Fabricating SiC whiskers of different sizes by controlling only the CVD deposition position

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Silicon carbide (SiC) whiskers were produced at different positions in the chemical vapor deposition (CVD) furnace. The effect of shifts in specimen position on vapor–solid (VS) whisker growth was studied. First, we confirmed the major factors influencing CVD whisker growth by controlling the specimen position. The source reactant depletion effect and temperature gradient acted to reduce the whisker diameter by 33.3 and 61.7%, but the gas residence time only accounted for 4.2% of whisker diameter reduction. The specimen upon which all three factors acted showed a 74.2% decrease in diameter. Transmission electron microscopy (TEM) observation showed that all whiskers had highly crystalline FCC structures. The front perpendicular specimen showed higher stacking fault densities, whereas the back horizontal specimen possessed no stacking faults. These results suggest that position variation led to a growth rate difference, which affected the stability of whisker growth. Based on this idea, we confirmed the possibility of synthesizing whiskers of two different diameters on the same substrate. This can propose a new network structure consisting of combined whiskers. This report focuses on varying the whisker deposition size by controlling the deposition position instead of changing the deposition conditions as is common.

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Key-words : SiC, Whisker, Vapor–solid mechanism, Deposition position, CVD, TEM

[Received August 31, 2010; Accepted September 16, 2010]

1. Introduction

Silicon carbide (SiC) is an important material due to its excellent mechanical, physical, and chemical properties.^{1),2)} SiC whiskers have been grown by several processes including the carbothermal reduction of silica,³⁾ reactions between silicon halides and CCl₄,⁴⁾ and chemical vapor deposition (CVD) using a metallic catalyst such as Ni or Fe.⁵⁾ Another technique is the growth of SiC whiskers through a CVD vapor–solid mechanism using no catalysts.⁶⁾

Previous studies focused on changing whisker growth by controlling the deposition factors.^{7),8)} These studies proved that the major factors affecting whisker growth in CVD are temperature, pressure, the input gas ratio, gas residence time, and reactant depletion effect. Moreover, catalyst features (e.g., material, size) can also affect CVD whisker growth.^{9),10)} These studies controlled the deposition factors by changing the deposition process conditions. In this study, we focused on synthesizing various diameters of SiC whiskers by controlling the specimen position in the CVD furnace while maintaining the other deposition conditions. We attempted to involve the major deposition factors by controlling the specimen position. Our method creates whiskers via a vapor–solid (VS) route which does not use any catalyst; therefore, we did not consider catalyst issues. The morphology and microstructure of the SiC whiskers, which were deposited in different positions, were investigated in this study.

2. Experimental procedure

The whiskers were grown in a horizontal hot-wall furnace^{6),11)} using low-pressure chemical vapor deposition (LPCVD). Carbon

woven fabric (Hankuk Carbon Co., Ltd.) with a filament diameter of 8 μm was used as a substrate. Circular substrates with diameters of 1.5 cm were used, and the substrate was held in the furnace perpendicularly to the gas flow by a specimen holder, as shown in Fig. 1(a). The lengths of the furnace and the specimen holder were 48.4 and 10 cm. Methyltrichlorosilane (CH₃SiCl₃, MTS, Acros Organics Co., USA) was used as a source, and hydrogen (H₂) gas was used as the dilute and carrier gasses. SiC whiskers were deposited at an input gas ratio ($\alpha = \text{H}_2/\text{MTS}$) of 40, and the total pressure was fixed at 646 Pa. The deposition temperature and time was held at 1,300°C and 60 min for all specimens. The specimen holder was placed in the middle of the furnace, which was the center of the hot zone. As shown in Fig. 1, each specimen was placed at a different position. A detailed description of specimen location is provided in the next section. The morphology and microstructure were characterized using scanning electron microscopy (SEM) (FESEM, JOEL JSM-6700F) and transmission electron microscopy (TEM) (JEM-2100 JEOL).

3. Results and discussion

Figure 1 shows the configurations of the specimens placed at different locations in the CVD furnace. The specimens were moved from the center to their locations, and the resulting mean diameters of the whiskers are recorded in Table 1. Each specimen's position was determined by considering the major CVD deposition factors in whisker growth. The specimen in Fig. 1(a) was arranged to be perpendicular to the gas flow, and the diameters of the whiskers on the front and back sides of the specimen were compared. As the front and back side were located at the same position which is the center of the hot zone in the furnace, both sides reached the same deposition temperature. A porous media was used for the specimen which allowed for

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Fig. 1. Configurations of specimens placed at different locations in the CVD furnace (a)–(d). Experimental results are recorded in Table 1.

Table 1. Results of experiments in Fig. 1. The mean diameter and diameter reduction ratio of each whisker deposited at positions shown in Fig. 1

Configuration	Initial position	Mean diameter (μm)	Shifted position	Mean diameter (μm)	Reduced ratio (%)
Fig. 1(a)	A1	2.4	A2	1.6	33.3
Fig. 1(b)	B1	2.4	B2	2.3	4.2
Fig. 1(c)	C1	2.4	C2	1.45	39.6
			C3	0.92	22.1
Fig. 1(d)	D1	2.4	D2	0.62	74.2

delivery of the source gas to its back side. The permeability of the substrate was reported in a previous study.¹²⁾ In Table 1, the mean diameter of the whiskers on the front side (A1) was 2.4 μm and on the back side (A2) was 1.6 μm. The diameter of back side whiskers was 33.3% smaller than that of the front side whiskers. This reduction could be due to the source reactant depletion effect. In Lee's study,¹³⁾ the back specimen growth rate of the SiC film decreased when another specimen was placed in front. Also, in our experiment, the source gas primarily reacted on the front side of the specimen and then the remaining diluted source gas penetrated to the back side, resulting in 33.3% thinner whiskers. This indicates that source reactant gas depletion could be a critical factor influencing whisker growth and could be utilized for controlling whisker diameter.

Next, we checked the relationship between whisker growth and the gas residence time during deposition. Figure 1(b) shows the configuration of each specimen, wherein B1 is vertically arranged and B2 is horizontal. Both specimens were located at the center of the hot zone to exclude the influence of temperature on whisker growth. In Table 1, the mean diameter of the vertical specimen (B1) was 2.4 μm, and that of the horizontal specimen (B2) was only 2.3 μm. The horizontal specimen possessed 4.2% thinner whiskers, but this difference seemed to be insignificant. According to A. Josiek,¹⁴⁾ gas residence times do not play a role in the growth rate when the source decomposition is sufficient and the growth rate is high. In our previous study,¹⁵⁾ the SiC film

deposited at 1300°C showed a high growth rate, indicating that the source decomposition rate could be high. Therefore, our whiskers deposited at 1300°C could also be showing a high source decomposition rate, causing the whisker size to be almost independent of the gas residence time. Thus, in our experiment, the gas residence time didn't have an obvious effect on whisker growth, but this could be different at low deposition temperatures.

Figure 1(c) shows the change in mean diameter of the whiskers at different specimen distances from the hot zone. Each specimen was located 2 or 4 cm away from the center of the hot zone, representing distances of 4.1 and 8.2% of the total heated furnace length. Because each specimen was 0 (C1), 2 (C2), or 4 cm (C3) farther from the hot zone, the mean diameter of the whiskers varied from 2.4 to 1.45 or 0.92 μm. The reduction ratios of C1 to C2 and C2 to C3 were 39.6 and 22.1%. Moreover, the total diameter reduction ratio of C1 to C3 was 61.7%. This showed that the temperature gradient greatly affected whisker growth which can be utilized to control whisker diameter. Consequently, Fig. 1 suggests that the temperature gradient and source reactant depletion effect could be critical factors in controlling whisker diameter. The gas residence time had a slight effect and made only a slight contribution in our experiment.

To maximize the deposition factors, we controlled the specimen position in the furnace. Figure 1(d) shows a new configuration for depositing two different whisker diameters. The first specimen, D1, was located at the center of the hot zone for deposition of thick whiskers. Then, the second specimen, D2, was placed 4 cm back from D1, horizontally positioned and slightly out of the hot zone. The position of D2 was a combination position of A2, B2, and C3. Results showed a large diameter difference between the whiskers of D1 and D2 which had mean diameters of 2.4 and 0.62 μm, respectively. The second D2 whiskers were 74.2% smaller than the first D1 whiskers. Thus, the growth factors we controlled affected whisker synthesis and could be manipulated to efficiently synthesize thinner whiskers.

Figures 2(a) and (b) show the whisker morphology following the configuration of Fig. 1(d). We can easily compare the

Fig. 2. (a), (b) Morphology of SiC whiskers deposited on locations shown in Fig. 1(d) ($T_{\text{dep}} = 1,300^{\circ}\text{C}$, $\alpha = 40$). (c) Morphology of combined SiC whiskers deposited twice at two different positions (first at the center and then 4 cm back from the center) ($T_{\text{dep}} = 1,300^{\circ}\text{C}$, $\alpha = 40$).

Fig. 3. Microstructures of SiC whiskers: (a) TEM image of the whisker deposited for 60 min on the perpendicular sample located at the center, (b) high-resolution TEM image of whisker in (a), (c) FFT pattern of whisker in (a), (d) TEM image of the whisker deposited for 60 min on the horizontal sample located 4 cm back from the center, (e) high-resolution TEM image of whisker in (d), (f) FFT pattern of whisker in (d). The specimen deposition positions follows as, (a)(b)(c) = Fig. 1(D1) and (c)(d)(f) = Fig. 1(D2). The black and white arrows indicate the direction of whisker growth and stacking faults.

whisker diameter difference between the first and second specimens. Figure 2(a) shows thick whiskers but Fig. 2(b) shows thin whiskers of similar length. Thus, the second specimen possessed a higher number of whiskers per unit area than the first. On the other hand, all whiskers in Figs. 2(a) and (b) grew in a similar corn-shaped formation. In Fig. 2(c), we tried to combine two different whisker diameters on the same substrate. We first deposited whiskers for 60 min at the front position to produce thick whiskers. Then the specimen was shifted 4 cm back in a horizontal position and re-deposited for 60 min using the same deposition conditions. The experimental configuration is shown in Fig. 1(d). The substrate morphology showed a high quantity of mixed whiskers. The thick whiskers first covered the substrate, and thin whiskers grew on their surfaces or filled in between them. In addition, as the first thick whiskers did not grow any larger after the second deposition (comparing Fig. 2(a) and Fig. 2(c)), we can see that the second deposition only synthesized thin whiskers. This means that the second horizontal position was

optimized for producing only thin whiskers and did not influence any additional thick whisker growth. This technique is a new method of synthesizing different types of whiskers and combining these whiskers together on a substrate without changing deposition conditions.

Figure 3 is the TEM microstructure of the specimen from Figs. 2(a) and (b). The observation region was at the top part of each whisker. Diffraction (FFT) patterns of Fig. 3(c) and Fig. 3(f) were taken at the electron beam directions of $[\bar{1}22]$, $[001]$, respectively. This pattern showed that the thin and thick SiC whiskers were highly crystalline FCC structures. In Fig. 3(b) several stacking faults were observed, but Fig. 3(e) possessed none. The black arrows on Figs. 3(b) and (e) indicate the direction of whisker growth, and by Fig. 3(b), the stacking faults were perpendicular to the growth direction. These stacking faults were also confirmed by the streaks in the diffraction pattern in Fig. 3(c). As the stacking fault density is dependent on the growth rate of a whisker¹⁶⁾ the formation of the stacking faults

can be explained by the difference in deposition rate between the front, Fig. 1(D1), and back, Fig. 1(D2), specimens. The front specimen located in the center of the hot zone quickly reached the highest temperature, leading to a high deposition growth rate. However, the back-side whiskers grew relatively slowly due to the decreasing temperature, source depletion, and the gas residence time reduction, which made the whisker growth more stable. Therefore, the result indicates that the macroscopic whisker sizes and microstructure of whiskers were obviously different by the change in location.

4. Conclusion

Whiskers of different diameters were successfully deposited under the same deposition conditions by changing only the specimen position in a CVD furnace. We confirmed the major factors influencing CVD whisker growth by controlling the specimen position. The source reactant depletion effect and temperature gradient acted to reduce the whisker diameters by 33.3 and 61.7%, but the gas residence time only influenced 4.2% of whisker diameter reduction. The specimen subjected to the effects of all three factors showed a 74.2% decrease in diameter. TEM observation showed that all whiskers were highly crystal-line FCC structures, and the front perpendicular specimen showed a high stacking fault density, whereas the back horizontal specimen possessed no stacking faults. These results suggested that position variation led to growth rate differences, and this affected the stability of whisker growth. Based on this finding, we confirmed the possibility of synthesizing a new network structure of two different whisker diameters on the same substrate. This fabrication technique can be used to vary whisker deposition size by controlling only the deposition positions instead of changing the deposition process conditions.

Acknowledgements This work was supported by DAPA and ADD.

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