

# Density and deposition rate of chemically vapour-deposited $\text{Si}_3\text{N}_4$ -TiN composites

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$\text{Si}_3\text{N}_4$ -TiN composites with an  $\text{Si}_3\text{N}_4$  matrix and TiN dispersion were prepared at deposition temperatures of 1050 to 1450°C and total gas pressures of 1.33 to 10.7 kPa by the chemical vapour deposition of a  $\text{SiCl}_4$ - $\text{TiCl}_4$ - $\text{NH}_3$ - $\text{H}_2$  system. The density and deposition rate were measured and the formation mechanism of the composites was considered. The density of the crystalline ( $\alpha$  or  $\beta$ )  $\text{Si}_3\text{N}_4$  matrix was practically equal to the theoretical values. However, the density of the amorphous  $\text{Si}_3\text{N}_4$  matrix was between 2.85 and 3.03  $\text{g cm}^{-3}$ , depending on the deposition conditions. The highest growth rate of thickness for the composites was 0.47  $\text{mm h}^{-1}$ . The deposition rate of the  $\text{Si}_3\text{N}_4$  matrix increased with the addition of  $\text{TiCl}_4$  vapour, the apparent activation energy being 68 to 84  $\text{kJ mol}^{-1}$ . The deposition rate of the TiN dispersion exhibited a minimum at a deposition temperature of 1250 or 1350°C.

## 1. Introduction

Chemically vapour-deposited (CVD)  $\text{Si}_3\text{N}_4$  has been investigated both as a dielectric or passivation film in electronic devices and as a refractory coating for high temperature applications. In recent years, some literature has become available on CVD of  $\text{Si}_3\text{N}_4$ -composites. Nickl and Braumühl [1] prepared Si- $\text{Si}_3\text{N}_4$  and Si-SiC- $\text{Si}_3\text{N}_4$  deposits from  $\text{SiCl}_4 + \text{N}_2 + \text{H}_2$  and  $\text{SiCl}_4 + \text{CCl}_4 + \text{N}_2 + \text{H}_2$  reactant gases, respectively, and reported that the composites were formed via carbidation and nitridation of the free silicon surface. Zirinsky and Irene [2] prepared films of mixtures of AlN and  $\text{Si}_3\text{N}_4$  by the ammonolysis of gaseous  $\text{AlCl}_3$  and  $\text{SiH}_4$  and found that the depositions of the AlN and  $\text{Si}_3\text{N}_4$  components were uncoupled. Tamaki *et al.* [3] carried out CVD of a  $\text{SiH}_4$ - $\text{NH}_3$ - $\text{GeH}_4$  system and found a steep increase in the deposition rate of Ge-doped  $\text{Si}_3\text{N}_4$  films with an addition of a small amount of  $\text{GeH}_4$ . Landingham and Taylor [4] attempted to prepare CVD-Sialon from  $\text{SiCl}_4 + \text{AlCl}_3 + \text{NH}_3 + \text{O}_2$  reactant gases and actually obtained a deposit composed of AlN,  $\text{Si}_3\text{N}_4$  and unknown phases, instead of Sialon. The present authors prepared  $\text{Si}_3\text{N}_4$ -C composites having an amorphous  $\text{Si}_3\text{N}_4$  matrix, by CVD of a  $\text{SiCl}_4$ -

$\text{NH}_3$ - $\text{H}_2$ - $\text{C}_3\text{H}_8$  system [5] and examined the density and deposition rate of the composites [6].

CVD of a  $\text{SiCl}_4$ - $\text{TiCl}_4$ - $\text{NH}_3$ - $\text{H}_2$  system was also conducted by the present authors in order to prepare  $\text{Si}_3\text{N}_4$ -TiN composites. The crystal structure, preferred orientation, Ti content, surface morphology and microstructure were previously reported [7-10]. This paper is concerned with the density and deposition rate of the  $\text{Si}_3\text{N}_4$ -TiN composites and includes a discussion on the formation mechanism.

## 2. Experimental procedure

### 2.1. Sample preparation

The  $\text{Si}_3\text{N}_4$ -TiN composites were prepared on a directly heated graphite substrate at deposition temperatures,  $T_{\text{dep}}$ , of 1050 to 1450°C and total gas pressures,  $P_{\text{tot}}$ , of 1.33 to 10.7 kPa. The flow rates of  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{NH}_3$  and  $\text{H}_2$  gases were kept at 136, 18, 120 and 2720  $\text{cm}^3 \text{min}^{-1}$ , respectively. The deposition time was 4 to 8 h. As shown in Fig. 1 [9], three kinds of composites having amorphous,  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  matrices were obtained, depending on  $T_{\text{dep}}$  and  $P_{\text{tot}}$ . The deposits were composed of  $\text{Si}_3\text{N}_4$  and TiN, not including free silicon, free titanium and titanium silicide phases. The TiN

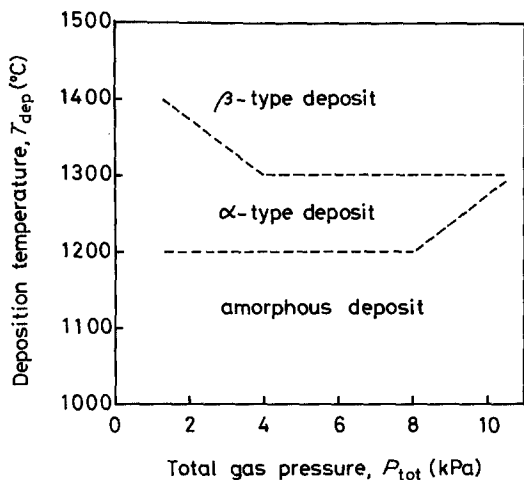


Figure 1 Effects of  $T_{\text{dep}}$  and  $P_{\text{tot}}$  on the structure of the  $\text{Si}_3\text{N}_4$  matrix in  $\text{Si}_3\text{N}_4$ -TiN composites.

weight fraction ( $f_{\text{TN}}$ ) in the composites depended on  $T_{\text{dep}}$  and  $P_{\text{tot}}$ , as shown in Fig. 2.

## 2.2. Density measurement

The sample deposited on the substrate was cut to about  $10\text{ mm} \times 10\text{ mm}$ . After the substrate was removed with SiC abrasive, the sample was ultrasonically cleaned in acetone. The density of the composite,  $\rho$ , was determined in toluene by the Archimedean method. The density of the  $\text{Si}_3\text{N}_4$  matrix,  $\rho_{\text{SN}}$ , was calculated from Equation 1.

$$\frac{1}{\rho} = \frac{f_{\text{TN}}}{\rho_{\text{TN}}} + \frac{1-f_{\text{TN}}}{\rho_{\text{SN}}} \quad (1)$$

Here  $\rho_{\text{TN}}$  is the density of TiN and a reported value of  $5.43\text{ g cm}^{-3}$  [11] was used.

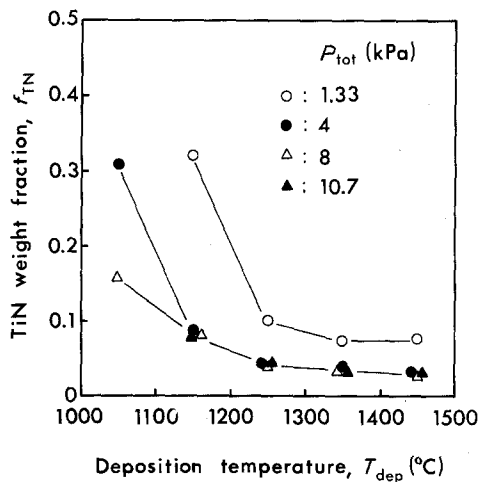


Figure 2 Effect of  $T_{\text{dep}}$  on the TiN weight fraction ( $f_{\text{TN}}$ ) in  $\text{Si}_3\text{N}_4$ -TiN composites.

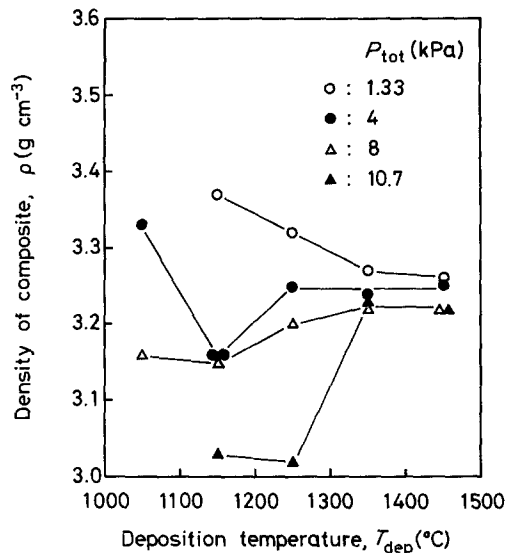


Figure 3 Effect of  $T_{\text{dep}}$  on the density,  $\rho$ , of  $\text{Si}_3\text{N}_4$ -TiN composites.

## 2.3. Thickness measurement and deposition rate

The sample was cut perpendicular to the substrate surface and polished with SiC abrasive. The thickness was determined by averaging the values measured at ten points of the sample using a travelling microscope.

As the thickness,  $x$ , of the deposit increases linearly with the deposition time,  $x/t$  is denoted as the growth rate of thickness. The product of  $x/t$  and  $\rho$ ,  $\rho(x/t)$ , is the deposition rate constant,  $k$ , of the composites, which means the weight increase of the deposit per unit surface of the substrate per unit time. The deposition rate constants of  $\text{Si}_3\text{N}_4$  and TiN in the composite, denoted as  $k_{\text{SN}}$  and  $k_{\text{TN}}$ , respectively, can be calculated from Equations 2 and 3.

$$k_{\text{SN}} = k(1 - f_{\text{TN}}) \quad (2)$$

$$k_{\text{TN}} = kf_{\text{TN}} \quad (3)$$

## 3. Results

### 3.1. Density

As shown in Fig. 3, the density of the composites,  $\rho$ , was in the range from  $3.02$  to  $3.37\text{ g cm}^{-3}$ . Since  $\rho$  is a function of the density of the  $\text{Si}_3\text{N}_4$  matrix,  $\rho_{\text{SN}}$ , and the TiN content, the relation between  $\rho$  and  $T_{\text{dep}}$  is complicated. The value of  $\rho$  decreased with increase in  $P_{\text{tot}}$ , as shown in Fig. 4. However, the change of  $\rho$  with  $P_{\text{tot}}$  was not significant for the composites prepared at  $T_{\text{dep}}$  of 1350 and  $1450^\circ\text{C}$ .

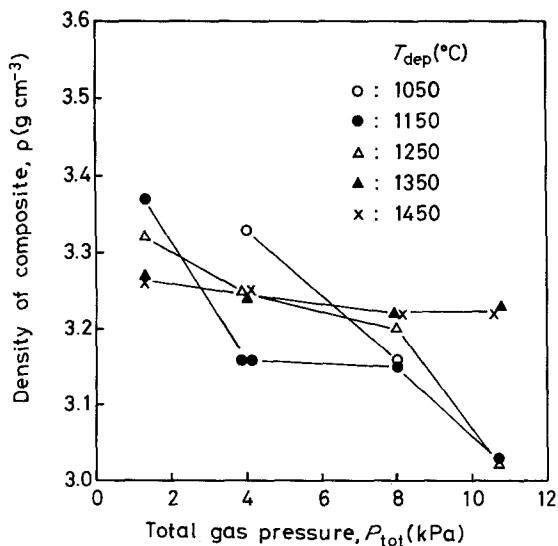


Figure 4 Effect of  $P_{tot}$  on the density,  $\rho$ , of  $\text{Si}_3\text{N}_4$ -TiN composites.

Fig. 5 shows the relation between  $T_{dep}$  and  $\rho_{SN}$  calculated using Equation 1.  $\rho_{SN}$  for the crystalline  $\text{Si}_3\text{N}_4$  was 3.15 to 3.20  $\text{g cm}^{-3}$ , being practically independent of  $T_{dep}$  and  $P_{tot}$ . For the amorphous matrix however,  $\rho_{SN}$  increased with increasing  $T_{dep}$  at each  $P_{tot}$ , the maximum and minimum being 3.03 and 2.85  $\text{g cm}^{-3}$ , respectively.

### 3.2. Growth rate of thickness

The growth rate of thickness of the composites increased with increasing  $T_{dep}$ , as shown in Fig. 6. The maximum value was 0.47  $\text{mm h}^{-1}$  at a  $T_{dep}$  of 1450°C and a  $P_{tot}$  of 4 kPa and the minimum was

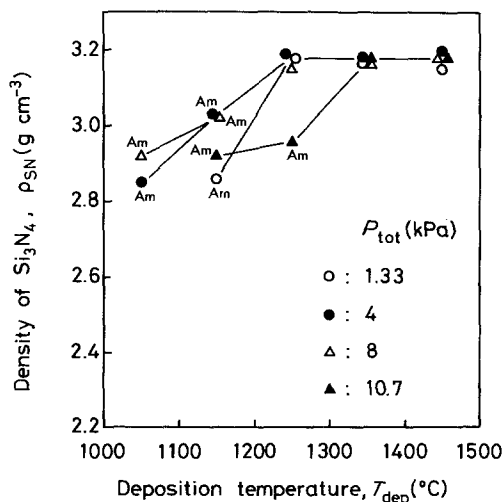


Figure 5 Effect of  $T_{dep}$  on the density,  $\rho_{SN}$ , of the  $\text{Si}_3\text{N}_4$  matrix in  $\text{Si}_3\text{N}_4$ -TiN composites. Am: amorphous  $\text{Si}_3\text{N}_4$ .

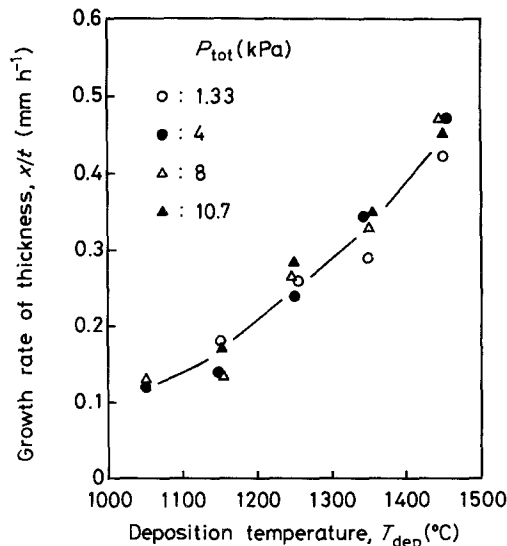


Figure 6 Effect of  $T_{dep}$  on the growth rate of thickness,  $x/t$ , of the  $\text{Si}_3\text{N}_4$ -TiN composites.

0.12  $\text{mm h}^{-1}$  at a  $T_{dep}$  of 1050°C and a  $P_{tot}$  of 4 kPa.

### 3.3. Deposition rate constant

Fig. 7 shows the Arrhenius plots of the deposition rate constant for the  $\text{Si}_3\text{N}_4$  matrix,  $k_{SN}$ , which was calculated using Equation 2. At each  $P_{tot}$ , linear relations were seen and the apparent activation energy was 68 to 84  $\text{kJ mol}^{-1}$ . The value of  $k_{SN}$  at each  $T_{dep}$  was almost independent of  $P_{tot}$ , as shown in Fig. 8.

In the Arrhenius plots of the deposition rate constant for the TiN dispersion,  $k_{TN}$ , as shown in Fig. 9, linear relations were not seen; the minimum of  $k_{TN}$  appeared at a  $T_{dep}$  of 1250 or 1350°C. In contrast to  $k_{SN}$  of Fig. 8, a marked dependence of  $k_{TN}$  on  $P_{tot}$  was noticed in Fig. 10.

## 4. Discussion

Pore-free and highly dense materials can be produced by the CVD technique. As shown in Fig. 5, the density of the crystalline  $\text{Si}_3\text{N}_4$  matrix in the composites is 3.15 to 3.20  $\text{g cm}^{-3}$  and is very close to the theoretical values for  $\alpha$ - $\text{Si}_3\text{N}_4$  (3.18  $\text{g cm}^{-3}$ ) and  $\beta$ - $\text{Si}_3\text{N}_4$  (3.19  $\text{g cm}^{-3}$ ) [12]. This result indicates the validity of estimating the density of the  $\text{Si}_3\text{N}_4$  matrix using Equation 1. Fig. 11 gives a comparison of the density of  $\text{Si}_3\text{N}_4$  prepared from a  $\text{SiCl}_4$ - $\text{NH}_3$ - $\text{H}_2$  system with that of the  $\text{Si}_3\text{N}_4$  matrix from the  $\text{SiCl}_4$ - $\text{TiCl}_4$ - $\text{NH}_3$ - $\text{H}_2$  system (Fig. 5). The density of the amorphous  $\text{Si}_3\text{N}_4$  for both systems increased with increasing  $T_{dep}$ . At a

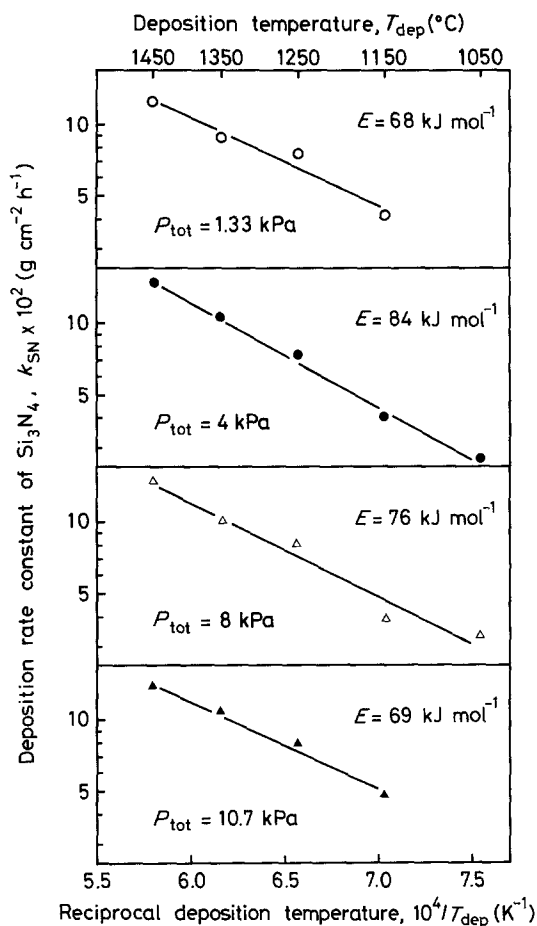


Figure 7 Arrhenius plot of the deposition rate constant,  $k_{\text{SN}}$ , of the  $\text{Si}_3\text{N}_4$  matrix in  $\text{Si}_3\text{N}_4$ -TiN composites.

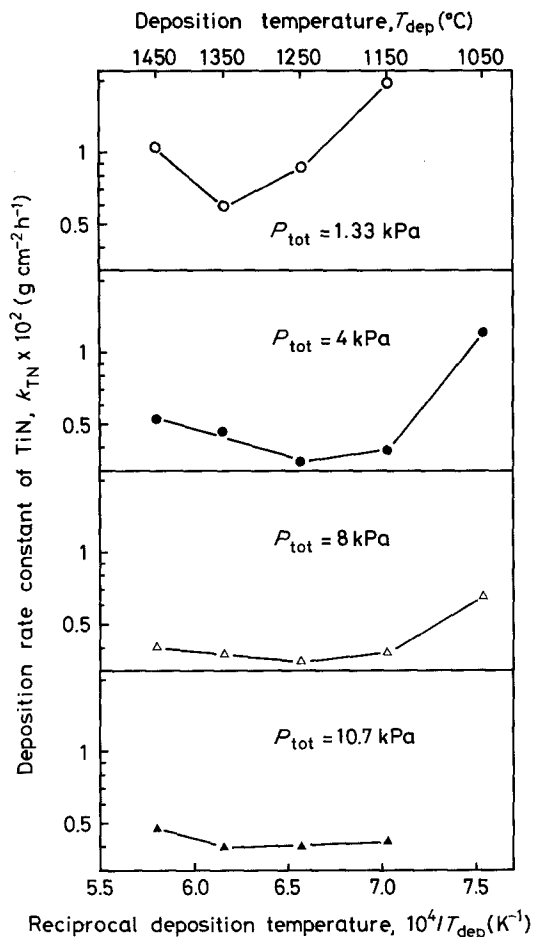


Figure 9 Arrhenius plot of the deposition rate constant,  $k_{\text{TN}}$ , of the TiN dispersion in  $\text{Si}_3\text{N}_4$ -TiN composites.

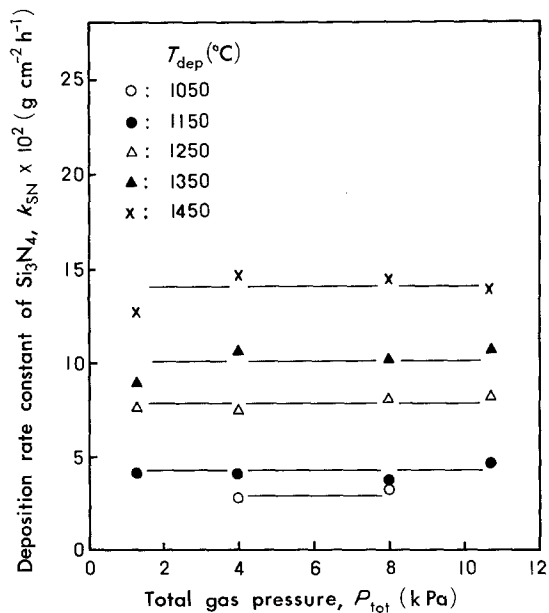


Figure 8 Effect of  $P_{tot}$  on the deposition rate constant,  $k_{\text{SN}}$ , of the  $\text{Si}_3\text{N}_4$  matrix in  $\text{Si}_3\text{N}_4$ -TiN composites.

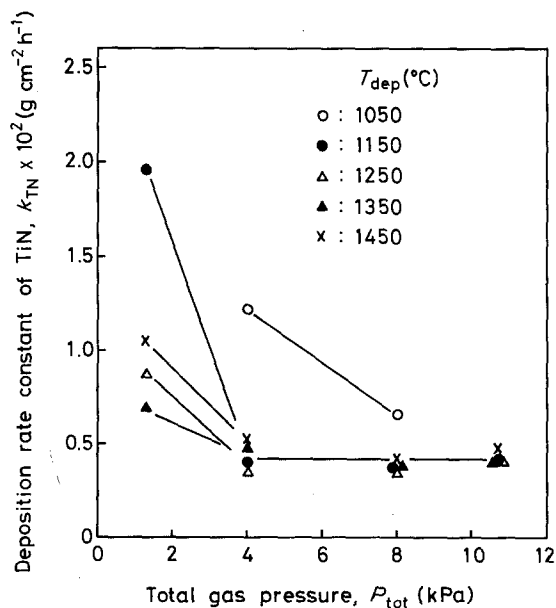


Figure 10 Effect of  $P_{tot}$  on the deposition rate constant,  $k_{\text{TN}}$ , of the TiN dispersion in  $\text{Si}_3\text{N}_4$ -TiN composites.

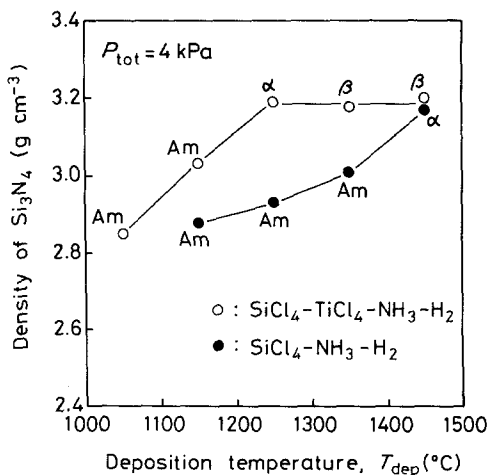


Figure 11 Comparison of the density of  $\text{Si}_3\text{N}_4$  prepared from the  $\text{SiCl}_4\text{-NH}_3\text{-H}_2$  system with that of the  $\text{Si}_3\text{N}_4$  matrix from the  $\text{SiCl}_4\text{-TiCl}_4\text{-NH}_3\text{-H}_2$  system. Am: amorphous  $\text{Si}_3\text{N}_4$ ,  $\alpha$ :  $\alpha\text{-Si}_3\text{N}_4$ ,  $\beta$ :  $\beta\text{-Si}_3\text{N}_4$ .

$T_{\text{dep}}$  of  $1150^\circ\text{C}$ , the density for the  $\text{SiCl}_4\text{-TiCl}_4\text{-NH}_3\text{-H}_2$  system ( $3.03\text{ g cm}^{-3}$ ) is higher than that for the  $\text{SiCl}_4\text{-NH}_3\text{-H}_2$  system ( $2.88\text{ g cm}^{-3}$ ). Therefore, the  $\text{TiCl}_4$  addition has an influence on the amorphous structure of  $\text{Si}_3\text{N}_4$  as well as the polymorphism of  $\text{Si}_3\text{N}_4$ .

Fig. 12 gives a comparison of the deposition rate of  $\text{Si}_3\text{N}_4$  from the  $\text{SiCl}_4\text{-NH}_3\text{-H}_2$  system with that of the  $\text{Si}_3\text{N}_4$  matrix from the  $\text{SiCl}_4\text{-TiCl}_4\text{-NH}_3\text{-H}_2$  system (Fig. 7). The apparent activation energy for the  $\text{SiCl}_4\text{-NH}_3\text{-H}_2$  system is  $120\text{ kJ mol}^{-1}$  which agrees well with the previously reported value,  $130\text{ kJ mol}^{-1}$  [13]. It can be seen

from Fig. 12 that the  $\text{TiCl}_4$  addition caused an increase in the deposition rate of  $\text{Si}_3\text{N}_4$  and a decrease in the apparent activation energy. Neumann and Kofler [14] investigated the effect of addition of nickel-carbonyl vapour on the deposition of pyrocarbon from acetylene and found that Ni-particles derived by decomposition of carbonyl catalyzed the deposition of pyrocarbon. They stated that Ni-particles acted as nucleation centres for high molecular weight hydrocarbons generated as intermediate products of the acetylene disproportion.  $\text{SiCl}_4$  reacts with  $\text{NH}_3$  to form  $\text{Si}(\text{NH})_2$ , even at room temperature, and  $\text{Si}(\text{NH})_2$  readily polymerizes with increasing temperature to intermediates such as  $[\text{Si}_3(\text{NH})_3\text{N}_2]_n$  and  $[\text{Si}_2(\text{NH})\text{N}_2]_n$  [13]. It is thought, therefore, that the  $\text{TiCl}_4$  addition promotes the formation of the above Si-N-H intermediate polymers, causing the increased deposition rate of  $\text{Si}_3\text{N}_4$ .

The complicated relation between the deposition rate of TiN and  $T_{\text{dep}}$ , as seen in Fig. 9, suggests that different processes for the TiN deposition may take place at the high and low  $T_{\text{dep}}$ . Hojo and Kato [15] obtained an attractive result from a study on the synthesis of TiN powders using  $\text{TiCl}_4$  and  $\text{NH}_3$  gases; when the mixing temperature for  $\text{TiCl}_4$  and  $\text{NH}_3$  is below  $250^\circ\text{C}$ ,  $\text{TiCl}_4\text{-NH}_3$  adducts are first formed, followed by the thermal decomposition of the adducts into TiN particles in the higher temperature zone. On the other hand, when the mixing temperature is above  $600^\circ\text{C}$ , TiN particles are directly formed by

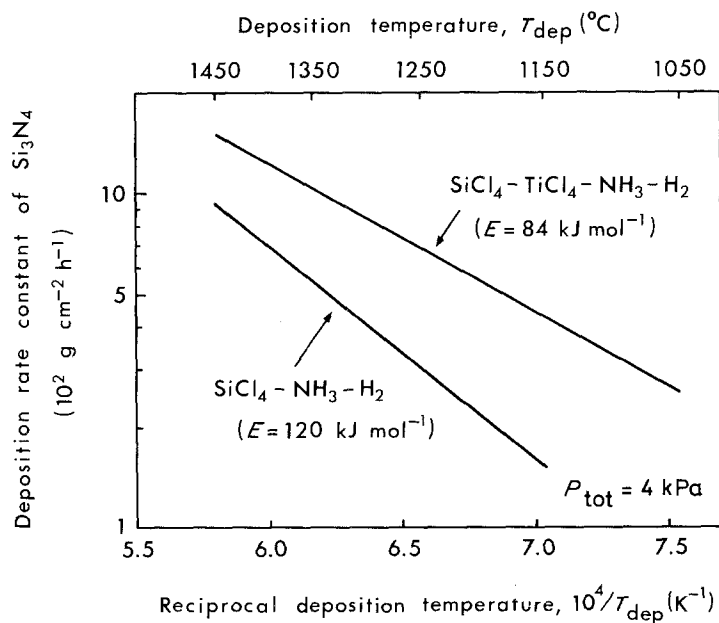


Figure 12 Comparison of the deposition rate constant of  $\text{Si}_3\text{N}_4$  prepared from the  $\text{SiCl}_4\text{-NH}_3\text{-H}_2$  system with that of the  $\text{Si}_3\text{N}_4$  matrix from the  $\text{SiCl}_4\text{-TiCl}_4\text{-NH}_3\text{-H}_2$  system.

the vapour phase reaction of  $\text{TiCl}_4$  with  $\text{NH}_3$ . In the present study, we adopted a cold-wall technique by which only the substrate was heated and designed a configuration so that the mixing of  $\text{SiCl}_4$ ,  $\text{TiCl}_4$  and  $\text{NH}_3$  gases occurs at a place 20 mm from the substrate [9]; the mixing temperature in the present study is lower than the substrate temperature,  $T_{\text{dep}}$ . Thus, the two types of processes as suggested by Hojo and Kato seem to be related to the behaviour of the TiN deposition, as shown in Fig. 9.

## 5. Conclusions

(a) The density of  $\text{Si}_3\text{N}_4$ -TiN composite depended on  $T_{\text{dep}}$  and  $P_{\text{tot}}$ . The maximum and minimum were  $3.37$  and  $3.02 \text{ g cm}^{-3}$ , respectively.

(b) The density of the crystalline  $\text{Si}_3\text{N}_4$  matrix was  $3.15$  to  $3.20 \text{ g cm}^{-3}$ . The density of the amorphous matrix increased with increasing  $T_{\text{dep}}$ ; the minimum was  $2.85 \text{ g cm}^{-3}$  and the maximum  $3.03 \text{ g cm}^{-3}$ .

(c) The growth rate of thickness of the composite increased with increasing  $T_{\text{dep}}$ , the maximum being  $0.47 \text{ mm h}^{-1}$ .

(d) The apparent activation energy for the deposition of the  $\text{Si}_3\text{N}_3$  matrix was  $68$  to  $84 \text{ kJ mol}^{-1}$ . The  $\text{TiCl}_4$  addition increased the deposition rate of  $\text{Si}_3\text{N}_4$ .

(e) The deposition rate of the TiN dispersion exhibited a minimum at  $T_{\text{dep}}$  of  $1250$  or  $1350^\circ\text{C}$ .

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