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Density and deposition rates of amorphous CVD-Si_3N_4 including carbon

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Amorphous Si_3N_4 containing uniformly distributed carbon was prepared by chemical vapour deposition [Am. CVD-(Si_3N_4–C)] using $SiCl_4$ vapour and NH_3, H_2 and C_3H_8 gases at deposition temperatures (T_{dep}) of 1100 to 1300° C and at total gas pressures (P_{tot}) of 30 to 70 torr. The density of Am.CVD-(Si_3N_4–C) is between 2.80 and 3.00 g cm^{-3}, depending upon the deposition conditions. Rate of growth in thickness increases with increasing T_{dep} and P_{tot}, and has the largest value of 0.6 mm h^{-1} at T_{dep} = 1300° C, P_{tot} = 70 torr and propane gas flow rates [$FR(C_3H_8)$] of 0 to 20 cm^3 min^{-1}. The activation energy of the formation decreases from 38 to 20 kcal mol^{-1} with increasing P_{tot} and $FR(C_3H_8)$.

1. Introduction

The chemical vapour deposition (CVD) technique can be used to synthesize not only powder and film but also bulk materials. Nickl and Braunmühl [1] and Jacobson [2] prepared Si–N–C system material using the CVD technique. Nickl and Braunmühl [1] have prepared deposits of Si–N–C material at temperatures between 1100 and 1300 °C using $SiCl_4$, CCl_4, H_2 and N_2 as the source gases and they examined the structure and morphology of the resulting deposits. They showed that the deposits are a mixture of Si + SiC + Si_3N_4, however, they did not report any properties of these deposits. Jacobson [2] prepared an amorphous Si–N–C system powder using $SiCl_4$, NH_3, N_2 and CH_4, and showed that the powder is useful as a starting material for SiAlON.

TABLE I Deposition conditions

Parameter		Conditions
Heating method		Direct heating of graphite substrate
Deposition temperature (T_{dep})		1100, 1200, 1300° C
Total gas pressure (P_{tot})		39, 50, 70 torr
Gas flow rate (FR)		
H_2 gas	$FR(H_2)$	700 cm^3 min^{-1}
$SiCl_4$ vapour	$FR(SiCl_4)$	170 cm^3 min^{-1}
NH_3 gas	$FR(NH_3)$	60 cm^3 min^{-1}
C_3H_8 gas	$FR(C_3H_8)$	0, 10, 25, 40, 70 100 cm^3 min^{-1}
Deposition time (t)		0.5 to 8 h

The present authors have previously reported the CVD conditions for the formation of plate-like amorphous Si_3N_4 containing carbon [Am. CVD-Si_3N_4–C)] [3]. This paper describes the density, deposition rate and deposition mechanism of Am.CVD-(Si_3N_4–C).

2. Experimental procedures

2.1. Preparation of amorphous Si_3N_4–C

The Am.CVD-(Si_3N_4–C) was prepared on a directly heated graphite substrate by the CVD technique using $SiCl_4$, NH_3, H_2 and C_3H_8. The detailed procedures for the above sample preparation have been reported previously [3]. The deposition conditions of Am.CVD-(Si_3N_4–C) are summarized in Table I. The carbon content is shown in Fig. 1.

2.2. Density measurements

The samples, together with the graphite substrate, were cut to approximately 10 mm by 10 mm using a diamond cutter. The graphite substrate was then removed by SiC abrasive and the specimens were ultrasonically cleaned in acetone. The density was measured by the displacement technique using toluene.

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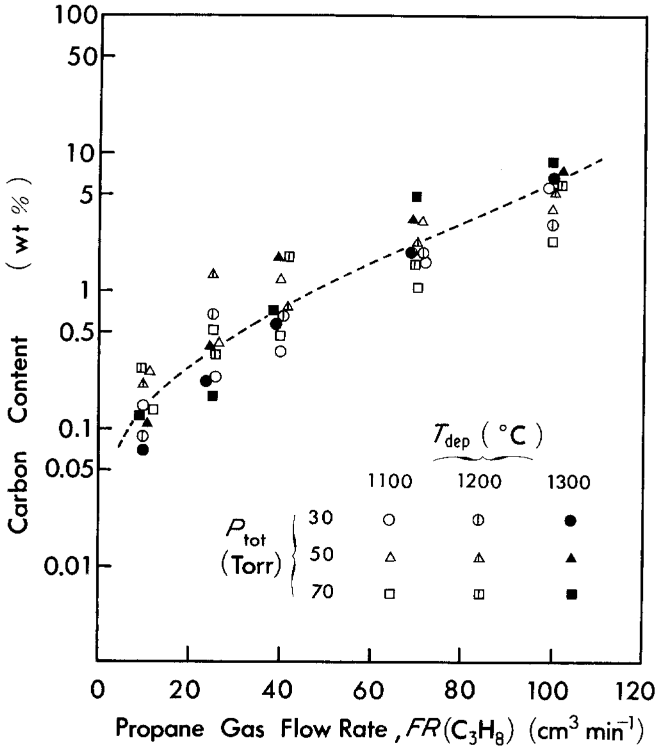

Figure 1 Carbon content of Am.CVD-(Si_3N_4–C).

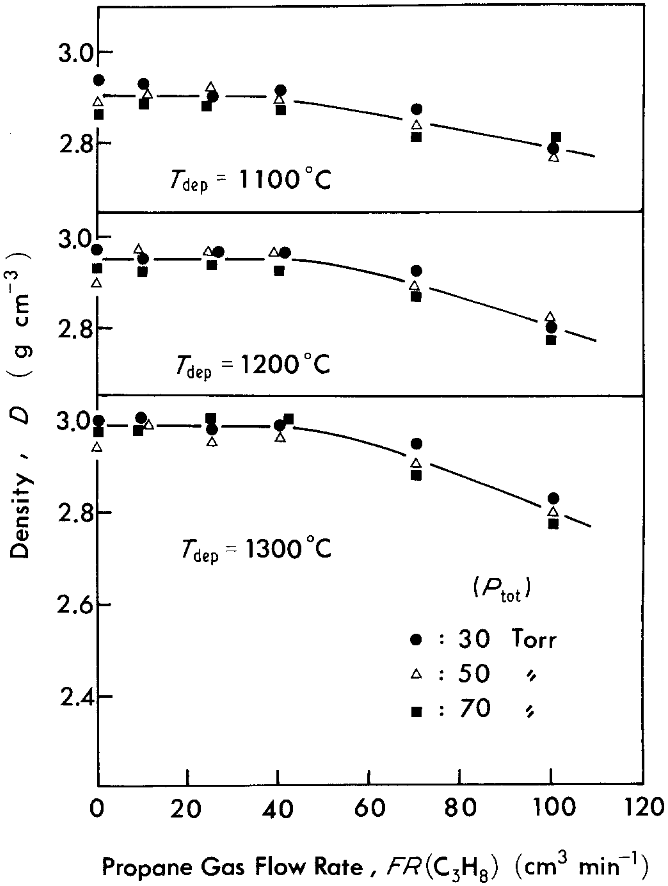

Figure 2 Effect of propane gas flow rate [$FR(C_3H_8)$] on density (D).

2.3. Thickness measurements

The thickness of Am.CVD-(Si_3N_4–C) was determined from the cross-section of the prepared specimens. The final thickness was obtained by averaging the values measured at about ten points on the specimen by using a travelling microscope (accuracy: 0.01 mm). The variation of the thickness was within a few per cent of the mean.

2.4. Deposition rates

Since the thickness (x) of the deposit increases linearly with the deposition time (t) [4], (x/t) is defined as the growth rate of the thickness. The product of the density (D) and the growth rate of the thickness (x/t), $D\,(x/t)$, is defined as the deposition rate constant (k). The value of k represents the weight increase of Am. CVD-(Si_3N_4–C) per unit time per unit surface area of the substrate.

3. Results

3.1. Density

Fig. 2 shows the relationship between the density (D) and the propane gas flow rate [$FR(C_3H_8)$] at T_{dep} = 1100 to 1300 °C. As shown in Fig. 2, the measured density at $FR(C_3H_8) = 0$ to $40\,cm^3\,min^{-1}$ is almost constant at each T_{dep}. The density above $FR(C_3H_8) = 40\,cm^3\,min^{-1}$ decreases with increasing value of $FR(C_3H_8)$, in such a way that the extent of the decrease is larger at the higher T_{dep}. The variation of D with T_{dep} at $FR(C_3H_8)$ = 0, 40, 70 and 100 $cm^3\,min^{-1}$ is presented in Fig. 3. As shown in Fig. 3, D increases with increasing T_{dep}, although the effect of T_{dep} on D decreases with increasing $FR(C_3H_8)$ in the range $FR(C_3H_8) = 0$ to $70\,cm^3\,min^{-1}$. At $FR(C_3H_8) = 100\,cm^3\,min^{-1}$, D is little affected by T_{dep} and indicates a constant value of about $2.80\,g\,cm^{-3}$.

3.2. Growth rate of the thickness

Fig. 4. illustrates the effect of $FR(C_3H_8)$ on the growth rate of the thickness (x/t) at T_{dep} = 1100 to 1300 °C. At T_{dep} = 1100 and 1200 °C, (x/t) is little affected by $FR(C_3H_8)$ at $P_{tot} = 30$ torr, however, (x/t) decreases with increasing $FR(C_3H_8)$ at both P_{tot} = 50 and 70 torr. At T_{dep} = 1300 °C, (x/t) decreases with increasing $FR(C_3H_8)$ at every P_{tot}.

3.3 Deposition rate constant

Fig. 5 indicates the Arrhenius plot of the deposition rate constant (k) at $FR(C_3H_8)$ = 0, 40, 70 and 100 $cm^3\,min^{-1}$. The slope of each line in Fig. 5 decreases with increasing P_{tot} and $FR(C_8H_8)$. The values of the activation energy obtained from these slopes are represented in Table II.

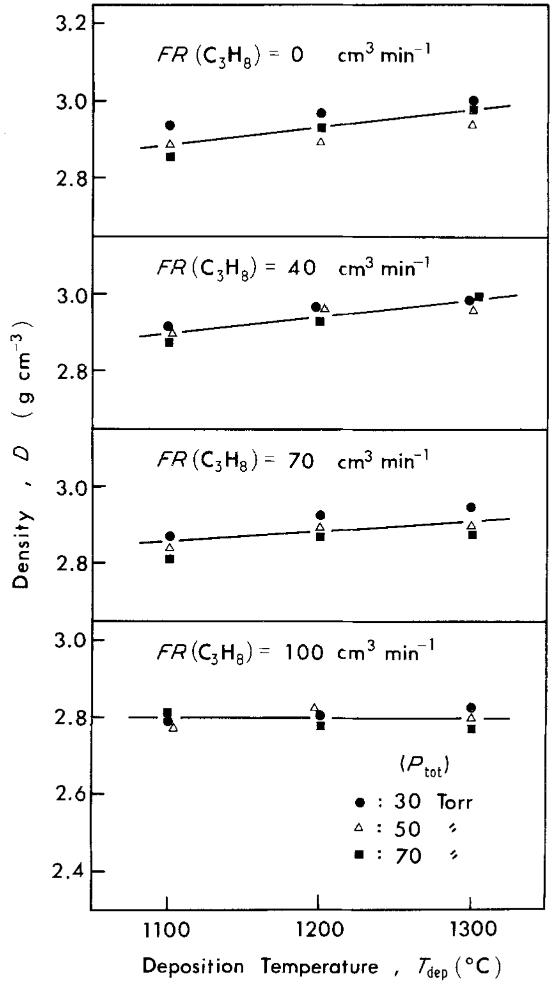

Figure 3 Effect of deposition temperature (T_{dep}) on density (D).

4. Discussion

4.1. Density

It has been reported that the density of Am.CVD-Si_3N_4 varies with deposition conditions [4–7]. The results for Am.CVD-Si_3N_4 in the present work at $FR(C_3H_8) = 0\,cm^3\,min^{-1}$ are compared with those of the previous works [4–7] in Fig. 6. The reasons for the difference among these results shown in Fig. 6 is not yet known.

Fig. 7 represents the relationship between density (D) and carbon content at various T_{dep}. The values of D decrease linearly with increasing carbon content at each T_{dep}. The density of carbon

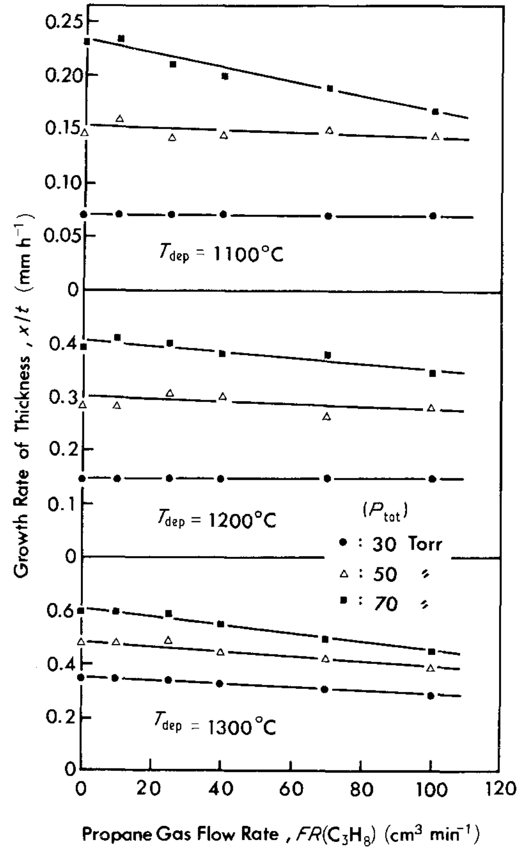

Figure 4 Effect of propane gas flow rate [$FR(C_3H_8)$] on the thickness growth rate (x/t).

is calculated to be about 1.6 g cm^{-3} at each T_{dep} assuming that the density of Am.CVD-(Si_3N_4–C) is represented by the linear combination of the density of Am.CVD-Si_3N_4 and that of carbon. The lines in Fig. 7 indicate the calculated value using the density of carbon to be 1.6 g cm^{-3}. However, the density value of 1.6 g cm^{-3} is similar to that of pyrolytic carbon obtained at T_{dep} = 1600 to 1800° C (1.3 to 1.5 g cm^{-3}) [8] but is smaller than that obtained at T_{dep} = 1100 to 1300 ° C (2.1 to 2.2 g cm^{-3}) [8].

The studies on the structure of Am.CVD-Si_3N_4 matrix and the existence state of the carbon are currently underway.

4.2. Deposition rate and activation energy

The growth rate of the thickness at $FR(C_3H_8)$ = 0 cm^3 min^{-1} increases with increasing T_{dep} and P_{tot}. Previous work by the authors [4] indicated that (x/t) has a maximum value in the range P_{tot} = 40 to 60 torr at a given T_{dep}. This result is interpreted as follows; when the source gases, issuing from some distance above the substrate, flow around the substrate down its length, the gas flow near the substrate changes from downward forced convection flow to upward natural convection flow in the range P_{tot} = 40 to 60 torr. However, such an (x/t) maximum was not observed in the present work, because the source gases were supplied vertically upward on to the surface of the substrate and thus no change in the nature of the

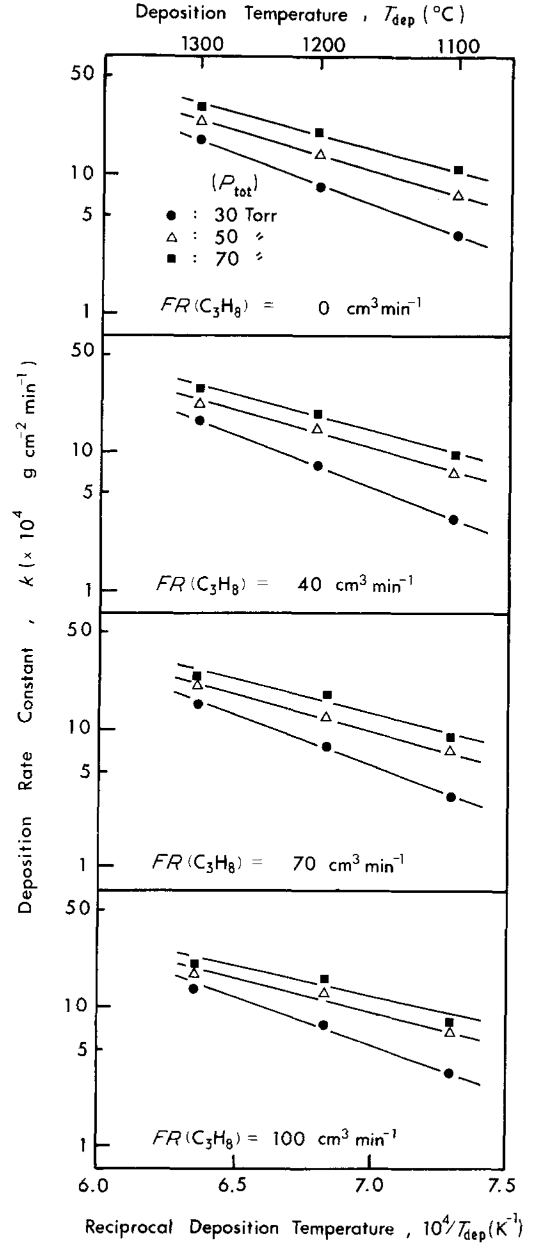

Figure 5 Arrhenius plot of the deposition rate constant (k).

TABLE II Activation energies of Am.CVD-Si_3N_4 and Am.CVD-(Si_3N_4–C) formation.

P_{tot} (torr)	$FR(C_3H_8)$ ($cm^3\ min^{-1}$)	Activation energy ($kcal\ mol^{-1}$)
30	0	38
30	40	35
30	70	34
30	100	33
50	0	28
50	40	26
50	70	26
50	100	24
70	0	25
70	40	24
70	70	23
70	100	20

gas flow as described above occurred at each P_{tot}. The result of the present work is compared with that obtained previously by the authors [4] in Fig. 8.

As shown in Table II, the activation energy (E) decreases with increasing P_{tot} and $FR(C_3H_8)$. It is speculated that this decrease is caused by the formation of by-products such as $Si(NH)_2$ and NH_4Cl powders [9] which are easily formed with increasing T_{dep}, P_{tot} and $FR(C_3H_8)$.

5. Conclusions

(1) The density of Am.CVD-(Si_3N_4–C) increases with increasing T_{dep} from 2.86 to 3.00 $g\,cm^{-3}$ and it is little affected by $FR(C_3H_8)$ in the range $FR(C_3H_8) = 0$ to $40\,cm^3\,min^{-1}$. Above $FR(C_3H_8) = 40\,cm^3\,min^{-1}$, the density decreases with increasing $FR(C_3H_8)$.

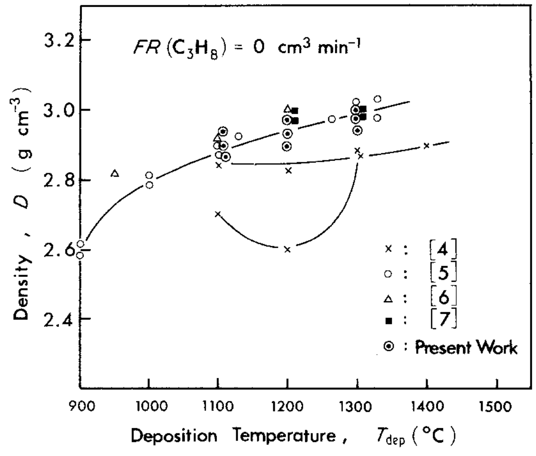

Figure 6 Density of Am.CVD-Si_3N_4. Present work and previous works [4–7].

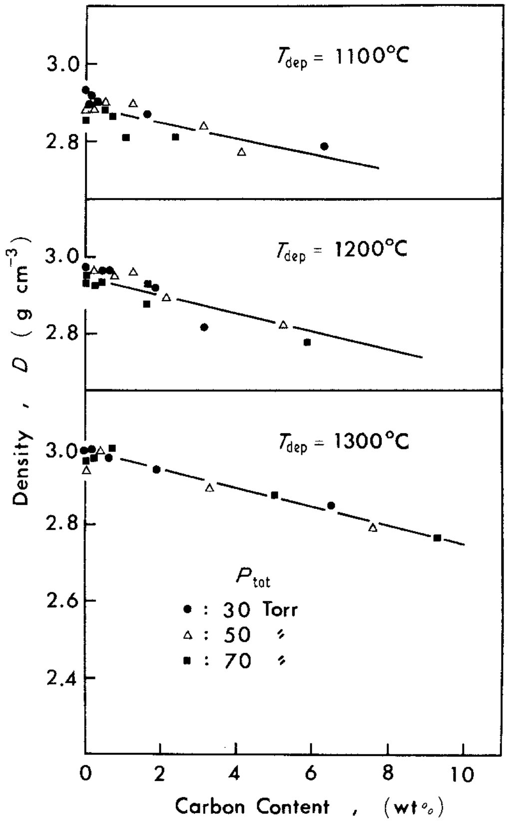

Figure 7 The relationship between carbon content and density (D).

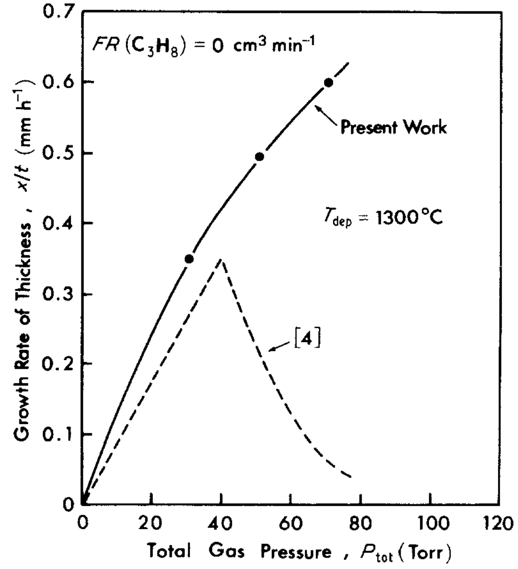

Figure 8 The thickness growth rate (x/t) of Am.CVD-Si_3N_4. Present work and previous work [4].

(2) The density decreases with increasing carbon content at each T_{dep}. At $T_{\mathrm{dep}} = 1300°\mathrm{C}$, the density varies from about 3.00 to 2.75 $\mathrm{g\,cm^{-3}}$ with an increase in carbon content from about 0 to 10 wt%.

(3) The growth rate of the thickness (x/t) increases with increasing T_{dep} and P_{tot}. The value of (x/t) is not affected by $FR(C_3H_8)$ at $P_{\mathrm{tot}} = 30$ torr and at $T_{\mathrm{dep}} = 1100$ and 1200° C. (x/t) decreases with increasing $FR(C_3H_8)$ at $P_{\mathrm{tot}} = 50$ and 70 torr at $T_{\mathrm{dep}} = 1100$ and 1200 ° C, and at every P_{tot} at $T_{\mathrm{dep}} = 1300°\mathrm{C}$. The largest value of (x/t) of about 0.6 $\mathrm{mm\,h^{-1}}$ was obtained at $T_{\mathrm{dep}} = 1300$ ° C, $P_{\mathrm{tot}} = 70$ torr and $FR(C_3H_8) = 0$ to 20 $\mathrm{cm^3\,min^{-1}}$.

(4) The activation energy decreases from 38 to 20 $\mathrm{kcal\,mol^{-1}}$ with increasing P_{tot} and $FR(C_3H_8)$.

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