JOURNAL OF MATERIALS SCIENCE 17 (1982) 1320–1328

Preparation and some properties of chemically vapour-deposited Si_3N_4-TiN composite

TOSHIO HIRAI, SHINSUKE HAYASHI
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan

Chemically vapour-deposited (CVD) Si_3N_4–TiN composite (a plate with the maximum thickness of 1.9 mm) has been prepared on a graphite substrate using a mixture of $SiCl_4$, $TiCl_4$, NH_3 and H_2 gases. The CVD was carried out at deposition temperatures, T_{dep}, in the range of 1050 to 1450° C, total gas pressures, P_{tot}, from 1.33 to 10.7 kPa and gas flow rates of 136 ($SiCl_4$), 18 ($TiCl_4$), 120 (NH_3) and 2720 (H_2) $cm^3 min^{-1}$. The deposits thus obtained appeared black. The Ti content in the composites ranged from 2.1 to 24.8 wt % and was found in the form of TiN. The structure of the Si_3N_4 matrices varied from amorphous (initially) to the α- and β-type, with increasing T_{dep}. Most of the α- and β-type deposits had a preferred orientation (001) parallel to the deposition surface. While the deposition surface of the amorphous deposits showed a pebble structure, the surfaces of the α- and β-type deposits were composed of various kinds of facets. The heat-treating experiment suggested that β-Si_3N_4 obtained in the present work was formed directly via a vapour phase, and not from crystallization of amorphous Si_3N_4 or from transformation of α-Si_3N_4.

1. Introduction

One approach in the course of developing a new material is to combine different components of various substances, i.e. the exploration of composites. Compared to the well-known sintering technique for producing composites, the chemical vapour deposition (CVD) technique can be successfully used to prepare composites having components with low sinterability. Some studies have been conducted on producing composites of a Si_3N_4 matrix by CVD for application in electronic and high temperature structural uses. As materials for electronic applications, Si_3N_4–Si, with a non-ohmic d.c. conduction property [1], Si_3N_4–Ge, with a reduced stress in the film [2], and Si_3N_4–AlN, with an enhanced charge storage property [3] have been reported. As high temperature structural materials, CVD of a Sialon has been attempted [4]. For the same application CVD of Si_3N_4–Si–SiC composites was also conducted [5].

A Si_3N_4–C composite having an amorphous Si_3N_4 matrix with dispersed carbon was prepared by the present authors via CVD of a $SiCl_4$–NH_3–H_2–C_3H_8 system, and it was found that this composite has a good electrical conductivity [6]. Recently, the present authors obtained a Si_3N_4–TiN composite in a plate form from CVD of a $SiCl_4$–NH_3-H_2–$TiCl_4$ system. A brief description on a part of this work has been previously reported [7].

The present paper describes detailed procedures for the preparation of the plate-like Si_3N_4–TiN composite and the influences of CVD conditions on the various characteristics of the resulting composites, such as, its crystal structure, preferred orientation, surface morphology and Ti content.

2. Experimental procedure

2.1. Sample preparation

The deposits were prepared by adding $TiCl_4$ vapour into a $SiCl_4$–NH_3–H_2 system which was

 0022–2461/82/051320–09$03.58/0 © 1982 Chapman and Hall Ltd.

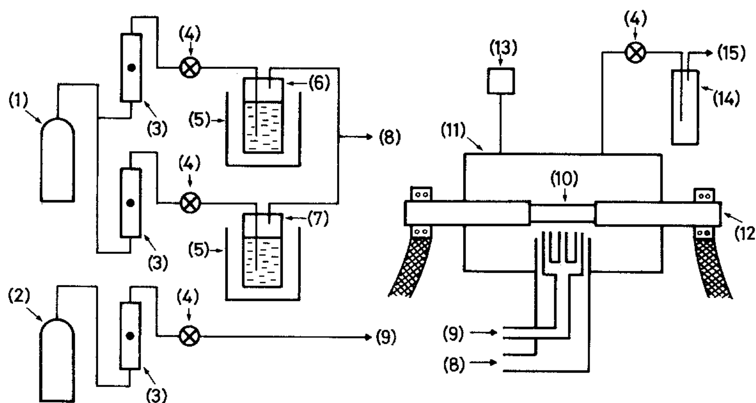


Figure 1 A schematic diagram of the deposition apparatus. (1) H_2 gas, (2) NH_3 gas, (3) flow meter, (4) valve, (5) constant temperature bath, (6) $SiCl_4$ reservoir, (7) $TiCl_4$ reservoir, (8) $SiCl_4$ + $TiCl_4$ + H_2 gas inlet, (9) NH_3 gas inlet, (10) graphite heater (substrate), (11) reaction chamber, (12) water-cooled electrode, (13) manometer, (14) cold trap and (15) rotary pump.

previously used for the preparation of the CVD-Si_3N_4 [8]. The deposition apparatus is schematically illustrated in Fig. 1. The substrate is a graphite plate with dimensions of 80 mm x 25 mm x 4 mm. The substrate was heated by applying an electric current. The deposition temperature, T_{dep}, was measured using a two-colour pyrometer. The $SiCl_4$ and $TiCl_4$ vapours were transported by the H_2 gas by introducing it in the $SiCl_4$ and $TiCl_4$ reservoirs which were kept at temperatures of 0 and 20° C, respectively. The H_2 gas, containing these chloride vapours, was introduced into a reaction chamber through the outer tube of an annular nozzle and NH_3 gas was introduced through the inner tube. The purities of $SiCl_4$, $TiCl_4$ and NH_3 were 99.9 % and that of H_2 was 99.9999 %. The total gas pressure, P_{tot}, in the reaction chamber was controlled using a needle valve. Table I summarizes the CVD conditions used in the present experiment.

2.2. Characterization of samples

The structure of the deposits was examined by an X-ray diffractometer (JEOL DX-GO-S) using Ni-filtered CuKα radiation. The contents of α- and β-Si_3N_4 in the crystalline deposites were determined from the peak heights of the (201) reflection for the α-phase, and the (110) reflection for the β-phase, for pulverized samples (under 325 mesh) using a calibration curve for the ratio α/β obtained from the mixtures of α- and β-Si_3N_4 powders. The lattice parameters of α- and β-Si_3N_4 were determined by the Nelson–Riley extrapolation method using the Debye–Scherrer camera. The deposition surface was coated with gold film and observed by a scanning electron microscope (Hitachi Akashi MSM-4). The Ti content in the deposits was determined by a chemical analysis.

3. Results

Under every CVD condition used in the present experiment the black plate-like deposits were obtained on the graphite substrate. The maximum thickness of the deposit was 1.9 mm.

3.1. Crystal structure of the Si_3N_4 matrices

Fig. 2 shows the typical X-ray diffraction patterns for pulverized deposit samples. It was found from the X-ray diffraction results that, depending on the CVD condition, the prepared deposits have a matrix consisting of either amorphous, α- or β-Si_3N_4. In this paper, each of above is denoted as amorphous, α-type or β-type deposits.

Fig. 3 shows the Si_3N_4 matrix structures found in deposits prepared at various T_{dep} and P_{tot}. At T_{dep} = 1050 and 1150° C, the deposits obtained were amorphous (Δ) irrespective of P_{tot} values. At T_{dep} = 1250° C and P_{tot} = 1.33 to 8 kPa α-type deposits (●) were obtained and at the same T_{dep} the amorphous deposit was prepared when P_{tot} = 10.7 kPa. At T_{dep} = 1350° C, the α-type deposit was obtained at P_{tot} = 1.33 kPa,

TABLE I CVD conditions

Deposition temperature, T_{dep} (°C)	Total gas pressure, P_{tot} (kPa)	Gas flow rate ($cm^3 min^{-1}$)				Deposition time (h)
		$SiCl_4$	$TiCl_4$	NH_3	H_2	
1050–1450	1.33–10.7	136	18	120	2720	4–8

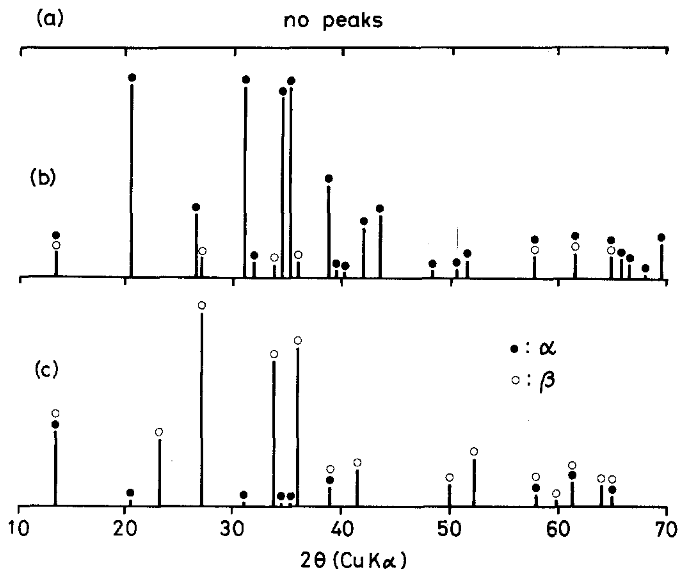


Figure 2 X-ray diffraction patterns of pulverized samples. (a) T_{dep} = 1150° C, P_{tot} = 4 kPa; (b) T_{dep} = 1250° C, P_{tot} = 4 kPa; (c) T_{dep} = 1350° C, P_{tot} = 4 kPa.

while the β-type deposits (○) were obtained at P_{tot} = 4 to 10.7 kPa. At T_{dep} = 1450° C, the β-type deposits were prepared at every P_{tot}.

Fig. 4 demonstrates the relationship between T_{dep} and β-Si_3N_4 content, i.e. β/(α + β), in the crystalline deposits. At P_{tot} = 1.33 kPa, β/(α + β) is as low as 4 to 9 wt % when T_{dep} = 1250 and 1350° C, but it has a value as high as 91 wt % at T_{dep} = 1450° C. At P_{tot} = 4 to 10.7 kPa, β/(α + β) was 95 to 100 wt % at T_{dep} = 1350 and 1450° C.

The lattice parameters, a_o and c_o, of β-Si_3N_4 obtained at T_{dep} = 1350° C and P_{tot} = 4 kPa and those of α-Si_3N_4 obtained at T_{dep} = 1250° C and P_{tot} = 4 kPa were determined. The values of a_o and c_o of β-Si_3N_4 were 0.7609 and 0.2909 nm, respectively. Those of α-Si_3N_4 were 0.7758 and 0.5622 nm, respectively.

3.2. Preferred orientation

Fig. 5 shows typical X-ray diffraction patterns for deposition surfaces of the crystalline deposits. While the deposit prepared at T_{dep} = 1250° C and P_{tot} = 1.33 kPa gave a strong diffraction peak of α(112) (Fig. 5a), that prepared at T_{dep} = 1250° C and P_{tot} = 4 kPa gave a strong diffraction peak of α(004) (Fig. 5b). As for the β-type

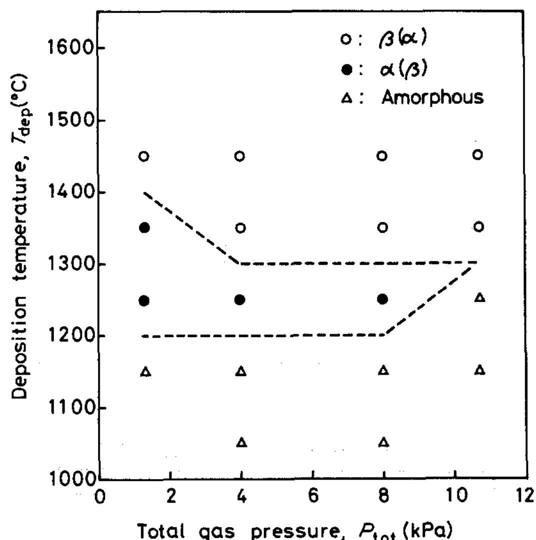


Figure 3 Effect of T_{dep} and P_{tot} on the structure of Si_3N_4 matrices.

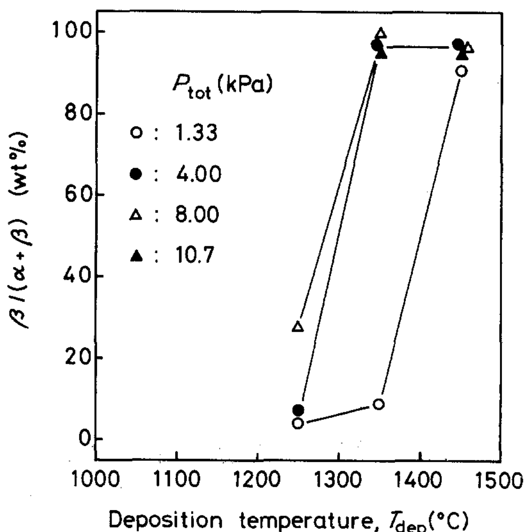


Figure 4 Effect of T_{dep} on the content of β-Si_3N_4, β/(α + β), in the crystalline deposits.

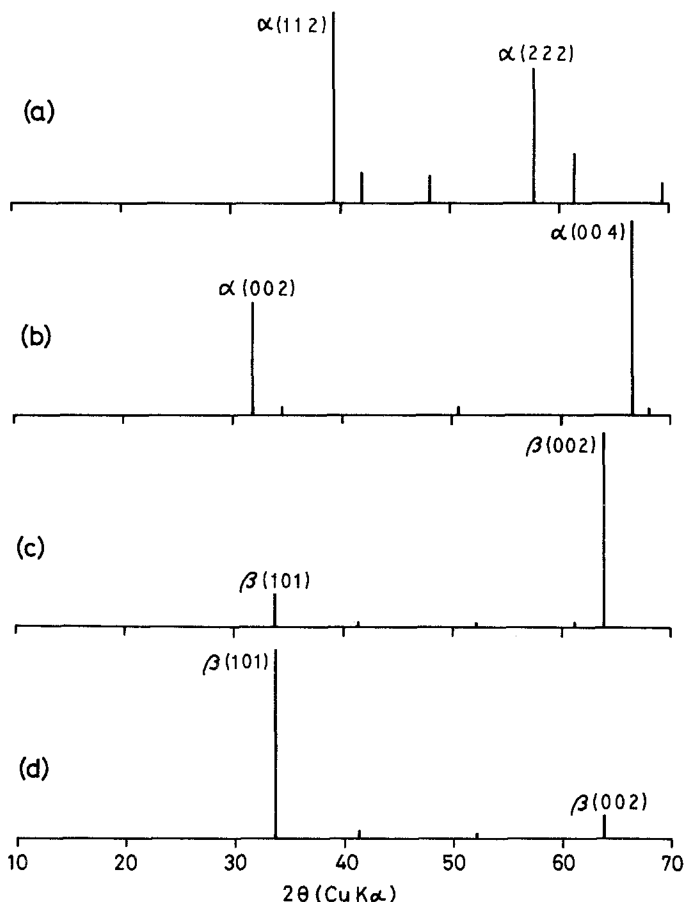


Figure 5 X-ray diffraction patterns for deposition surfaces of the crystalline deposits. (a) T_{dep} = 1250° C, P_{tot} = 1.33 kPa; (b) T_{dep} = 1250° C, P_{tot} = 4 kPa; (c) T_{dep} = 1350° C, P_{tot} = 4 kPa; (d) T_{dep} = 1350° C, P_{tot} = 10.7 kPa.

deposits, two types of preferred orientations were observed; a diffraction peak of β(002) was dominant at T_{dep} = 1350° C and P_{tot} = 4 kPa (Fig. 5c), while β(101) was strong at T_{dep} = 1350° C and P_{tot} = 10.7 kPa (Fig. 5d).

Table II summarizes the preferred orientation of the crystalline deposits prepared at the various T_{dep} and P_{tot}. Most of the α-type deposits showed the (001) preferred orientation. The β-type deposits showed the (001) preferred orientation at lower T_{dep} and P_{tot} and the (101) preferred orientation at higher T_{dep} and P_{tot}.

TABLE II Preferred orientation of the crystalline deposits

T_{dep} (° C)	P_{tot} (kPa)	Strongest diffraction peak
1250	1.33	α(112)
1250	4	α(004)
1250	8	α(004)
1350	1.33	α(004)
1350	4	β(002)
1350	8	β(002)
1350	10.7	β(101)
1450	1.33	β(002)
1450	4	β(002)
1450	8	β(101)
1450	10.7	β(101)

3.3. Surface morphology

Fig. 6 shows a typical scanning electron micrograph for the deposition surface of the amorphous deposits. All the amorphous deposits had a pebble structure as shown in Fig. 6. The size of the pebbles ranged from 0.1 to 0.4 mm and remained practically constant with T_{dep} and P_{tot}.

The surface morphology of the crystalline deposits was markedly different from that of the amorphous deposits. Fig. 7 shows that scanning electron micrographs for the deposition surfaces of the α-type deposits obtained at T_{dep} = 1250° C and P_{tot} = 1.33 to 8 kPa. The deposit prepared at P_{tot} = 1.33 kPa had a pebble-like structure as shown in Fig. 7a, however, the observation at a higher magnification revealed that those pebbles were actually composed of crystalline facets (Fig. 7b). This deposit has a (112) preferred orientation. At P_{tot} = 4 kPa, the deposits were

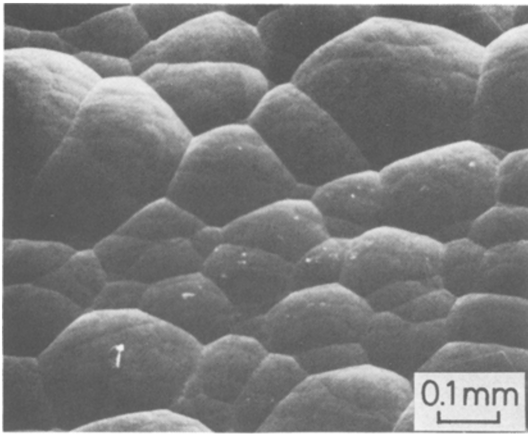
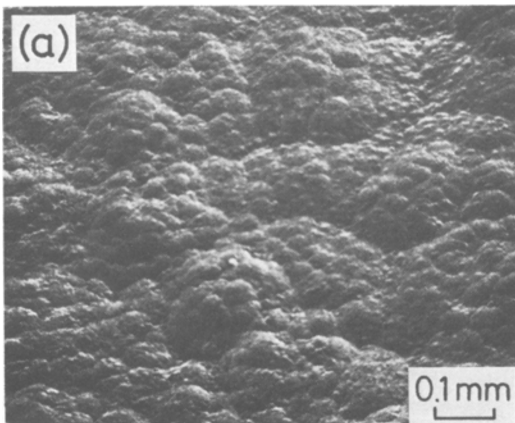
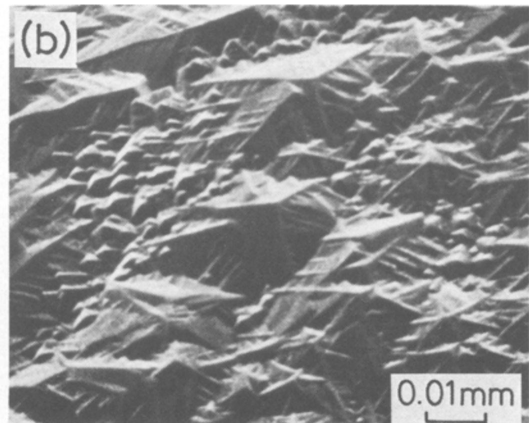


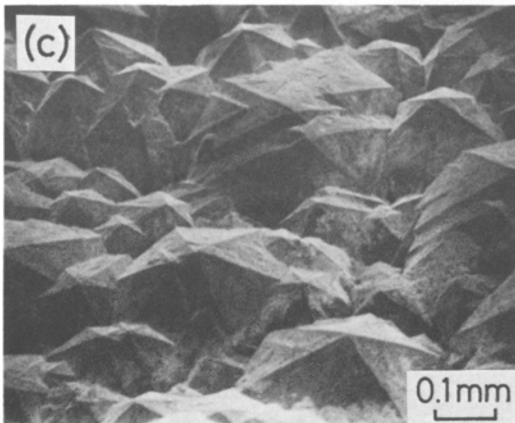
Figure 6 A scanning electron micrograph of the amorphous deposit prepared at T_{dep} = 1050° C and P_{tot} = 4 kPa.

in the form of hexagonal pyramids with sizes of 0.1 to 0.3 mm having a preferred orientation of (001) (Fig. 7c). At P_{tot} = 8 kPa, they appeared as grains of sizes 0.1 to 0.2 mm, consisting of piled up hexagonal plates with a preferred orientation of (0 0 1) (Fig. 7d).

Fig. 8 shows the scanning electron micrographs for the deposition surfaces of the β-type deposits prepared at T_{dep} = 1450° C and P_{tot} = 1.33 to 10.7 kPa. At P_{tot} = 1.33 kPa, they appeared as grains with sizes below 0.1 mm. Their facets were observed to be not well developed (Fig. 8a). This deposit had a (001) preferred orientation. At P_{tot} = 8 kPa, grains consisting of piled *c*-facets of β-Si_3N_4, having a (001) preferred orientation, were observed (Fig. 8b). At P_{tot} = 10.7 kPa, the well developed hexagonal *c*-facets have appeared







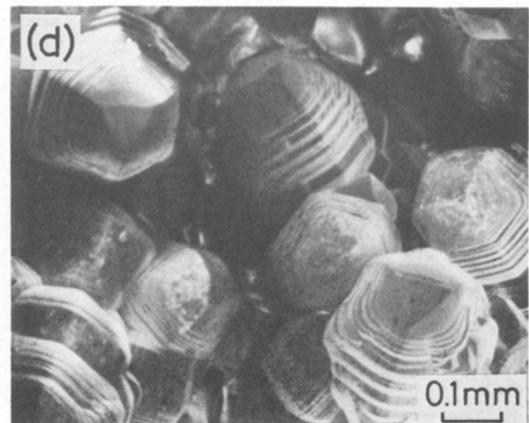
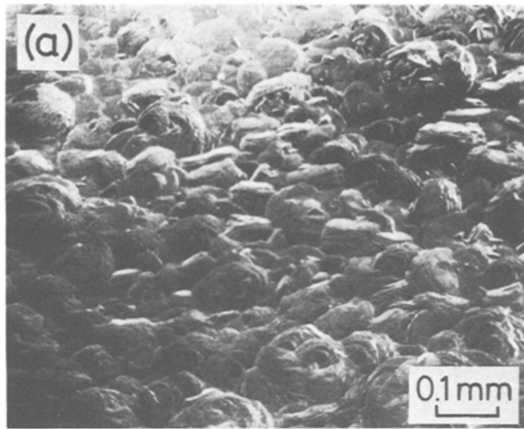
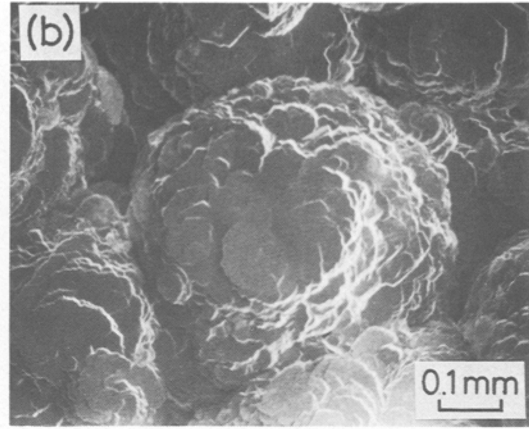


Figure 7 Scanning electron micrographs of the α-type deposits prepared at T_{dep} = 1250° C. (a)P_{tot} = 1.33 kPa; (b) a higher magnification of (a); (c) P_{tot} = 4 kPa; (d) P_{tot} = 8 kPa.





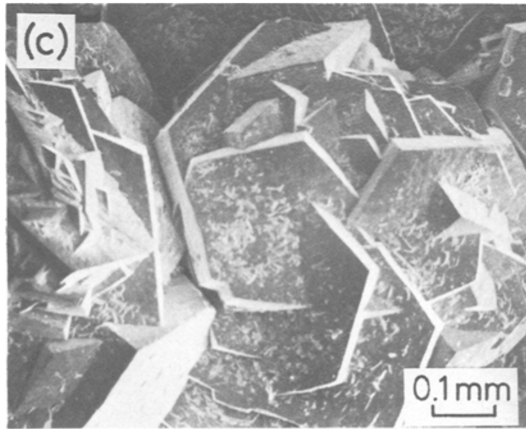


Figure 8 Scanning electron micrographs of the β-type deposits prepared at T_{dep} = 1450° C. (a) P_{tot} = 1.33 kPa; (b) P_{tot} = 8 kPa; (c) P_{tot} = 10.7 kPa.

(Fig. 8c). This deposit had a (101) preferred orientation.

3.4. Ti content

Figs 9 and 10 show the influences of T_{dep} and P_{tot} on the Ti content in the deposits. As is clear from Fig. 9 the Ti content decreases with increasing T_{dep} in the T_{dep} range of 1050 to 1450° C. In Fig. 10, the Ti content decreases with increasing P_{tot} in the range of 1.33 to 4 kPa. The Ti content remained almost constant in the range of 4 to 10.7 kPa at T_{dep} between 1150 and 1450° C. The maximum content was 24.8 wt % at T_{dep} = 1150° C and P_{tot} = 1.33 kPa, and the minimum was 2.1 wt % at T_{dep} = 1450° C and P_{tot} = 8 kPa.

3.5. State of Ti in deposits

Fig. 11 shows an X-ray diffraction pattern of the amorphous deposit having a high Ti content (24.1 wt %) prepared at T_{dep} = 1050° C and P_{tot} = 4 kPa. Very broad peaks at 2θ = 36.6, 42.5, and 62.0° are observed. These peaks correspond to (111), (200) and (220) reflections of TiN, respectively. From the half-value width of these peaks, the crystallite size of TiN was roughly estimated to be 3 nm. X-ray diffraction peaks of TiN were not detected for the α- and β-type deposits. This absence of the peaks may be due to the low Ti content and overlapping of the diffraction peaks of TiN with those of α- and β-Si_3N_4. As reported in [9], the existence of TiN in that crystalline deposits was confirmed by a transmission electron microscopic observation. Therefore, the deposits prepared by CVD of the $SiCl_4$–$TiCl_4$–NH_3–H_2 system are composites of Si_3N_4–TiN.

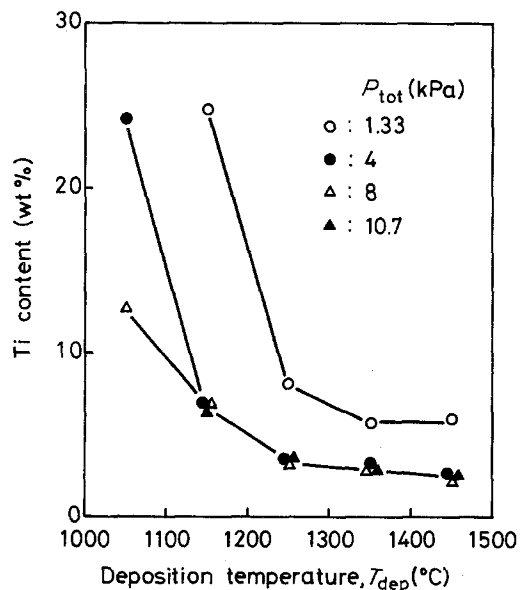


Figure 9 Effect of T_{dep} on the Ti content in the deposits.

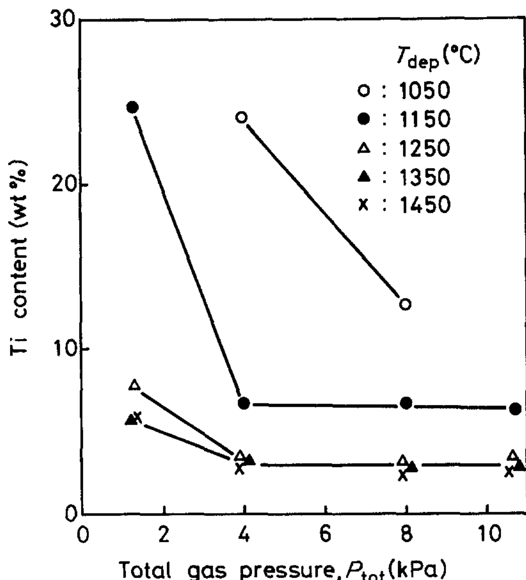


Figure 10 Effect of P_{tot} on the Ti content in the deposits.

4. Discussion

The structure of CVD–Si_3N_4 prepared by many investigators in powder, thin film, coating and bulk forms were mostly amorphous or α-crystalline. In some works [4, 5, 10], however, the formation of β-Si_3N_4 has been recognized. Landingham and Taylor [4] reported the formation of crystalline deposits composed of α-Si_3N_4, β-Si_3N_4, AlN and some unknown phases at the end of the gas-inlet tube when they performed CVD of a $SiCl_4$–$AlCl_3$–NH_3–H_2–O_2 for the purpose of preparing a Sialon. However, no description of the β-Si_3N_4 content was given in their paper. Nickl and Braunmühl [5] obtained a deposit consisting of free Si and α-Si_3N_4 at a temperature of 1300° C from CVD of a $SiCl_4$–N_2–H_2 mixture, and also reported the observation of some diffraction lines which may be attributed to the existence of β-Si_3N_4. Kijima *et al.* [10] obtained a mixture of α- and β-Si_3N_4 at 1300 to 1400° C from CVD of $SiCl_4$–N_2–H_2 and reported that a large number of crystals were identified as α-Si_3N_4.

For a comparison, CVD of a $SiCl_4$–NH_3–H_2 system was conducted at the following conditions: T_{dep} = 1050 to 1450° C, P_{tot} = 4 kPa and flow rates of 136 ($SiCl_4$), 120 (NH_3) and 2720 (H_2) cm^3 min^{-1}. α-Si_3N_4 was formed at T_{dep} = 1450° C and amorphous Si_3N_4 was obtained at T_{dep} below 1350° C. On the other hand, for the $SiCl_4$–$TiCl_4$–NH_3–H_2 system, as shown in Fig. 3, α-Si_3N_4 was formed together with a small amount of β-Si_3N_4 at T_{dep} = 1250° C. Moreover, β-Si_3N_4 was the main product at the higher temperatures of T_{dep} = 1350 and 1450° C. This result indicates that the addition of $TiCl_4$ lowers the deposition temperature of α-Si_3N_4 and promotes the formation of β-Si_3N_4.

In order to confirm this finding on the effect of adding $TiCl_4$, CVD of the $SiCl_4$–NH_3–H_2 system was conducted at T_{dep} = 1350° C and P_{tot} = 4 kPa, followed by CVD of the $SiCl_4$–$TiCl_4$–NH_3–H_2 system at the same T_{dep} and P_{tot}. Fig. 12 shows a scanning electron micrograph of a cross-section of the deposit: Part a corresponds to the amorphous Si_3N_4 deposit and Part b is the β-type deposit. In Fig. 12, Parts a and b have different fractographs, corresponding to the characteristics of the amorphous and the polycrystalline ceramics, respectively.

In order to obtain some information on the formation mechanism of β-Si_3N_4, a heat-treatment was performed on the amorphous deposit prepared at T_{dep} = 1150° C and P_{tot} = 4 kPa from the $SiCl_4$–$TiCl_4$–NH_3–H_2 system. A six hour heat-treatment at a temperature of 1400° C in Ar flow crystallized amorphous Si_3N_4 to α-Si_3N_4 but not to β-Si_3N_4. On the other hand, as described earlier, β-Si_3N_4 was obtained at the low T_{dep} of 1250° C. These results imply that the formation of β-Si_3N_4 is a direct result of the CVD process.

The lattice parameters of α- and β-Si_3N_4 have been measured by many investigators. The values that have been reported are: a_o = 0.7748 to 0.7818 nm and c_o = 0.5591 to 0.5627 nm for α-Si_3N_4 [11–21] and a_o = 0.7595 to 0.7609 nm and c_o = 0.2902 to 0.2911 nm for β-Si_3N_4 [11–15, 22–24]. Because the lattice parameters of α-

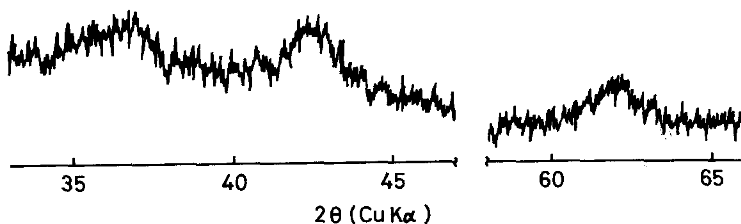


Figure 11 An X-ray diffraction pattern of the amorphous deposit prepared at T_{dep} = 1050° C and P_{tot} = 4 kPa.

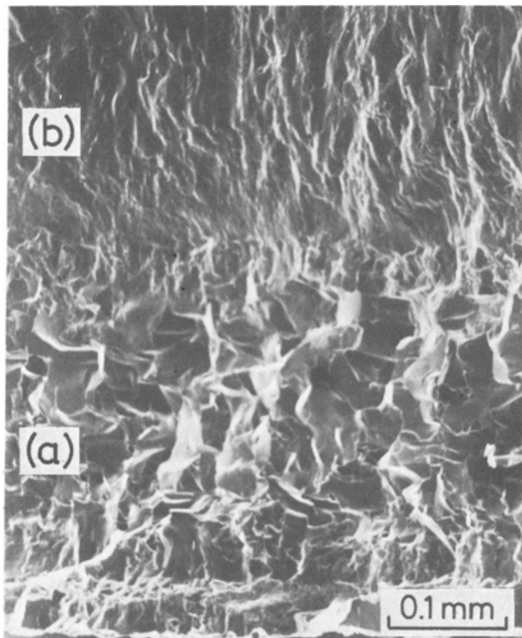


Figure 12 Cross-sectional structure of the deposit prepared at $T_{dep} = 1350^\circ C$ and $P_{tot} = 4$ kPa (a) the amorphous deposit obtained from the $SiCl_4-NH_3-H_2$ system; (b) the β-type deposit obtained from the $SiCl_4-TiCl_4-NH_3-H_2$ system.

and β-Si_3N_4 matrices found in CVD Si_3N_4–TiN composites lie in the range of these reported values, the solid solubility of TiN in Si_3N_4 is not thought to be significant. At the present time measurement of the lattice parameters for α- and β-Si_3N_4, obtained under different conditions, are underway.

There have been several studies made on the preferred orientation of CVD Si_3N_4 (α-Si_3N_4). Niihara and Hirai [20] reported that the preferred orientation of the α-Si_3N_4 deposit from $SiCl_4-NH_3$ was (1 1 1) at a low P_{tot} and high T_{dep} and was (1 1 0) and (2 1 0) at a high P_{tot} and low T_{dep}. Moreover, Hirai *et al.* [21] pointed out that in the CVD of the same system the (1 1 1) orientation became more prominent as the flow rate of $SiCl_4$ is increased. Gebhardt *et al.* [25] found a (0 0 1) orientation for an α-Si_3N_4 deposit prepared from $SiCl_4-NH_3$, and a (1 1 0) orientation for a deposit from SiF_4-NH_3. Galasso *et al.* [19] conducted a CVD of SiF_4-NH_3 and reported that most of the α-Si_3N_4 deposits had the (1 1 1) orientation but (0 0 1) orientation was also sometimes observed. The α-type deposits obtained in the present study have none of the (1 1 1), (1 1 0), and (2 1 0) orientations. Although various factors such as the raw materials, the substrate, deposition temperature, gas flow rate, and the total gas pressure have an effect on the preferred orientation, the emergence of the (0 0 1) orientation of the α- and β-type deposits in the present study may be related to the co-deposition of TiN. A configuration of TiN in the Si_3N_4–TiN composites has been described in [9]. forthcoming paper [9].

5. Conclusions

(a) CVD of the $SiCl_4-TiCl_4-NH_3-H_2$ system was carried out in the range of $T_{dep} = 1050$ to $1450^\circ C$ and $P_{tot} = 1.33$ to 10.7 kPa. In the process a black deposit in the form of plate, with the maximum thickness of 1.9 mm, was obtained.

(b) The Ti content in the deposits decreased with increasing T_{dep} and P_{tot}. The maximum content was 24.8 wt % at $T_{dep} = 1150^\circ C$ and $P_{tot} = 1.33$ kPa, and the minimum was 2.1 wt % at $T_{dep} = 1450^\circ C$ and $P_{tot} = 8$ kPa. Since Ti existed in a form of TiN, the deposits obtained in this study can be explained as composites of Si_3N_4 and TiN.

(c) The structure of the Si_3N_4 matrices depended on T_{dep} and P_{tot}. At $T_{dep} = 1050$ and $1150^\circ C$, the amorphous deposit was obtained. At $T_{dep} = 1250^\circ C$, the crystalline Si_3N_4 deposit, mainly consisting of α-phase (72 to 96 wt %), was formed at $P_{tot} = 1.33$ to 8 kPa and the amorphous deposit was formed at $P_{tot} = 10.7$ kPa. At $T_{dep} = 1350$ and $1450^\circ C$, the crystalline deposit, consisting mainly of β-phase (91 to 100 wt %) was preferentially obtained.

(d) The addition of $TiCl_4$ to the $SiCl_4-NH_3-H_2$ system had the effect of lowering the deposition temperature of the α-Si_3N_4 and promoting the formation of the β-Si_3N_4.

(e) The lattice parameters of α- and β-Si_3N_4 in the CVD Si_3N_4–TiN composites were close to those of pure Si_3N_4. The α-Si_3N_4 matrix mainly showed (0 0 1) preferred orientation and the β-Si_3N_4 matrix had (0 0 1) and (1 0 1) preferred orientations, depending on T_{dep} and P_{tot}.

(f) The surface morphology of Si_3N_4–TiN composites well reflected the structure of the Si_3N_4 matrix; i.e., while the deposition surface of the amorphous deposits showed the pebble structure, that of the crystalline deposits consisted of various kinds of facets.

Acknowledgements
The authors wish to express their appreciation to Mr A. Ohkubo for his assistance in preparing the test samples and Mr H. Kimura for carrying out the chemical analysis.

References
1. D. DONG, E. A. IRENE and D. R. YOUNG, *J. Electrochem. Soc.* **125** (1978) 819.
2. Y. TAMAKI, S. ISOMAE, A. SHINTANI and M. MAKI, *ibid.* **126** (1979) 2271.
3. S. ZIRINSKY and E. A. IRENE, *ibid.* **125** (1978) 305.
4. R. L. LANDINGHAM and R. W. TAYLOR, "Energy and Ceramics", edited by P. Vincenzini (Elsevier New York, 1980) p. 494.
5. J. J. NICKL and C. V. BRAUNMÜHL, *J. Less-Comm. Met.* **37** (1974) 317.
6. T. HIRAI and T. GOTO, *J. Mater. Sci.* **16** (1981) 17.
7. T. HIRAI and S. HAYASHI, *J. Amer. Ceram. Soc.* **64** (1981) C-88.
8. K. NIIHARA and T. HIRAI, *J. Mater. Sci.* **11** (1976) 593.
9. T. HIRAI and S. HAYASHI, Proceedings of the 8th International Conference on CVD, edited by J. M. Blocher, Jr, G. E. Vuillard and G. Wahl (Electrochemical Society, 1981) p. 790.
10. K. KIJIMA, N. SETAKA and H. TANAKA, *J. Crystal Growth* **24/25** (1974) 183.
11. D. HARDIE and K. H. JACK, *Nature* **180** (1957) 332.
12. W. D. FORGENG and B. F. DECKER, *Trans. Metall. Soc. AIME* **212** (1958) 343.
13. S. N. RUDDLESDEN and P. POPPER, *Acta Cryst.* **11** (1958) 465.
14. D. S. THOMPSON and P. L. PRATT, "Science of Ceramics", Vol. 3, edited by G. H. Stewart (Academic Press, New York, 1967) p. 33.
15. S. WILD, P. GRIEVESON and K. H. JACK, "Special Ceramics 5", edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, 1972) p. 385.
16. R. MARCHAND, Y. LAURENT, J. LANG and M. Th. LEBIHAN, *Acta Cryst.* **B25** (1969) 2157.
17. K. KATO, Z. INOUE, K. KIJIMA, I. KAWADA, H. TANAKA and T. YAMANE, *J. Amer. Ceram. Soc.* **58** (1975) 90.
18. H. F. PRIEST, F. C. BURNS, G. L. PRIEST and E. C. SKAAR, *ibid.* **56** (1973) 395.
19. F. GALASSO, U. KUNTZ and W. J. CROFT, *ibid.* **55** (1972) 431.
20. K. NIIHARA and T. HIRAI, *J. Mater. Sci.* **12** (1977) 1233.
21. T. HIRAI, K. NIIHARA and T. GOTO, *J. Japan Inst. Met.* **41** (1977) 358.
22. L. J. GAUCKLER, H. L. LUKAS and T. Y. TIEN, *Mater. Res. Bull.* **11** (1976) 503.
23. I. C. HUSEBY, H. L. LUKAS and G. PETZOW, *J. Amer. Ceram. Soc.* **58** (1975) 377.
24. R. GRÜN, *Acta Cryst.* **B35** (1979) 800.
25. J. J. GEBHARDT, R. A. TANZILLI and T. A. HARRIS, *J. Electrochem. Soc.* **123** (1976) 1578.

Received 28 August and accepted 29 September 1981