# Chemical Vapor Growth of Titanium Diboride Whisker

Seiji MOTOJIMA, Fumio SUGIMORI, Yasutaka TAKAHASHI, and Kohzo SUGIYAMA
*Department of Synthetic Chemistry, Faculty of Engineering, Gifu University, Gifu 504*

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Titanium diboride whisker was grown by chemical vapor deposition from a gaseous mixture of $TiCl_4$, $BCl_3$, $H_2$, and Ar. The relations between the growth conditions and the crystal morphologies were investigated. The predominant factors for whisker growth were found to be the substrate temperature and the kind of impurities painted on the substrate. The optimum temperature was determined as 1050—1070 °C where whiskers grew up to 250 μm in length and 0.1 to 1 μm in diameter for 30 min. Au, Pt, and Pd were found to be promissing impurities for whisker growth. From an observation of the droplet on whisker tip, the growth mechanism for the whiskers was supposed to be VLS mechanism. The form of whisker grown was tetragonal and hexagonal pillar, and the growth direction was determined as [100]direction.

A few investigations have been reported on the single crystal growth of titanium diboride by Verneuil's process,[1,2] and from fused metal solutions.[3,4] However, few papers have been published on the single crystal growth by chemical vapor deposition (CVD) except for polycrystalline coatings.[5-7] In this paper, chemical vapor growth conditions of titanium diboride whisker were studied in relation to the effects of impurities to the whisker morphology and growth mehcanism.

## Experimental

Figure 1 shows the apparatus for whisker growth. A gaseous mixture of hydrogen and argon passed through a $TiCl_4$ saturator which consisted of an evaporator and a condenser, the top temperature of which was regarded as saturating temperature. Another gas stream of chlorine was flowed into a boron trichloride generator filled with boron carbide regulated at 800 °C. Two gas streams were mixed to flow into reaction tube of quartz glass (27 mm i.d.). Substrate and atmosphere were heated doubly by four rods of outer and a rod of inner carborundum resistants. A quartz glass tube (8 mm i.d.) was used as substrate for whisker growth,

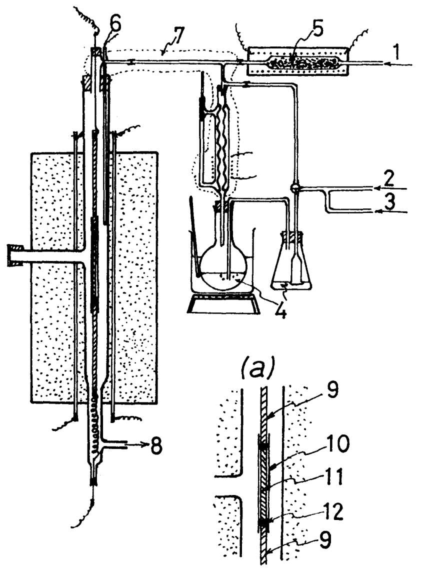


Fig. 1. Schematic diagram of the experimental apparatus. (1) $Cl_2$, (2) $H_2$, (3) Ar, (4) $TiCl_4$, (5) $B_4C$, (6) Pt-PtRh thermocouple, (7) thermal insulator, (8) outlet, (9) electrode, (10) quartz substrate, (11) SiC heater, (12) carbon powder.

and the inner carborundum rod was inserted to the substrate tube. Surface temperature of the substrate was measured by an optical pyrometer and was corrected by a calibration curve. As an impurity, various salts of metals were painted on the substrate scratched by abrasives in the form of the aqueous solutions, and decomposed or reduced to the respective metal, in hydrogen atmosphere at 1000 °C.

The term of whisker length in this paper means the average length of ten samples selected in the order from the longest in the field of microscope magnified by 150.

## Results and Discussion

*The Effects of Impurities.* In preliminary experiments, the optimum conditions were roughly determined as follows; substrate temperature of 1070 °C, gas phase temperature of 870 °C, total gas flow rate of 2.3 cc/s (NTP), and the concentration of boron trichloride, titanium tetrachloride, hydrogen, and argon of 9, 17, 44, and 30 vol%, respectively. Under these conditions, the impurities of In, Cr, Cu, Co, Ni, Fe, Mn, and V

TABLE 1. IMPURITY EFFECTS ON WHISKER GROWTH AND EUTECTIC TEMPERATURE OF BINARY ALLOYS

| | Impurity effects[a)] | | Eutectic temperature (°C)[b)] | |
|---|---|---|---|---|
| | $TiB_2$ | Boron[8)] | Ti-impurity | Boron-impurity |
| Co | − | ++ | 1135 (22.4) | 1095 (18.5) |
| Ni | − | ++ | 955 (75.5) | 1080 (18.4) |
| Mn | − | | 1175 (60.8) | |
| Fe | − | + | 1080 (71 ) | 1149 (17 ) |
| In | − | | | |
| V | − | | | |
| Cr | − | + | | *ca.* 1570 (*ca.* 13) |
| Cu | − | ++ | 880 (27 ) | 1060 (10.7) |
| Ag | + | | | |
| Pd | + | ++ | 1080 (71.5) | 845 (27 ) |
| Rh | + | ++ | | |
| Pt | + | ++ | 1310 (84.4) | 830 (40 ) |
| Au | ++ | ++ | peritectic | |

Reaction temperature: 1070 °C; $BCl_3/TiCl_4/H_2/Ar$= 8.8/17.5/43.4/30.2 (vol%). a) (−): Non or negative effect; (+): Weak positive effect (up to 200—300 μm); (++): Positive effect (longer than 300 μm). b) Atomic percent of titanium and boron metal in corresponding binally alloy systems, are shown in the parenthesis, respectively.

compounds resulted in no or even negative effects for whisker growth. In these cases, titanium diboride deposition took place in a form of homogeneous coatings or fine crystallites, and the thickness of the coatings or deposits on impurity painted zone was the same as or rather thinner than those on upainted zone. On the contrary, the compounds of Au, Ag, Pt, Pd, and Rh resulted in positive effects to titanium diboride deposition. Whisker grew on the half part of substrate near to outlet, while coatings or fine crystallites on the other half part near to inlet. Of the positive effect elements, Au was the most effective one, and Pt and Pd were found to be considerably effective. Rh exhibited weak effect and Ag also gave an effect only at somewhat lower temperature range than that of Au. These impurity effects for titanium diboride whisker growth are summarized in Table 1 together with those for the boron whisker growth[8] and the eutectic temperature of relevant binary systems. It is interesting that the excellent impurities for boron whisker growth such as Co, Ni, Cu metals are in effective in titanium diboride whisker growth.

Figure 2 shows the appearance of whiskers commonly grown with Au impurity at 1050 °C (a) and hexagonal pillar crystals grown with Pd impurity at 1120 °C (b and c). Hereafter the results were taken under painting of 2% chloroauric acid unless otherwise described.

a)
b)
c)

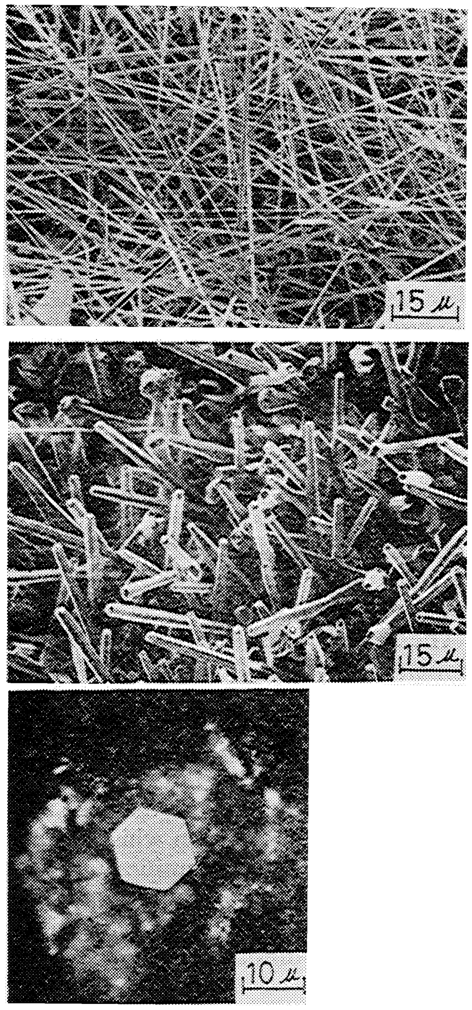


Fig. 2. Appearances of $TiB_2$ whiskers and pillar crystals. (a) Whiskers, impurity: Au; substrate tempeature: 1050 °C. (b) Pillar crystals, impurity: Pd; substrate temperature: 1120 °C. (c) Cross section of pillar crystal.

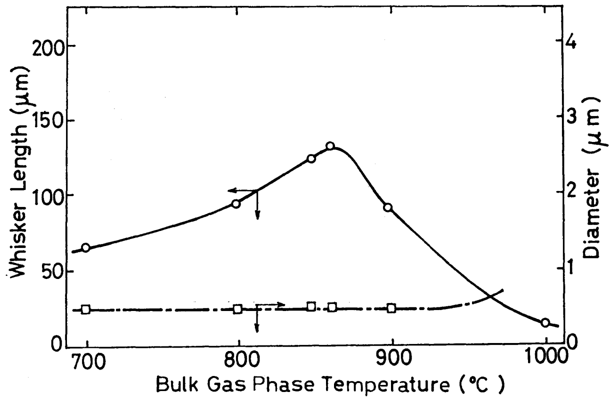


Fig. 3. Effect of temperature of bulk gas phase.
Substrate temperature: 1100 °C; reaction time: 30 min.

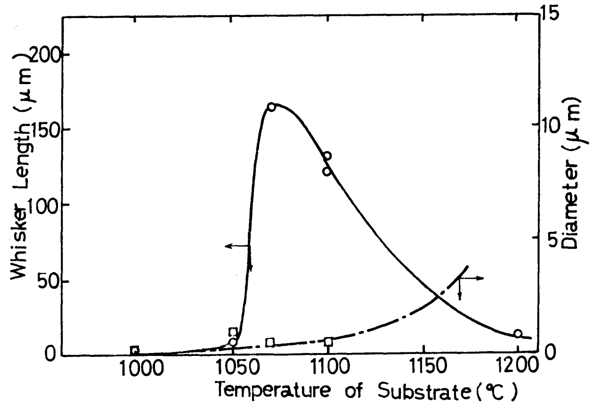


Fig. 4. Effect of substrate temperature.
Bulk gas phase temperature: 870 °C; reaction time: 30 min; total flow rate: 2.3 cc/s; $TiCl_4/BCl_3/H_2/Ar=$ 8.8/17.5/43.5/30.2 (vol %).

*The Effect of Temperature.* When the substrate temperature was kept at 1100 °C, whisker length and its diameter after 30 min are moderately varied with the gas phase temperature as shown in Fig. 3. The whisker length became the shorter above 870 °C. Therefore, the gas phase temperature of 870 °C was selected hereafter. On the other hand, the substrate temperature exhibited a sharp effect for whisker growth (Fig. 4). The longest whisker grew at 1060—1080 °C, above which decrease of length and increase of diameter took place gradually, and at the temperature higher than 1100 °C, pillar crystals and thick polycrystalline coatings deposited (Fig. 5). On the contrary, at the substrate temperature lower than 1050 °C whiskers did not grow to observable length.

*Time Dependence of Whisker Growth.* Average whisker length increased with time up to 30 min, then decreased apparently as shown in Fig. 6. This results may be explained by rapid linear growth, followed by gradual thickning to touch each other especially at the foot part of the whiskers.

In Fig. 7, whisker length and diameter are plotted

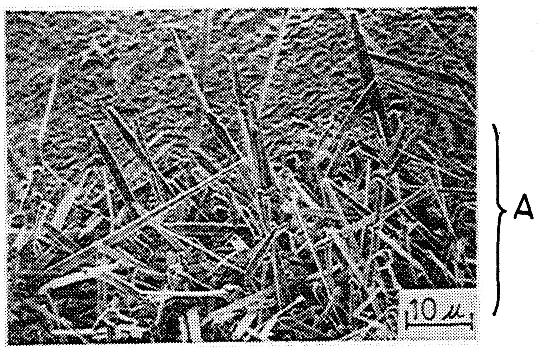


Fig. 5. Appearances of pillar crystals.
Substrate temperature: 1100 °C.

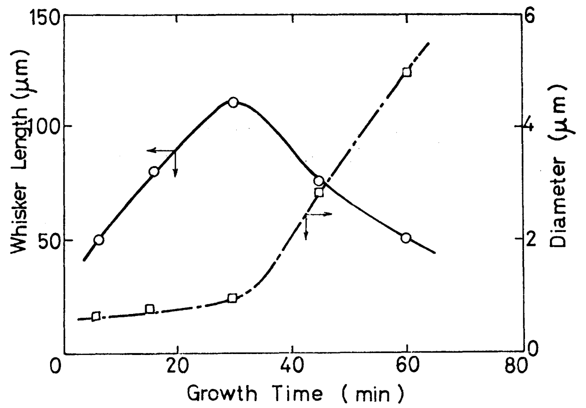


Fig. 6. Effect of reaction time.
Bulk gas phase temperature: 870 °C; substrate temperature: 1070 °C; total flow rate: 2.3 cc/s; $TiCl_4/BCl_3/H_2/Ar = 13.1/13.1/45.6/28.2$ (vol %).

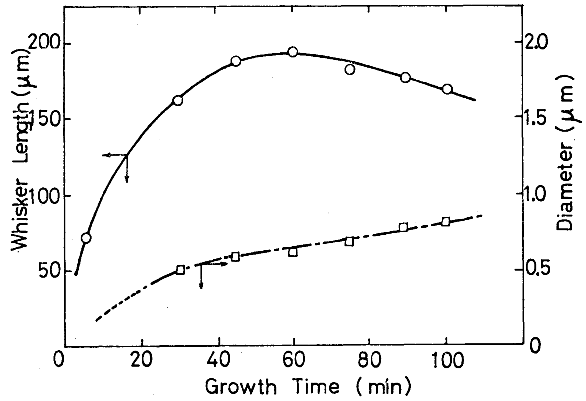


Fig. 7. Effect of growth time with repeptive painting of gold.

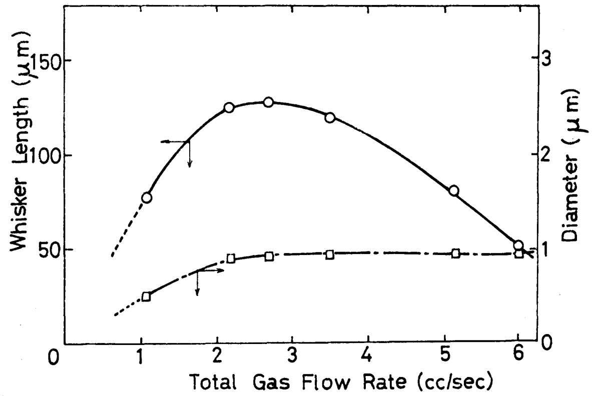


Fig. 8. Effect of total gas flow rate.
Bulk gas phase temperature: 870 °C; substrate temperature: 1070 °C; reaction time: 30 min; $TiCl_4/BCl_3/H_2/Ar = 10/20/50/20$ (vol %).

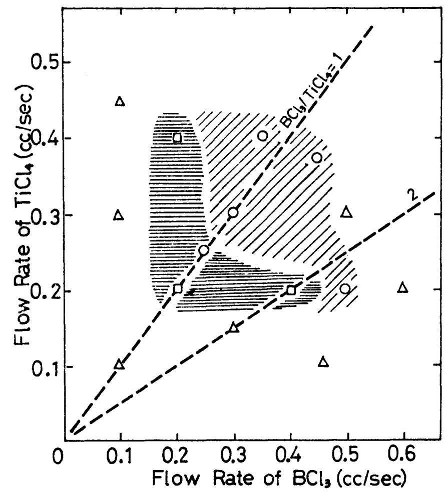


Fig. 9. Effects of the gas flow rate and its composition
Bulk gas phase temperature: 870 °C; substrate temperature: 1070 °C; reaction time: 30 min; total flow rate: 2.3 cc/s, (△): below 100 μm; (○): 100—150 μm; (□): above 150 μm.

against the reaction time during which repetitive gold paintings of about 0.05 mg/cm$^2$ of substrate area were carried out. It is found that the repetitive paintings resulted in only a slight effect and the average whisker length increased to 200 μm (maximum length of 350 μm) up to 60 min of growth time, and average diameters also increased up to 0.9 μm for 100 min.

*Effect of the Gas Flow Rate and its Composition.* In Fig. 8, total flow rate for obtaining the longest whisker is found at 2.0—3.0 ml/s. The average whisker diameters retain 0.9—1.0 μm above the flow rate of 2.5 ml/s. In Fig. 9, the concentration of titanium tetrachloride is plotted against that of boron trichloride in relation to whisker length under a total flow rate of 2.3 ml/s, and the optimum growth conditions are in the hatched range. The longest whiskers were not obtained at the concentration ratio of $BCl_3/TiCl_4=2$, which corresponds to the stoichiometric ratio of the reaction of

$$2BCl_3 + TiCl_4 + 5H_2 = 10HCl + TiB_2,$$

but at a ratio of $BCl_3/TiCl_4 \approx 1$. At the concentration range of boron trichloride higher than the range shown in Fig. 9 the formation of boron whisker was detected, however, which could not be identified by X-ray diffraction for its low diffraction ability, but was discriminated against the titanium diboride whisker by thin curled appearance and by easy dissolution in nitric acid.

*Morphologies and Growth Mechanism of $TiB_2$ Crystals.* Some interesting morphologies are shown in Fig. 10. The whisker growth along the hexagonal edges (10a), and from a center of a hexagonal to the six corners of it (10b) are seen when Ag was painted as impurity. When substrate was scratched by pure gold plate, the gold are

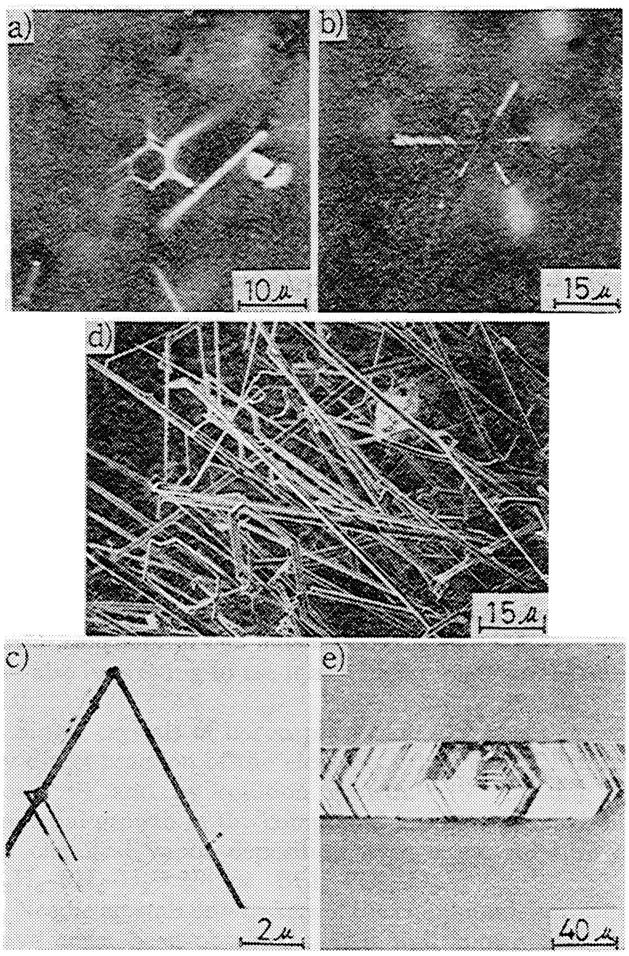


Fig. 10. Some interesting morphologies of $TiB_2$ whiskers.
a) Whisker grown along a hexagonal edges, b) whiskers grown from the center of hexagonal, c) and d) kinked whiskers, e) growth steps on the side of pillar crystal.

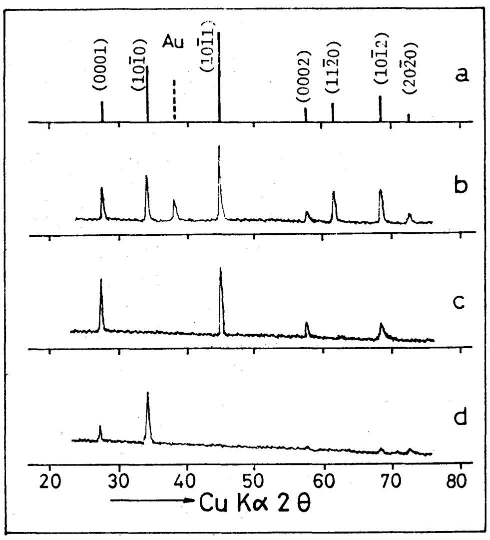


Fig. 11. X-ray diffraction profiles.
a) ASTM data for pulverized $TiB_2$, b) whiskers as grown, c) hexagonal piles as grown, d) whiskers dispersed on glass.

a)

b)

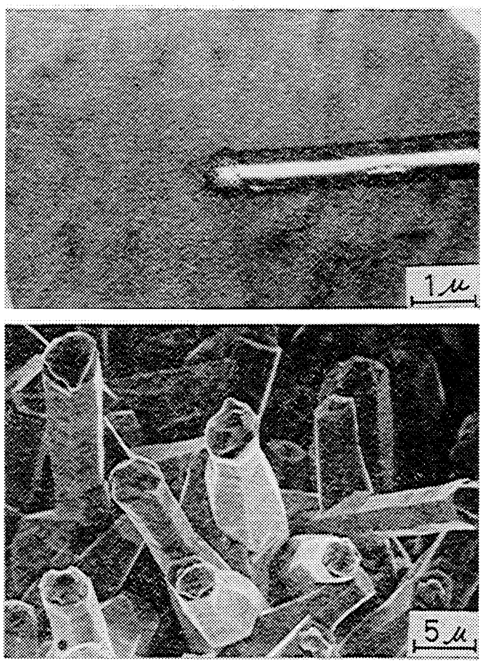


Fig. 12. The tips of the whiskers and pillar crystals.
a) Impurity: Au, substrate temperature: 1050 °C.
b) Impurity: Pd, substrate temperature: 1120 °C.

regarded as one of the heaviest dopings. On the zone scratched by gold, whiskers are apt to grow with two kinds of kink angles of 60° (Fig. 10c) and 120° (Figs. 10c and 10d). On the sides of tetragonal pillar crystals (Fig. 10e), multiple growth steps of hexagonal patterns are found, and six fold symmetry axis perpendicular to the side plane was confirmed by Laue photograph. Also additional information for growth direction was obtained from X-ray diffraction diagrams as shown in Fig. 11. The whiskers as grown gave a diagram (Fig. 11b) having peak intensities like those of powder diffraction (Fig. 11a). On the contrary, when about one milligram of whiskers was thoroughly disintegrated in a few drops of water, poured on a holder glass, and dried, the X-ray diffraction diagram is deficient of (10$\bar{1}$1) peak (Fig. 11d) which is the strongest one in powder diffraction peaks (Fig. 11a). From above results, the whisker shape is considered to be tetragonal pile, and the growth direction to be ⟨100⟩axis. Then the kink angles of 60° and 120° are reasonable for equivalent ⟨100⟩directions.

It may be seen in Fig. 5 that pillar whiskers grow only on the part of Au impurity painted zone (A-part), furthermore, on the tip of whisker a droplet can be seen as in Fig. 12a. The existence of a cap on the whisker tip leads to the VLS mechanism for whisker growth. There is, however, a problem to support the mechanism, that is, no liquid phase is found in the binary systems Ti–Au,[9] Ti–B,[9] and Au–B, below 1063 °C which is the melting point of Au. Whiskers grew above 1050 °C. Then the liquid phase may be formed by contamination with silicon from the substrate as reported on the titanium nitride whisker growth[10] or by lowering of liquidus in ternary system Ti–Au–B compared with any of relevant binary systems.

On the other hand, the growth process of hexagonal piles are supposed from their appearance (Figs. 2b and 2c) that the piles grew to [001] direction under the influence of impurity at first, followed by the growth to the direction perpendicular to c-axis.

In Fig. 12b, which is the sample grown on the Pd painted zone near inlet, droplets are also found on the tips, but have different figure from that of Fig. 12a. These hexagonal piles are grown from a $BCl_3$ rich atmosphere relative to that for the whisker which was grown on the half part substrate near outlet. By the deposition of polycrystalline $TiB_2$ on the half part of substrate near inlet, the ratio of $BCl_3/TiCl_4$ in gas stream may steeply decrease from unity at inlet to nearly zero outlet. Then, hexagonal piles grown on the zone painted of Pd near inlet are considered to grow under a condition of VS (Vapor-Solid) growth, that is, high concentrations of reactants and high temperature (1120 °C). It is supposed that VS growth rate to [001] direction is low as seen from the hexagonal steps in Fig. 10e. The stacking of the atomic planes to the direction of [001] of titanium diboride consisted of alternative planes of boron and titanium, whereas the stacking to the direction of [100] is that of self-consistent plane of titanium diboride. If one of the reasons for the low growth rate to [001] direction is assumed to be the nucleation of boron, the role of palladium impurity is recognized by easier nucleation of boron plane from a liquid phase of Pd–B alloy, and VS growth from the nuclear along the (0001) plane develops the figure shown in Fig. 12b.

**References**

1) S. A. Mersol, C. T. Lynch, and F. W. Vahldick, Anisotropy Single Cryst. Refract. Compounds Proc. Int. Symp. Dayton, Ohio, **2**, 41 (1967).

2) A. D. Kiffer, U. S. Dept. Com., Office Tech. Serv., PB Report 161792, 24 (1960).

3) I. Higashi and T. Atoda, *J. Cryst. Growth*, **1**, 251 (1970).

4) V. N. Gurin, A. P. Obukhov, T. I. Mazina, Z. P. Terenteva, I. R. Kozlova, and M. M. Korsukova, *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, **5**, 11 (1969).

5) P. Peshev, *Izv. Inst. Obshta. Neorg. Khim., Bulg. Akad. Nauk.*, **4**, 53 (1966).

6) R. L. Hough, *AIAA J.*, **4**, 107 (1966).

7) T. Takahashi, K. Sugiyama, and Y. Suzuki, *J. Cryst. Growth*, **10**, 139 (1971).

8) S. Motojima, Y. Miura, Y. Takahashi, and K. Sugiyama, Unpublished data.

9) M. Hansen, "Constitution of Binary Alloys," McGraw-Hill, London (1958), pp. 237, 260.

10) K. Sugiyama, Y. Takahashi, and S. Motojima, *Chem. Lett.*, **1975**, 363.