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OBSERVATION OF SINGLE CRYSTAL DIAMOND WHISKERS BY FE-SEM AND TEM

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We have formed two type very thin whiskers on a diamond substrate using a RIE technique. We have found by observation of TEM that the whisker is a single crystal diamond. Diamond whiskers using $O_2 = 100\%$ gas have a size of <200 nm and the minimum size of approximately 2 nm. Diamond whiskers using $CF_4/O_2 = 1\%$ gas have a size of 50 to 200 nm and the minimum top size of <5 nm.

Keywords: diamond; whisker; RIE; TEM; FE-SEM

I. INTRODUCTION

Diamond is an important material for an electron emitter device because of its negative electron affinity. There are many reports on a field emission from diamond films and emitter arrays fabricated by a transfer mold

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method. We also have fabricated a new type tip on a single crystal diamond using a novel reactive ion etching (RIE) technique [1,2], which has a high performance; a very high etching rate (9 μm/h), a smooth etching surface, a high selective etching ratio of diamond/Al and a vertically etched side wall. Tips are very sharp and aligned at a controlled position. We have found that the upside of tip was a whisker. Therefore, we can form only a whisker by the same method. As a diameter of Al mask is smaller, thinner whiskers are formed on diamond. The smallest mask is a micro-mask occurred naturally in a RIE chamber. Using this mask, the thinnest whisker is formed. Diamond whiskers have ever been reported, but it is not satisfied for characterization of their crystalline quality [3–5]. It is important to estimate a size and to characterize a structure of tips and whiskers, because they are as thin as other nanocarbons.

In this paper, we report an observation of whiskers by a field emission type scanning electron microscopy (FE-SEM) and a transmission electron microscopy (TEM).

II. EXPERIMENTAL

Samples were prepared by a reactive ion etching (RIE) of diamond substrate. Diamond substrate was etched under the condition of $O_2 = 100\%$ or $CF_4/O_2 = 1\%$ in a conventional RIE chamber. The other etching conditions were as follows. The r.f. power was 200 W, the pressure 5 Pa, and the O_2 gas flow rate 50 sccm. Then, whiskers were formed on diamond. Diamond was used Ib (100) single crystal substrate synthesized at high temperature and high pressure (HTHP). The size was $1.5 \times 2.0 \times 0.3\,\text{mm}^3$. Sample was treated in a HF acid after RIE in order to remove some layer, which is not diamond. Some samples were observed by a field emission type scanning electron microscope (FE-SEM). Whiskers in another sample were separated from diamond substrate in order to observe by a transmittance electron microscope (TEM).

III. RESULTS AND DISCUSSION

Figure 1 shows FE-SEM photograph of a diamond surface after RIE in O_2 of 100%. It was found that the surface had many whiskers. Figure 1(a) shows whiskers on the surface after RIE and (b) shows whiskers treated in a HF acid after RIE. The diameter of whiskers in (a) was in the range of 0.5 to 1.0 μm. The density of whiskers was 0.1 to $0.5\,\mu\text{m}^{-2}$. On the other hand, whiskers after a HF treatment were thinner and much more than whiskers after RIE. These figures show that whiskers just after RIE were covered by a layer, which is removable in a HF acid. We guess that the layer was iron

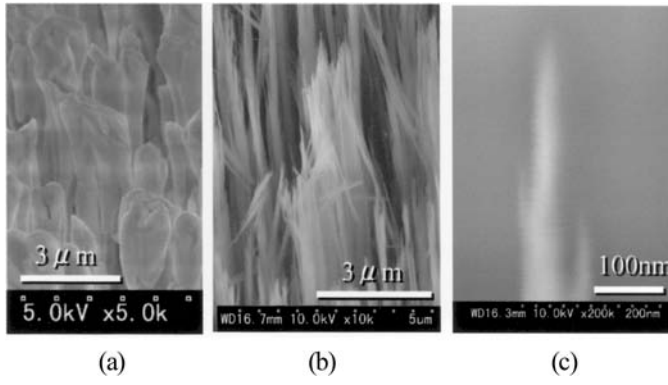

FIGURE 1 FE-SEM photograph of whiskers on a diamond surface (a) after RIE using $O_2 = 100\%$ gas, (b) after HF acid treatment after (a), and (c) the top of a whisker in (b).

oxide or silicon oxide, because they were observed by measuring of XPS before a HF treatment. We also have estimated that the whisker treated in a HF acid was mainly diamond, because a homoepitaxial growth of diamond on it was confirmed. Figure 1(c) shows an expansion of a whisker in (b). Any whisker in Figure 1(b) was less than 0.2 μm. Moreover, the thinnest whisker has the diameter of less than 25 nm, as shown in Figure 1(c). Although diamond is etched easily using only O_2 gas, a micro–mask of metal, which cause in a RIE chamber because of plasma, cannot be removed. Therefore, diamond remained under the very small micro–mask and very thin diamond whisker was formed. Then a metal oxide was covered on whisker. We guess that Figure 1(a) shows diamond whiskers covered by metal oxide.

Figure 2 shows SEM photograph of a diamond surface after RIE in CF_4/O_2 of 1%. It was found that a few whiskers appeared on the diamond surface. Figure 2(a) is reactive ion etched sample and (b) is a sample treated in a HF acid after RIE. We have obtained smooth etching surface on some substrate under this condition, because a micro–mask was etched in plasma included F atoms. However, a few whiskers remained on some substrate with a metal inclusion or a deep and sharp groove, as shown in Figure 2(a) and (b). The whisker became also thinner after a HF treatment. Then, the whisker was very sharp and less than 0.5 μm, but it was thicker than that of RIE using only O_2 gas.

Figure 3 shows TEM photograph of a diamond whisker by RIE in O_2 of 100%. Figure 3(a) is a bright field image, (b) is a diffraction pattern, and (c) is a dark field image. Whiskers were treated in a HF acid. Although we cannot observed clearly the thinnest diamond whisker by FE–SEM, as

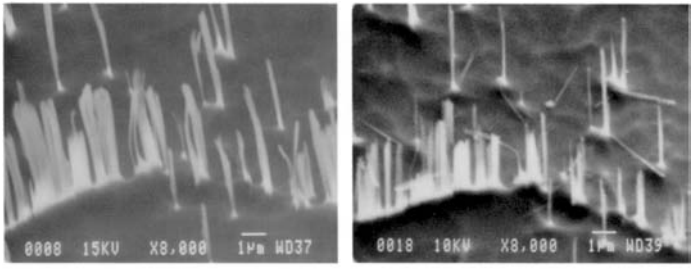

FIGURE 2 FE-SEM photograph of whiskers on a diamond surface (a) after RIE using $CF_4/O_2 = 1\%$ gas and (b) after HF acid treatment after (a) occurs.

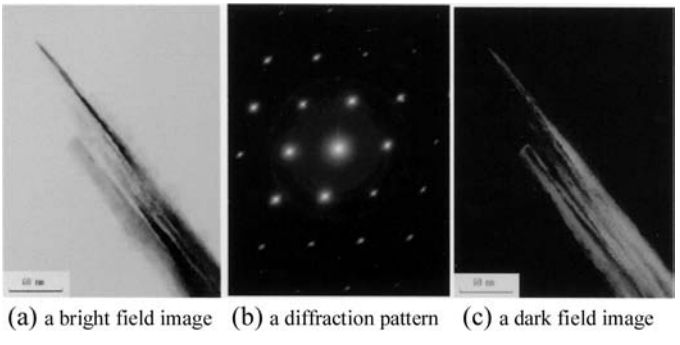

FIGURE 3 TEM photograph of a whisker formed on diamond surface by RIE using $O_2 = 100\%$ gas.

shown in Figure 1(c), it was found by measuring of TEM that the thinnest whisker has the diameter of 2 or 3 nm. Spot patterns in Figure 3(b) shows that a whisker is mainly a single crystal diamond and that the direction of whisker is a (100) direction. This agreed with a substrate of a (100) plane. Spot patterns are a little streaky to the vertical direction of a whisker, because whiskers have a very small diameter. Moreover, ring patterns included spotty patterns in (b) were also observed. This suggests that whisker includes a nanopolycrystalline phase or a graphite phase. Therefore a polycrystalline or amorphous phase was also observed on outside of whiskers in Figure 3(a) and (c). Figure 3(c) shows that a top of a whisker was a single crystal diamond and that a diamond whisker of 2 or 3 nm was formed.

TEM photograph of a typical diamond whisker formed by RIE in CF_4/O_2 of 1% showed the same results with that of $O_2 = 100\%$. The diameter of

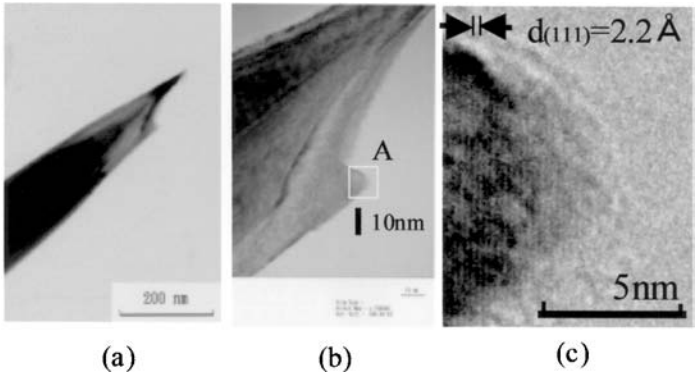

FIGURE 4 The top of a very sharp whisker formed by RIE using $CF_4/O_2 = 1\%$ gas (a) the bright field image of whisker, (b) the expansion image of (a) and (c) the lattice image of area A in (b).

whiskers was in the range of 50 to 200 nm and larger than that of RIE in only O_2. It was also found that the direction of whisker was a (100) direction and that a whisker was a single crystal diamond. However, there are no ring patterns in a diffraction pattern. It was observed in a bright and dark field image that no polycrystalline phase and few amorphous phases existed on outside of whiskers. A diamond whisker under the condition of $CF_4/O_2 = 1\%$ is shown in Figure 4. Figure 4(a) is a bright field image, (b) is the expansion image of (a), and (c) is a lattice image of the area A in (b). Although some diamond whisker of $CF_4/O_2 = 1\%$ had a wide top, some diamond whiskers had a sharp top. The whisker in Figure 4 had two sharp tops. First top seemed to be smaller than second top. The size of both tops was less than 5 nm. A lattice image was observed in all area of Figure 4(b), which was near the top of (a). This shows that the top of a whisker is a single crystal diamond. The expansion of second top "A" in (b) was shown in (c). A lattice image and an amorphous layer were observed in this figure. That lattice showed (111) planes and the distance was about 2.2 A. The degree between the direction of the (111) plane and the direction of whisker was about 51°, because the substrate was a (100) plane. It was found that the top of diamond whisker was less than 5 nm, as shown in Figure 4(c).

IV. CONCLUSIONS

We have formed two type whiskers by a RIE. These whiskers are almost same with the top of emitter tip, which we have fabricated by a RIE. It was

found that the diamond whisker is very thin. The size of whiskers formed by RIE in O_2 was less than 0.2 μm. The minimum size was approximately 2 nm. The size of whiskers formed by RIE in CF_4/O_2 of 1% was 50 to 200 nm. The minimum top size of the whisker was approximately 5 nm. The whisker under two conditions was a single crystal diamond. We have formed single crystal diamond whiskers of <5 nm.

REFERENCES

[1] Ando, Y., Nishibayashi, Y., Kobashi, K., Hirao, T., & Oura, K. (2002). *Diamond and Related Materials*, to be published.
[2] Y. Nishibayashi, Y. Ando, K. Kobashi, K. Meguro, T. Imai, T. Hirao, & K. Oura; Proceedings of the Sixth Applied Diamond Conference/Second Frontier Carbon Technology Joint Conference (ADC/FCT 2001), Y. Tzeng, K. Miyoshi, M. Yoshikawa, M. Murakawa, Y. Koga, K. Kobashi, & G.A.J. Amaratunga (Editors), Auburn, August 6–10, 2001, p. 110.
[3] Shiomi, H. (1997). *Jpn. J. Appl. Phys.*, *36*, 7745.
[4] Baik, E. S. & Baik, Y. J. (2000). *J. Mater. Res.*, *15*(4), 923.
[5] Kobashi, K., Tachibana, T., Yokota, Y., Kawakami, N., Hayashi, K., & Inoue, K. (2001). *Diamond and Related Materials*, *10*, 2039.