Effect of the Crystal Plane on the Catalytic Etching Behavior of Diamond Crystallites by Cobalt Nanoparticles

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Catalytic etching of synthetic diamond crystallites using small cobalt particles in a hydrogen atmosphere was found to be dependent on the crystal planes of diamond crystallites. The etched surface formed on the {100} planes at 900 °C consisted of reversed pyramid-like etch pits with {111} walls. Those on the {111} planes conversely showed a characteristic morphology consisting of nanochannels with flat walls perpendicular to the flat {111} base.

Although chemical etching of pure diamond with KNO_3 or oxygen has been reported,[1] the catalytic creation of pores with hydrogen has not yet been well established. The different available forms of diamonds, such as crystallites, powders, and coatings[2] including BDDs (boron-doped diamonds)[3,4] have been utilized for a variety of purposes, such as polishing materials, surface coatings, electrodes or supporting materials of catalysts. In order to expand the uses of diamonds, optical material for example, morphological modification of them is needed.

The catalytic etching of diamond by metals under a hydrogen atmosphere for obtaining thin diamond films efficiently[5] and for the patterning of diamond surfaces[6] was reported. In the previous paper, we demonstrated the catalytic etching of crushed diamond crystallites by cobalt nanoparticles;[7] however, the effect of the crystal planes of diamond against the etching behavior has never been examined. We now report our discoveries concerning the effects of crystal plane on the catalytic etching of the surface layers of synthetic pure diamond crystallites by cobalt nanoparticles at 900 °C in a hydrogen atmosphere.

A 0.1 mol dm^{-3} aqueous solution of $Co(NO_3)_2$ was used as the source of the cobalt particles. After 10 µL of the precursor solution was dropped onto 10 mg of a synthetic single-crystal diamond powder [Tomei Diamond Co., Ltd.; No. MD-200; This synthetic diamond was statically produced at ultrahigh pressure (5 GPa, 1300 °C, 1 h).], the powder was placed in a Pt boat which was then placed in a fused silica furnace tube, dried at 60 °C in flowing N_2 gas, and then heated at 900 °C in a flowing gas mixture of H_2(10%) + N_2(90%) for 2 h. The specimen treated by this procedure was designated as "cobalt-treated diamond crystallites" in this study.

Figure 1 shows a typical SEM image of the synthetic diamond crystallite after being heated under a gas mixture stream of highly pure H_2(10%) + N_2(90%) at 900 °C for 2 h. Although some edges are seen on the surface, neither the etch pits nor channels can be observed. The surface morphology of this specimen is the same as that of the as-received specimen.

Thermogravimetry showed that the decomposition of $Co(NO_3)_2$ loaded on the diamond crystallites under the hydrogen atmosphere was achieved below 250 °C, and the consumption of the diamond began beyond ca. 700 °C. Figure 2 shows the typical surface of the {100} planes of the cobalt-treated diamond crystallites. As seen in this micrograph, many reversed pyramid-like etch pits consisting of flat {111} walls were formed by the cobalt-treatment. Thus, the catalytic etching behavior of the diamond crystallites by cobalt nanoparticles is dependent on the characteristic arrangement of the carbon atoms of the [100] direction. The reason for the formation of the etch pits surrounded by the {111} walls is that the {111} planes are the closest packing planes in the diamond structure. Although round-shaped cobalt particles are observed in some etch pits,

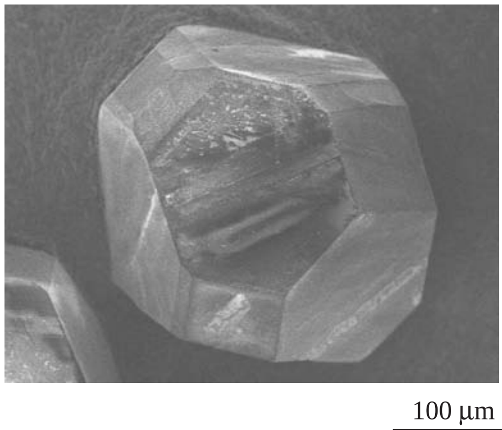

Figure 1. A typical SEM image of the synthetic diamond crystallites after being heated under a gas mixture stream of highly pure H_2(10%) + N_2(90%) at 900 °C for 2 h.

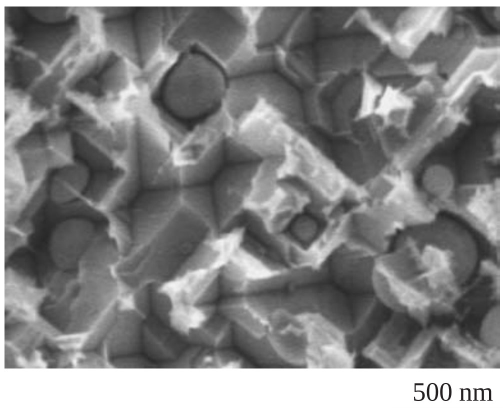

Figure 2. A typical SEM image of the {100} plane of the cobalt-treated synthetic diamond crystallite. The cobalt-treatment was made by the heating of a $Co(NO_3)_2$-loaded diamond under a gas mixture stream of highly pure H_2(10%) + N_2(90%) at 900 °C for 2 h.

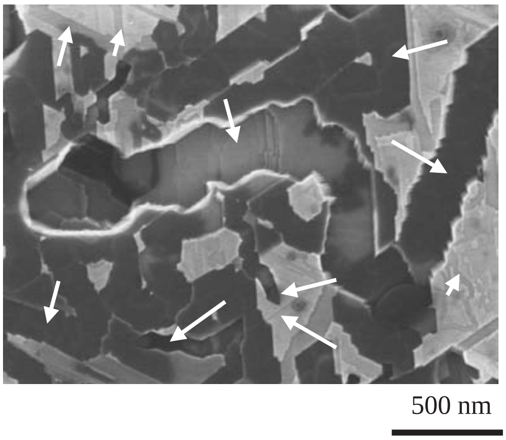

Figure 3. A typical SEM image of the {111} plane of the cobalt-treated synthetic diamond crystallite.

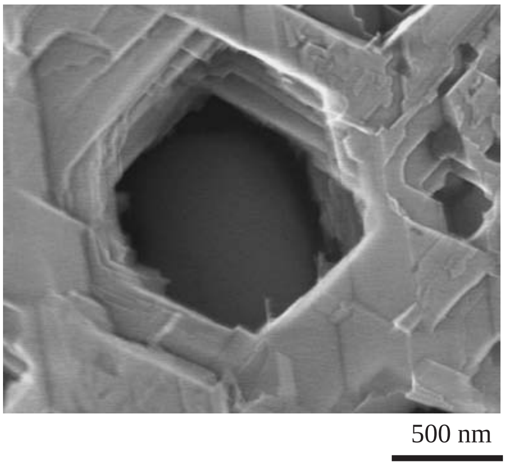

Figure 4. A typical SEM image of the {111} plane of the cobalt-treated synthetic diamond crystallite showing a large etch pit with a cobalt particle at the bottom.

no cobalt particles are seen in other etch pits. This strongly suggests that the cobalt particles seen in this micrograph must be formed as a result of the cohesion of finer cobalt particles which etched the diamond forming methane. The origin for the etching of a diamond by cobalt particles must be the formation of a carbide-like layer at the interface where the cobalt particles meet the diamond prior to the formation of methane. The successive formation of a carbide-like layer could have assisted the moving of the cobalt particles, resulting in the etching of the surface layer of the diamond crystallites.

Figure 3 shows a typical surface of the {111} planes of the cobalt-treated diamond crystallites. Contrary to the {100} planes, many channels with various sizes in width are observed on the surface, where they are not always straight channels (see white arrows in Figure 3). Formation of such nanochannels is similar to the phenomena observed on the HOPG (highly oriented pyrolytic graphite) which was etched by cobalt nanoparticles in a hydrogen atmosphere at a high temperature.[8] The bases of the channels formed on the {111} planes were flat and parallel to the surface. Other than such channels, etch pits were also observed on the {111} planes. An etch pit with a large cobalt particle on the {111} plane is shown in Figure 4. The etch pit is hexagonal in shape, reflecting the carbon atom arrangement in the {111} surface layers of the diamond structure.

In conclusion, we have discovered unique etching phenomena of pure diamond crystallites etched by cobalt particles under a hydrogen atmosphere at 900 °C. The shapes of the etch pits were affected by the arrangement of the carbon atoms in the diamond crystals. This simple method can be used to increase the real surface area of the diamonds, BDD and other carbon materials. The holes on the diamonds can also be utilized to form concave sites for any catalyst metals or compounds.

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