

Figure 7 shows the conversion of Si_2H_6 as a function of C_2H_2 concentration at various Si_2H_6 initial concentrations. In the high C_2H_2 concentration region, the Si_2H_6 conversions (about 45%) were independent of the concentration of Si_2H_6 at Si_2H_6 partial pressures of 0.075 torr and 0.15 torr while the conversion increased when Si_2H_6 partial pressure was raised to 0.3 torr and 0.6 torr. This result indicates a first order reaction with respect to Si_2H_6 when Si_2H_6 partial pressure is lower than 0.15 torr, and a higher reaction order when Si_2H_6 partial pressure is larger than 0.15 torr. This nonlinear kinetics is attributable to a reaction of the reactant Si_2H_6 with its initial gas-phase product, SiH_2 , to form Si_3H_8 or other high order silanes ($\text{Si}_n\text{H}_{2n+2}$, $n > 3$).

The pyrolysis of Si_2H_6 has been extensively studied.⁸⁻⁹ The primary step of the homogeneous reaction, most favored, is proposed to be the decomposition of Si_2H_6 into SiH_2 and SiH_4 . Buss *et al.*¹⁰ have studied the surface chemistry of Si_2H_6 . They showed that the reactive sticking probability of Si_2H_6 on a silicon surface was a function of both temperature and Si_2H_6 gas flux. Though different experimental conditions were used, the reactive sticking probability extrapolated at 873 K and Si_2H_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 Si_2H_6 reacts with the adsorbed C_2H_2 on the substrate surface to form SiC films.

2. Si_2H_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_2H_6 and C_2H_2 as follows:

The trapping reaction of SiH_2 and C_2H_2 may occur in the gas-phase or on the surface, i.e., SiH_2 may react with C_2H_2 in the gas phase or with the adsorbed C_2H_2 .

Fig. 8 Schematic representation of the SiC film formation mechanism by $\text{Si}_2\text{H}_6 + \text{C}_2\text{H}_2$

The surface reaction of Si_2H_6 is almost suppressed in the presence of an abundance of C_2H_2 , presumably due to the strong adsorption of C_2H_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 Si_2H_6 concentrations, the nonlinear reaction of Si_2H_6 and SiH_2 to form high order silanes may be the reason for the particle formation in the outlet of the reactor. When Si_2H_6 concentration is less than 0.15 torr, the gas-phase species SiH_2 , with a negligible extent of reaction with Si_2H_6 , mainly reacts with C_2H_2 to form SiC films.

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 $\text{PSiH}_6 = 0.15$ torr, $\text{PC}_2\text{H}_2 = 0.9$ torr, $d = 15.6$ mm, $T = 873$ K.

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

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.¹¹ 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 ($\text{PSi}_2\text{H}_6 = 0.15$ torr, $\text{PC}_2\text{H}_2 = 0.90$ torr, $d = 15.6$ mm, and $T = 873$ K) ensures that no nonlinear reaction respect to Si_2H_6 occurs and that most of the surface reaction is retarded. For this reason, the film forming species was expected to be SiH_2 or a chemically active species produced from SiH_2 and C_2H_2 .

Another approach named the Macro cavity Method¹² was applied to support the proposed mechanism. In this work, two pieces of silicon wafer (13×15 mm²) were processed to form a macro cavity by putting spacers (0.1 mm in width) between them. The macro cavity 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 macro cavity. 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 macro cavity indicates an active gas-phase intermediate does exist in this reaction system. The intermediate, accumulated in the gas-phase, diffuses into the macro cavity 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, Si_2H_6 , diffusing deeply into the macro cavity 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

$$\text{G.R.} = [k_s + (V/S)k_g]C\rho \quad (7)$$

where C is the Si_2H_6 concentration and ρ is the volume of solid product produced from a mole of Si_2H_6 . Since k_g , V/S (equals to $W/2$, W = cavity spacing), and G.R. are known and the Si_2H_6 concentration at the position where the macro cavity was placed can be estimated from k_g , the surface reaction rate constant (k_s) can be calculated. The result showed a value of $k_s = 4 \times 10^{-4}$ m/s, under the condition of sufficient addition of C_2H_2 . Compared with the reaction of Si_2H_6 in the absence of C_2H_2 ($k_s = 1.95 \times 10^{-2}$ m/s), the surface reaction rate constant is smaller by two orders, which suggests a complete retarding effect of C_2H_2 to the surface reaction of Si_2H_6 .

4.-Conclusions

In this study, SiC films were synthesized from Si_2H_6 and C_2H_2 by the LPCVD method at quite a low temperature of 873 K. The surface and gas-phase chemistry of Si_2H_6 in the presence of C_2H_2 was quantitatively investigated. Compared with the reaction of Si_2H_6 in the absence of C_2H_2 , the surface reaction of Si_2H_6 was strongly retarded by C_2H_2 while the gas-phase reaction was unaffected. Addition of C_2H_2 allowed us to separate the surface reaction of Si_2H_6 from the overall reaction. In this way, the sticking coefficient of Si_2H_6 was, for the first time, measured without using a high vacuum reactor system. Also, we found that the gas-phase reaction of Si_2H_6 obeyed a nonlinear kinetics when Si_2H_6 concentration was larger than 0.15 torr, which was attributed to the insertion reaction of SiH_2 with reactant Si_2H_6 to form high order silanes ($\text{Si}_n\text{H}_{2n+2}$, $n > 2$). Under the

condition of first order reaction with respect to Si_2H_6 and an abundance of C_2H_2 , an intermediate, which may be SiH_2 or a compound produced from SiH_2 and C_2H_2 , deposited on the substrate with a sticking probability of 0.1. A study of the detailed mechanism is now under way.

5.-References

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