# Chemical Vapor Deposition of Tetraboron Silicide Whiskers

Seizi MOTOZIMA, Kozoh SUGIYAMA, and Yasutaka TAKAHASHI

*Department of Synthetic Chemistry, Faculty of Egineering, Gifu University, Kakamigahara, Gifu 504*

(Received January 6, 1975)

Growth conditions of $B_4Si$ whiskers were investigated at the temperature range of 1000—1100 °C. Optimum composition of halides was determined as $BCl_3/SiCl_4$=2—0.5, and $BCl_3$= 1—6 vol%, $SiCl_4$= 1—7 vol%. Gold had an excellent impurity effect with optimum concentration of 20—50 μg/cm² on whisker growth, and gave wool like whiskers of 0.1—1 μm in thickness and 0.5—2 mm in length. $B_4Si$ whisker growth was explained in terms of a tip VLS mechanism, for a drop-like deposit of impurity was observed on each tip.

Boron silicides are well known to have useful properties of high stability in oxygen, high elastic modulus, high mechanical strength, and so on. In the system of B–Si, a number of stoichiometric compounds, BSi, $B_3Si$, $B_4Si$, $B_6Si$, $B_nSi(n=10-14)$,[1] $B_{16}Si$,[2] $B_nSi(n=20-30)$,[2] and a few of nonstoichiometric compounds[3] have been prepared. Of these silicides, tetraboron silicide is the most stable and inert for oxygen up to its decomposition temperature (above 1400 °C).[4] Therefore, it is frequentry used as one of refractories[5] or coating materials of graphite to improve its oxidation resistivity.[6] On the other hand, the semiconducting properties of tetraboron silicide have been extensively studied, and are of much interest in its anisotropy.

Up to date, $B_4Si$ has been prepared by various methods as follows: 1) solid-phase reactions between the elements,[7–10] 2) solid-vapor reactions of boron metal with silicon halides [11] and of silicon metal with boron trichloride or borane,[11] 3) vapor phase reactions in systems: $SiCl_4+BBr_3+H_2$,[12] $SiH_4+BCl_3+H_2$,[13] and $BCl_3+SiCl_4(SiHCl_3)$.[14] In these reactions, however, has never been reported the formation of $B_4Si$ whiskers, which are expected as an excellent composite material.

In present work, $B_4Si$ whiskers are found to grow from a vapor phase of $BCl_3$, $SiCl_4$, $H_2$, and Ar onto a quartz substrate at 1000—1100 °C and effects of various factors including gas concentration, temperature, and impurity in particular on whisker growth are examined.

## Experimental

*Materials.* Commercial guaranteed reagent grade silicon tetrachloride, boron carbide, and chlorine gas were used without further purification. Argon was purified by passing over titanium sponge kept at 800 °C, and hydrogen was also refined by passing through active copper nets heated about 400 °C, conc sulfuric acid and phosphorus pentoxide, successively. Boron trichloride was prepared *in situ* (*vide infra*).

*Preparation of $B_4Si$.* The equipment used in this study is shown schematically in Fig. 1. The quartz tube(1) (7 mm in outside diameter and 100 mm in length), in which a SiC heater was inserted, was placed as a substrate in the center of reaction tube (quartz of 24 mm in inside diameter). The substrate was heated at 950—1200 °C dually from outside and inside. Boron trichloride (bp 12.5 °C) was prepared by chlorination of boron carbide at 800 °C, and supplied into the reaction tube. Silicon tetrachloride (bp 57.6 °C) was carried into the reactor by argon or hydrogen which was bubbled through its saturator(3) maintained at a given temperature. Hydrogen was also introduced through an upper

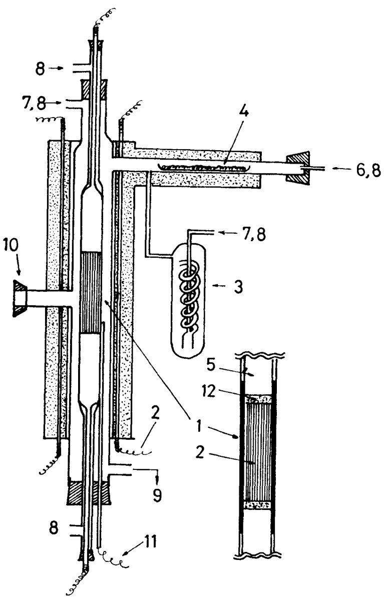



Fig. 1. Schematic diagram of the experimental apparatus.
1) Quartz substrate, 2) SiC heater, 3) $SiCl_4$ saturater, 4) $B_4Si$, 5) carbon electrode, 6) $Cl_2$, 7) $H_2$, 8) Ar. 9) outlet, 10) observation window, 11) alumel–chromel thermocouple, 12) carbon powder.

inlet (7) and allowed to be mixed with the streams of boron trichloride and silicon tetrachloride in the reaction zone. After the reactions had been quenched by stopping the supply of all reagent gases except argon, the furnace was allowed to cool below 200 °C to take out the substrate. The surface temperature of the substrate was measured by an optical pyrometer through a window(10), and the atmospheric temperature by an alumel–chromel thermocouple. The flow rates of each gas at room temperature were measured by an orifice type flow meter. The products formed on the surface of substrate were examined thoroughly by X-ray diffraction and an optical or electron microscope.

Whisker growth was found to be affected only when and where the substrate was painted with one of impurities such as gold, cobalt and nickel which were obtained by painting on the substrate in the form of aqueous solution of their salts: $HAuCl_4$, $CoCl_2$, and $NiCl_2$, followed by decomposition or reduction in the reactor below the reaction temperature.

## Results and Discussion

When a mixture of boron trichloride, silicon tetrachloride, hydrogen and argon was introduced on a substrate(quartz) heated around 1100 °C, no deposition was observed except formation of microcrystallites of boron metal at a condition of higher concentration of boron chloride. However, a large quantity of grayish wool-like crystals were obtained, only when the substrate was coated with gold. The X-ray diffraction profile of the crystals (Fig. 2) is consistent with that of ASTM data of tetraboron silicide,[15] and no peaks due to other products but gold were detected, even if a highly sensitive measurement was performed. In order to achieve the formation of well-formed and long crystals, the reaction conditions and impurity effects were thoroughly examined, and the results are discussed in the following sections in relation to the growth mechanism.

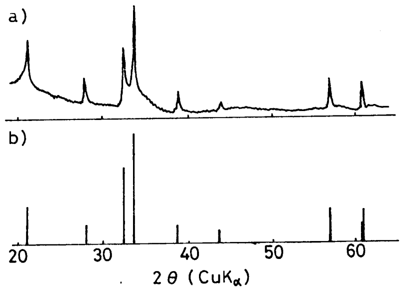



Fig. 2. X-Ray diffraction patterns.
a) $B_4Si$ whiskers as grown, b) ASTM powder data of $B_4Si$

*Growth conditions.* In this work, composition and concentration of reaction gas, which is considered to be the most impotant factors for whisker growth, were mainly studied.

The influences of $SiCl_4$ and $BCl_3$ flow rates on the whisker growth are shown in Fig. 3, where gold was used as an impurity. In this figure, it is found that optimum gas flow rates of $BCl_3$ and $SiCl_4$ are 0.02—0.14 $cm^3/s$ and 0.02—0.15 $cm^3/s$, respectively; in other words, the growth of tetraboron silicide whisker takes place in the narrow range of molar ratio $BCl_3/SiCl_4$ of 2—0.5. In condition of an excess of boron trichloride ($BCl_3/SiCl_4$ >2) or silicon tetrachloride ($SiCl_4/BCl_3$>3), whiskers of boron or silicon metal were obtained, respectively,

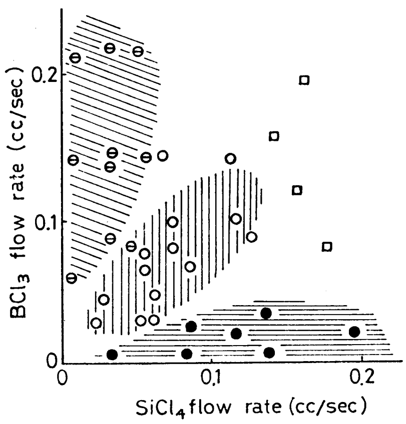



Fig. 3. Influence of $SiCl_4$ and $BCl_3$ flow rates on whisker growth.
(□): No-deposition; (⊖): boron whiskers; (○): $B_4Si$ whiskers: (●): silicon whiskers.
Temperature: 1050 °C; total gas flow rate: 2.3 ml/s.

but tetraboron silicide was not formed. The increase of concentration of both halides could not result in deposition of the silicide, perhaps due to insufficiency of reducing agent. Although the stoichimetric ratio of chlorides in the reaction $4BCl_3+SiCl_4+8H_2=B_4Si+16HCl$, $BCl_3/SiCl_4=4$, growth experiments show the ratio to be near unity. Such a tendency that boron compound whiskers grow from a gaseous mixture of poorer boron trichloride content than that expected from stoichiometry has been found also in the case of $TiB_2$[16] and $ZrB_2$[17] whisker growth. It is supposed that such a tendency came from the difference in reactivity of halides with hydrogen on the one hand, and from the lower activity of metals such as Ti, Si, and Zr in a impurity liquid phase from which whiskers grow on the other hand.

*Morphology.* Figure 4 is a micrograph of $B_4Si$ whisker typical in present experiments, where gold was used as an impurity. The appearance of whiskers was woolly and curled with dimensions of 0.5—2 mm in length and of 0.1—1 μm in diameter. The side surface of whisker was very smooth. Silicon or boron whiskers also have been obtained generally in the woolly form in contrast to a needle form of $ZrB_2$ or $TiB_2$.

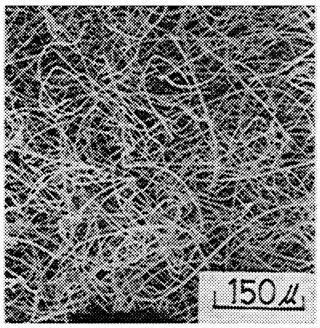



Fig. 4. Micrograph of typical $B_4Si$ whiskers.
Temperature: 1050 °C; reaction time: 30 min; $SiCl_4$: 0.05 ml/s; $BCl_3$: 0.05 ml/s; $H_2$: 2.1 ml/s.

TABLE 1. IMPURITY EFFECT ON WHISKER GROWTH AND EUTECTIC TEMPERATURE OF BINARY ALLOYS[18—20]

| | Impurity effect[a)] | | | Eutectic temperature (°C)[b)] | |
|---|---|---|---|---|---|
| | $B_4Si$ | Boron | Silicon | Boron-impurity | Silicon-impurity |
| Cu | − | ++ | − | 1060 (10.7) | 802 (30) |
| Ag | − | − | − | | 840 (10.6) |
| Au | ++ | ++ | ++ | | 370 (31) |
| Fe | − | + | − | 1149 (∼17) | 1200 (34) |
| Co | + | ++ | + | 1095 (18.5) | 1195 (23) |
| Ni | + | ++ | + | 1080 (18.4) | 964 (46) |
| Rh | − | ++ | ++ | | 1438 (10) |
| Pd | − | ++ | ++ | 845 (27) | 800 (15.5) |
| Pt | − | ++ | ++ | 830 (40) | 830 (25) |
| Nd | − | − | + | | |
| Tl | − | − | − | | |
| Al | − | − | − | | 577 (11.3) |
| Cr | − | − | | 1570 (13) | 1335 (85) |

a) (−): no or negative effects, (+): weak positive effects, (++): positive effects. b) Atomic percents of boron or silicon in corresponding binary systems are shown in the parentheses, respectively.

*Impurity effect.* In Table 1, impurity effects of various metals on whisker growth at 1050 °C are shown qualitatively together with the eutectic temperature of corresponding binary system.[18-20] Although many kinds of impurities affected whisker growth of boron and silicon, for $B_4Si$ gold alone showed an excellent effect, and Co and Ni weak effect. If vapor-liquid-solid(VLS) mechanism proposed by Wagner and Ellis[21] can be applied to $B_4Si$ whisker growth, the impurity metal must fulfil at least following requirements: 1) the binary or ternary system among the impurity, boron and silicon has eutectic temperature lower than growth temperature, and 2) the impurity metal is stable in the corrosive atmosphere of $BCl_3$, $SiCl_4$, $H_2$, HCl, *etc.* The reason why excellent impurities such as Pd, Rh, or Pt metals for boron or silicon whisker growth are ineffective in $B_4Si$ whisker growth is difficult to explain. However, it seems plausible that they have so strong affinity with both boron and silicon that the activities of both or one of elements in their ternary liquid may be lowered below the limit of $B_4Si$ growth. Though the system Si–B–Au has not been reported, it may be considered from the two binary systems, that is, soluble Au–Si system and insoluble Au–B system, that the ternary system contains trace of boron in homogeneity. Therefore, growth kinetic requires fast diffusion of boron.

Whisker growth was very slow below 1000 °C, but was fast at the temperature above 1100 °C, where radial growth or branchings became striking. At the higher temperature, no deposition was observed, probably due to the following reasons: 1) activity of relevant species in Au drops is low, 2) Au disappears due to the reaction with quartz, 3) etching temperature may be attained.

In Figs. 5 and 6, the influence of Au impurity concen-

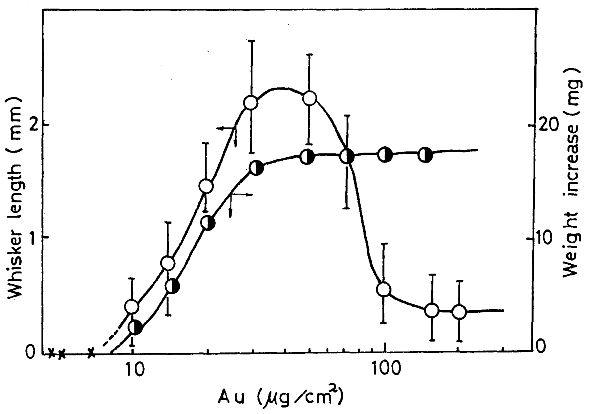
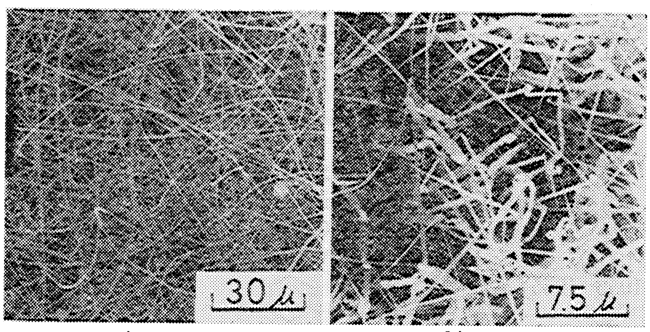
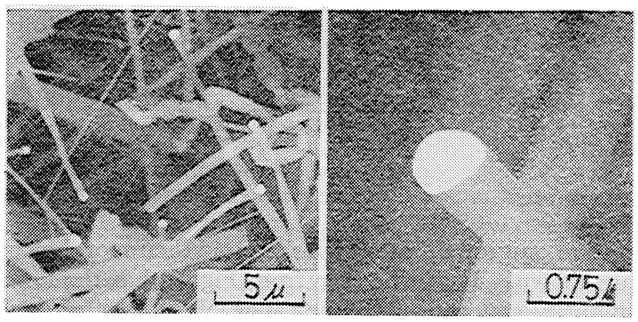



Fig. 5. Influence of impurity (Au) concentration on the growth.
Temperature: 1050 °C; total gas flow rate: 1.7 ml/s; reaction time: 1 hr.



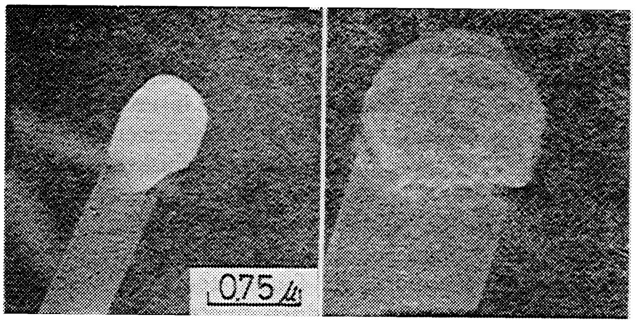

a) b)

Fig. 6. Whiskers grown in different Au concentration.
Temperature: 1050 °C; reaction time: 30 min; impurity (Au) concentration, (a): 0.03 mg/cm²; (b): 0.2 mg/cm².




a) b)

Fig. 7. The typical tip of whiskers.
Growth temperature: 1050 °C.




a) b)

Fig. 8. Whiskers with unique tips.
Growth temperature: 1050 °C; (a) hollow: (b): rough cap.

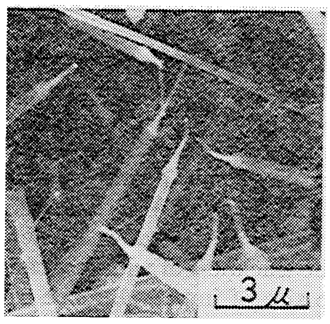



Fig. 9. The tip of whiskers (secondary growth).
Growth temperature: 1080 °C.

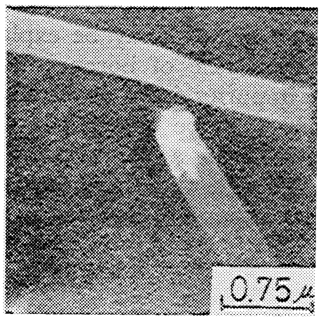
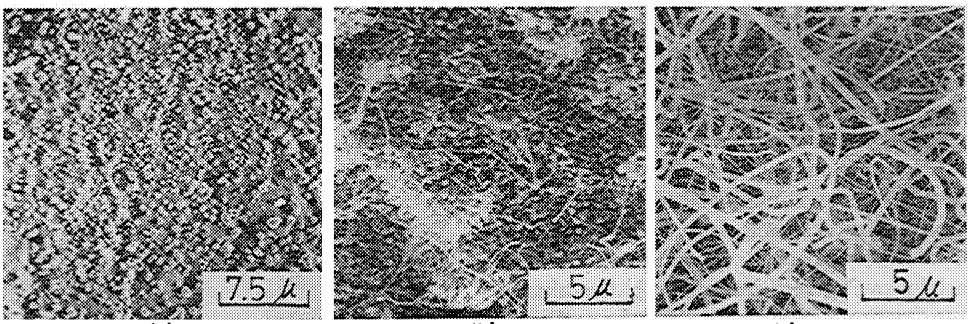



Fig. 10. The tip of whisker (tailing of liquid).



(a) (b) (c)

Fig. 11. Growth process of whiskers.
Au concentration: 0.05 mg/cm², reaction time (a): 0 min; (b) 5 min; (c) 30 min.

tration on growth rate of whiskers and their morphology are shown. It can be seen from Fig. 6 that the lower impurity concentration (the range of 20 to 50 μg/cm²) results in the more smooth whiskers and irregular whiskers are grown at the Au concentration of above 100 μg/cm². The lowest Au concentration for whisker growth is found to be 5 μg/cm² as seen in Fig. 5. Micrograph of the tip of typical whiskers obtained is shown in Fig. 7. There can be seen "cap" on each whisker which has a smooth surface with an apparent boundary with whisker. Rarely a hollow at the interface between the cap and crystal, and rough surface were observed (Fig. 8). The caps on the tips of whiskers look like Au or Au alloy. Accordingly, it is reasonable to consider that the wisker was grown by a tip VLS mechanism. Sometimes, whiskers with secondary growth of more thin crystals were found, too (Fig. 9), which may be attributed to a sudden fluctuation of reaction conditions such as temperature, or to precipitation during the cooling process. As shown in Figs. 7 and 9, a bright part which might be regarded as a residue of drop is frequentry observed to remain in side of the whiskers. Moreover, Fig. 10 indicates the creeping of cap material from tip to shoulder. The growing process of whiskers is shown in Fig. 11. When the quartz substrate which was painted with 2% aqueous $HAuCl_4$ solution was heated at 1050 °C in $H_2$ and cooled to room temperature, fine gold drops were found to be dispersed uniformly on the substrate and its size was about 0.5 μm (Fig. 11a) in diameter. This dimension is consistent with the diameter of whiskers, suggesting that the thickness of whiskers can be determined with the drop size of impurity. The number of drops per unit area quite agreed with that of whiskers ($10^{7-8}$ per square centimeter of the substrate). Whisker growth was observed 5 minutes later after the reactant gas mixture had been introduced. This "induction time" for whisker growth may be explained in terms of a slow diffusion rate of boron, silicon and other species into the impurity drops or of the time necessary to nucleation. It can be concluded therefore that a whisker is grown from a Au-drop by the tip VLS mechanism. Although the thermodynamic data tell the gross concentrations of species in vapor phase, whiskers are grown from an impurity drop as mentioned above in which each component must be ballanced for the sake of whisker growth. Therefore, the solubility of the components to the impurity (liquid) and/or the diffusions to crystallizing sites must be more impotant factors for the growth than the concentration in vapor phase.

## References

1) L. K. Lamikhov, *Izv. Akad. Nauk., SSSR, Neorg. Mater.*, **4**, 1076 (1968).
2) W. Dietze, M. Miller, and E. Amberger, *Electron Technol.*, **3**, 73 (1970).
3) M. Bergt and B. Cyrill, *Acta Chem. Scand.*, **16**, 449 (1962).
4) R. S. Fergelson and W. D. Kingery, *Spec. Ceram.*, *Proc. Symp. Brit. Ceram. Res. Assoc.*, **1962**, 27.
5) K. Aktiebolag, Swed. 201850 (1967).
6) C. Ervin, U. S. 3275467 (1966).
7) V. I. Matkovich and C. Ervin, U.S. 3138468 (1964).
8) G. V. Samsonov and V. M. Sleptsov, *Poroshkovaya Met., Akad. Nauk Ukr., SSSR*, **4**, 58 (1964).
9) V. I. Matkovich and C. Ervin, U.S. 3427131 (1969).
10) G. V. Samsonov and V. P. Latysheva, *Doklady Akad. Nauk, SSSR*, **105**, 499 (1955).
11) E. L. Kern and G. A. Jerone, Fr. 1538423 (1968).
12) I. V. Petrusvich, L. A. Niselson, A. I. Belyaev, and M. A. Gurevich. *Izv. Akad. Nauk., SSSR, Neorg. Mater.*, **3**, 1389 (1967).
13) L. C. McCandless and J. C. Withers, U.S. 3607367 (1971).
14) L. C. McCandless, J. C. Withers, and C. R. Brummett, U.S. 3549413 (1970).
15) V. I. Matkovich, *Acta Crystallogr.*, **13**, 679 (1960).
16) K. Sugiyama, Y. Takahashi, F. Sugimori, and S. Motozima, in preparation for publication
17) S. Motozima, F. Sugimori, Y. Takahashi, and K. Sugiyama, in preparation for publication
18) M. Hansen, "Constitution of Binary Alloys," McGraw-Hill, London (1958).
19) R. P. Elliot, *ibid.*, First Supplement (1964).
20) F. A. Shunk, *ibid.*, Second Supplement (1969).
21) R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.*, **4**, 89 (1964). R. S. Wagner and W. C. Ellis, *Trans. AIME*, **233**, 1053 (1965).