Selected Papers

Self-Embedment of Small Rectangular Parallelepiped Platinum Particle Array in Etch Pits on {100} Planes of Diamond Crystallites

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Small platinum particles less than about 200 nm in size with the unique form of a rectangular parallelepiped array were self-embedded in etch pits that were formed through partial gasification of the diamond with hydrogen and the platinum particles on the {100} planes of synthetic diamond crystallites at 1173 K.

Diamond has excellent physical properties, such as high hardness and strong chemical stability. To extend the functionality of diamond, including boron-doped diamond (BDD), researchers have focused on surface modifications, e.g., those involving surface morphology and embedment of small metal particles. Etching of diamond {111} surfaces with dry oxygen gas, oxygen/water vapor, and molten potassium nitrate resulted in the formation of triangular micron-order etch pits with smooth rounded corners.[1–3] Patterning of a diamond surface was conducted in a hydrogen atmosphere through a thin solid metal layer, such as Fe, Ni, and Pt.[4] A well-ordered nanoporous honeycomb was prepared on mirror-polished BDD by oxygen plasma etching through a porous alumina mask.[5–7] The honeycomb BDD electrodes with various pore diameters were modified with Pt nanoparticles, and their size-selective electrocatalytic properties were examined.[7] Applying microwave plasma-assisted chemical vapor deposition (MPACVD) to a Pt thin-film predeposited on diamond, spherical platinum particles were implanted in the diamond film.[8] Various nanometer-sized platinum particles were electrodeposited on BDD electrodes.[9] We previously reported the successful catalytic formation of channels and holes, i.e., etch pits, in the surface layers of both crushed pure diamond powder and BDD with a few metal nanoparticles (Co, Ni, Nb, Mo, W, and Pt) by heat treatment in a hydrogen atmosphere.[10–12]

Here, we report our discovery of the catalytic formation of etch pits in which rectangular parallelepiped platinum array particles are self-embedded in the surface layers of the {100} planes of synthetic pure diamond crystallites.

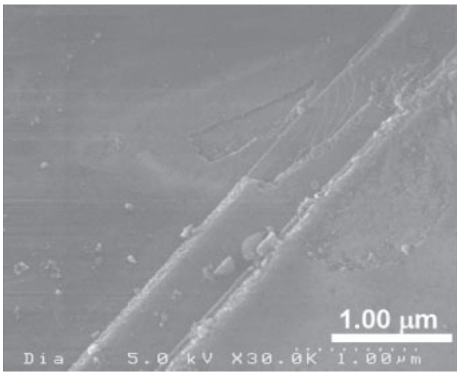

Figure 1. SEM micrograph of a (100) surface of the synthetic diamond crystallite heat-treated under a gas mixture stream of high-purity $H_2(10\%) + N_2(90\%)$ at 1173 K for 2 h.

The diamond crystallites (IMS-25, Tomei Diamond Co., Ltd.) used in this study were statically produced under 5 GPa at 1573 K. The average diameter was 0.3 mm. The morphology of the synthetic diamond crystallites was a cubo-octahedral structure with eight {111} and six {100} planes. A highly {100}-oriented diamond coating formed on a Si{100} single crystal wafer using MPACVD, was also used in this study (provided by Kobe Steel, Ltd.). Figure 1 shows an SEM image of a (100) surface of the diamond crystallites. Steps were found on the (100) surface of the diamond; however, no etch pits were observed.

Platinum loading on the diamond crystallites was conducted by impregnation. The aqueous suspension of diamond crystallites and $[Pt(NH_3)_2(NO_2)_2]$ was placed in a beaker, heated on a hot plate at 353 K while stirring, and then dried. The resulting powder was placed in a silica boat in a silica tube furnace, heated in a stream of $H_2(10\%) + N_2(90\%)$ at $5\,K\,min^{-1}$ to 1173 K, retained at that temperature for 2 h, and then cooled to room temperature in the hydrogen atmosphere, where high-purity N_2 and H_2 (both gases; 99.999% purity, TAIYO NIPPON SANSO CORPORATION) were used. Heating the diamond crystallites, on which the platinum complex was loaded, in the hydrogen atmosphere, decomposed the platinum complex below about 473 K, forming small platinum particles on the diamond. At 1173 K, the diamond crystallites underwent partial gasification with hydrogen and platinum as the catalyst, forming etch pits and channels. Methane was the only gaseous product detected by gas chromatography.

Figures 2a and 2b show SEM images of a typical (100) surface of the diamond crystallites, loaded with 5 mass % platinum on average, which was heat-treated in the hydrogen atmosphere at 1173 K. Many rectangular parallelepiped particles less than about 200 nm wide were embedded in the etch pits of the diamond, while the geometries of the portion of the metal particles embedded inside of the pits were unseen by SEM. The backscattering electron image shown in Figure 2b strongly suggests the particles to be platinum. However, the platinum particles might have contained carbon, because the equilibrium content of carbon in the phase diagram of Pt–C at 1173 K was about 0.7 atom %.[13] As shown in Figure 3, the

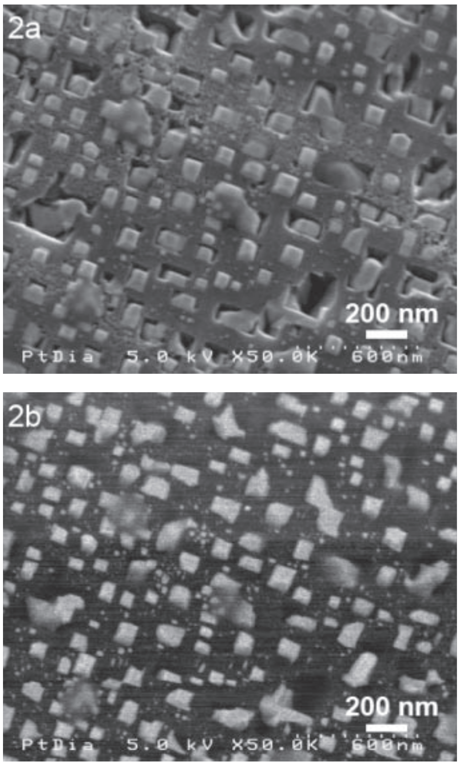

Figure 2. SEM micrographs of the Pt-loaded {100} surface of a diamond crystallite prepared by impregnation under a gas mixture stream of high-purity $H_2(10\%) + N_2(90\%)$ at 1173 K for 2 h. 2a is a secondary electron image, and 2b is its backscattering electron image.

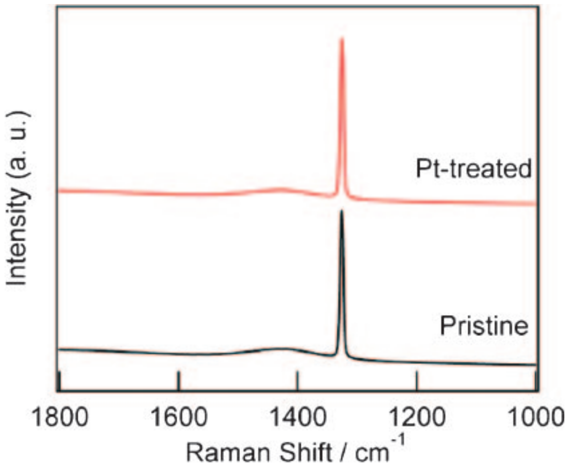

Figure 3. Raman spectra of the Pt-treated diamond crystallites prepared at 1173 K for 2 h and that of the pristine diamond crystallites.

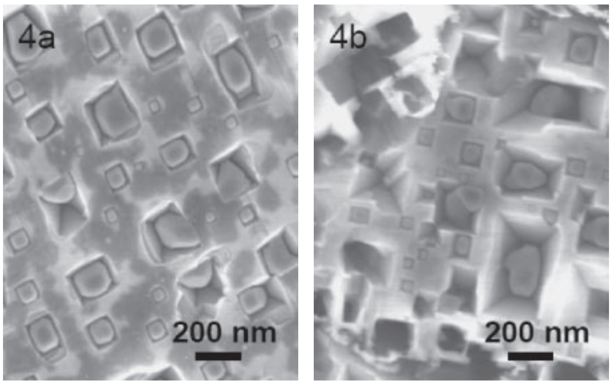

Figure 4. SEM micrographs of the Pt-loaded surface of the highly {100}-oriented diamond coatings heat-treated at (4a) 1173 or (4b) 1273 K for 2 h under a gas mixture stream of high-purity $H_2(10\%) + N_2(90\%)$. Platinum was loaded by vacuum evaporation.

Raman spectrum of the diamond crystallites, which was etched by platinum particles at 1173 K in the hydrogen atmosphere, was almost the same as that of the pristine diamond crystallites. This means that the surface of the diamond structure of the former specimens was retained even after the Pt treatment.

The form of the agglomerated platinum particles must have been affected by one or more factors, namely (1) thermodynamics governing the stable form of the platinum particles in the hydrogen atmosphere, (2) carbon content in the platinum particles, (3) amount of platinum in the etch pits, (4) shape of the etch pits, and (5) arrangement of the surface carbon atoms of the walls of the etch pits. As typically shown in Figure 2, the platinum particles could adhere closely to the walls of the etch pits of the diamond. Although the walls of the etch pits must consist of {111} planes of the diamond, as shown in a previous paper for cobalt particles embedded in the etch pits of diamond,[11] this is difficult to confirm from the SEM images presented in Figure 2. As the condition of platinum particles contributing to the etching of the diamond, two probabilities can be proposed. The first one is that the platinum particles were in a melted state, because the melting point of a metal nanoparticle generally decreases with smaller particle size.[14] The small platinum particles in a melted state must have behaved in various manners; etching of the diamond, coalescence with the other platinum particles or staying at the position where the etching of the diamond had initiated. The second probability is that the platinum particles were in a solid state, because, as Yoshida and his co-workers found, iron carbide particles are movable in a solid state and contribute to the formation of carbon nanotubes, even at 873 K.[15] To understand the process of the catalytic etching by platinum particles, platinum was loaded on a highly {100}-oriented diamond coating by vacuum evaporation (6.9×10^{17} Pt atoms cm^{-2}) and heat-treated under the hydrogen atmosphere at 1173 or 1273 K. The SEM micrographs in Figure 4 strongly suggest that; an increase in the heating temperature provokes not only the etching of diamond by Pt particles in each etch pit, but connecting of the pits.

The exposed crystal planes of the parallelepiped platinum particles appear to be {100} planes. We previously reported that the particle size appeared to determine the exposed crystal plane of nanosized platinum particles loaded on a BDD surface by vacuum evaporation followed by heat treatment in a hydrogen atmosphere; however, the morphology of the platinum particles was too small to be determined.[12] Figure 5 shows the size distribution of platinum particles evaluated from the SEM images of Figure 2 and the above assumption for the particle size, where platinum particles of less than 10 nm were excluded due to inadequate resolution of the SEM images.[16]

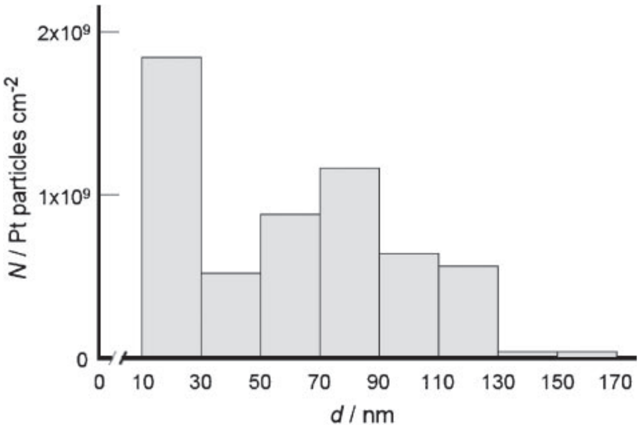

Figure 5. Size distribution of the platinum particles evaluated from the SEM images of Figure 2, where platinum particles of less than 10 nm were excluded due to inadequate resolution of the SEM images.

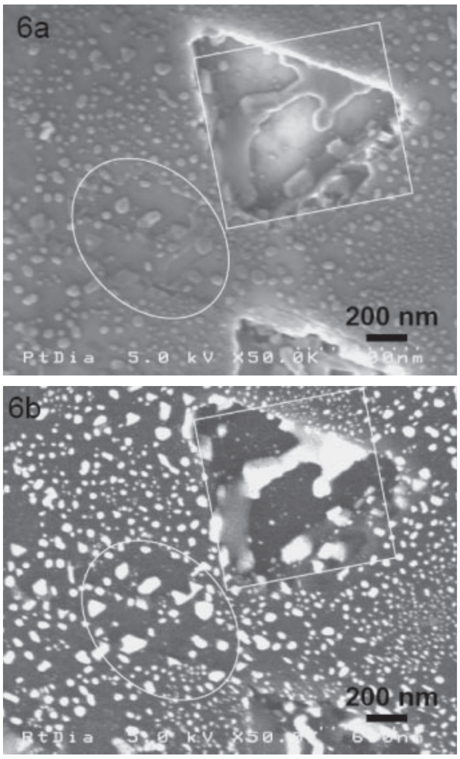

Figure 6. SEM micrographs of the Pt-loaded {111} surface of a diamond crystallite prepared at 1173 K for 2 h. 6a is a secondary electron image, and 6b is its backscattering electron image.

On the {111} surfaces of the Pt-loaded crystallites, channels (indicated with a white ellipse in Figure 6) and triangular hollows (indicated with a white square in Figure 6) with distorted sphere-shaped platinum particles are formed as shown in Figures 6a and 6b. The base of the channels and hollows formed in the surface layers of the {111} planes is flat with the close-packed {111} planes of the diamond.

In conclusion, we have prepared small platinum particles less than about 200 nm with the unique form of a rectangular parallelepiped platinum array in the surface layers of {100} planes of synthetic diamond crystallites by exposing the {100} planes by a catalytic method at 1173 K. The platinum particles were self-embedded in diamond-crystallite etch pits that were formed through partial gasification of the diamond with hydrogen and the platinum particles. This simple method not only contributes to fundamental research on small platinum particles but also introduces new functionalities to diamonds, including the development of agglomeration-resistant diamond-supported platinum particle catalysts and platinum particle catalysts with a specific crystal plane.

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16 The amount of platinum per specimen, 5 mass % Pt, would correspond to nearly 2.9×10^{18} Pt atoms $\mathrm{cm}^{-2}{}_{\mathrm{(dia)}}$, if the platinum had been uniformly coated on the diamond on every plane and crystallite; however, uniform coating of the platinum complex by impregnation is essentially very difficult. Assuming that all the platinum particles loaded on the plane shown in Figure 2 are spheres and that all the cross sections evaluated from the top view of the reflection SEM image in Figure 2b correspond to those of the spheres, the loading amount of Pt would be 1×10^{17} Pt atoms $\mathrm{cm}^{-2}{}_{\mathrm{(dia)}}$, where the amount of the platinum monolayer would be about 1.3×10^{15} Pt atoms cm^{-2}.