Synthesis of Diamond Cylinders with Triangular and Square Cross Sections Using Anodic Porous Alumina Templates

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Highly ordered arrays of diamond cylinders with square and triangular cross sections were prepared by CVD synthesis using anodic porous alumina templates with modified pore shapes. The CVD synthesis of diamond was carried out using a microwave enhanced CVD apparatus using alumina templates. By removing the alumina template in concentrated phosphoric acid, an ordered array of cylinders with a uniform size and shape was obtained. The obtained diamond cylinders could be isolated, and yielded the shape- and size-controlled diamond particles.

Diamond has attracted considerable interest because of its unique properties including hardness, chemical stability, and negative electronic affinity.[1–6] Control of the geometrical structures of diamond is important in the application of diamond to several types of devices such as field emitters,[2–4] functional electrodes,[5,6] and sensors. In our previous report,[7] we described the fabrication of ordered cylinder arrays of diamond with nanometer dimensions. In this process, anodic porous alumina with an ordered hole array was used as the template for the CVD synthesis of diamond. Anodic porous alumina, which is formed by anodization of Al in an acidic solution, has ordered hole array structures.[8–10] This material is suitable for the CVD synthesis of diamond because of its high thermal resistance in addition to its unique geometrical structures. In the present report, we describe the CVD synthesis of an ordered array of diamond cylinders with triangular and square cross sections using the anodic porous alumina template with modified pore shapes, that is, square and triangular openings.[11] The square and triangular diamond cylinder arrays are useful for the modification of the band-gap structures of the photonic crystals prepared by diamond cylinder arrays.[12] Highly shape-designed diamond cylinders can be also applied to control the electron emission properties of the electron emitters used for the flat display panels.[13] In addition, the uniformly shaped diamond nanocylinders (particles) obtained through the isolation of the synthesized diamond are promising as candidate building units for the fabrication of ordered nano-structures by self-assembly.

In Figure 1, the procedure for CVD synthesis of the shape-controlled diamond nanocylinders is shown. The anodic porous alumina used as the template was prepared based on the procedure described in a previous report.[11] In this process, anodic porous alumina with triangular and square openings was prepared based on the control of the initiation site of the hole development, and the close packing of the formed cells. The preparation of initiation sites for the hole development was carried out by imprinting Al (99.99% purity) using a SiC mold with a patterned array of convexes. The SiC mold was prepared by an electron-beam lithographic technique.[14,15] After the imprinting, anodization of Al was conducted in 0.5 M phosphoric acid solution under constant voltage anodization of 80 V at 17 °C. The Al substrate was removed using saturated $HgCl_2$, and the bottom part of the oxide layer was subsequently etched by 5 wt% phosphoric acid solution at 30 °C. Prior to the CVD synthesis, small diamond particles of 500 nm diameter were coated on one side of the alumina template for nucleation in the CVD synthesis of diamond. For the coating, a drop of acetone solution with dispersed diamond particles, which can act as seeds for nucleation, was placed on the alumina template, and was subsequently evaporated.

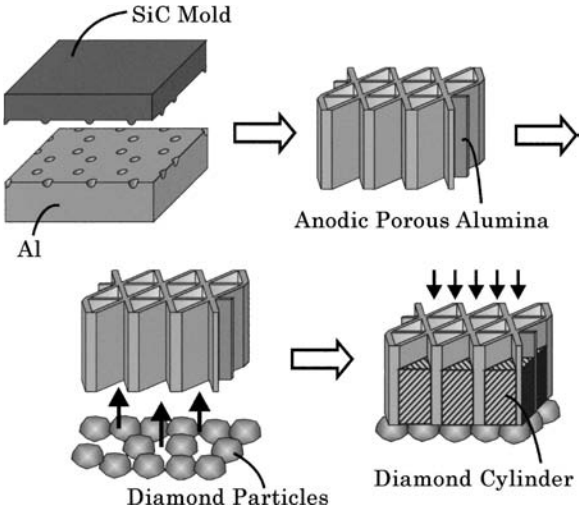

Figure 1. Schematic of preparation of the array of diamond cylinders with controlled shape: (a) control of initiation sites of hole development by imprinting of Al with SiC mold, (b) anodization of Al and removal of Al and bottom layer of the alumina, (c) nucleation of alumina template with diamond particles, (d) CVD synthesis of diamond on the template.

The CVD synthesis of diamond was carried out using a microwave enhanced CVD apparatus (ASTEX). After the CVD synthesis, the alumina template was removed by immersing the samples in concentrated phosphoric acid at 250 °C.

Figure 2 shows a typical SEM image of the ordered array of diamond cylinders with a square cross section. The CVD diamond was not deposited on the surface or inner wall of the pores of the alumina template. Diamond grew only from the particles loaded at the bottom of the membrane. The side length and period of the cylinders were 140 nm and 200 nm, respectively. The shape and the size of the obtained diamond cylinders were in good

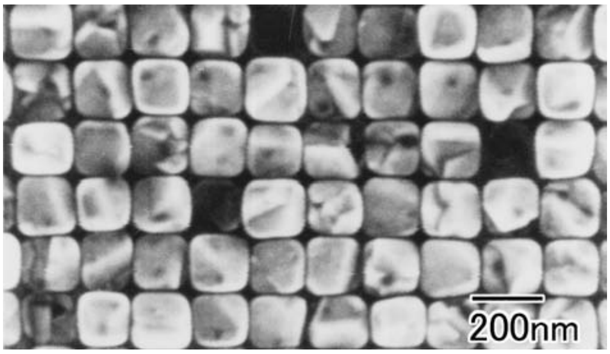

Figure 2. SEM micrographs of the array of diamond cylinders with a square cross section. CVD time was 240 min.

agreement with those of the porous alumina used as the template. This result indicates the high controllability of the shape of the diamond cylinders in the present method of synthesis. In our previous report, microscopic Raman analysis confirmed that the cylinders obtained by the present process mainly consist of diamond with small amounts of non-diamond carbon.[7]

For the case in which anodic porous alumina with triangular openings was used as the template, an ordered array of diamond cylinders with a triangular cross section was obtained as shown in Figure 3. From the surface view in Figure 3a, a highly ordered array of diamond cylinders with a triangular cross section was formed over the sample. As observed in the oblique SEM view in Figure 3b, cylinders were formed perpendicular to the surface, and were independent of each other. The height of the diamond cylinders was 1.3 μm based on the image in Figure 3b.

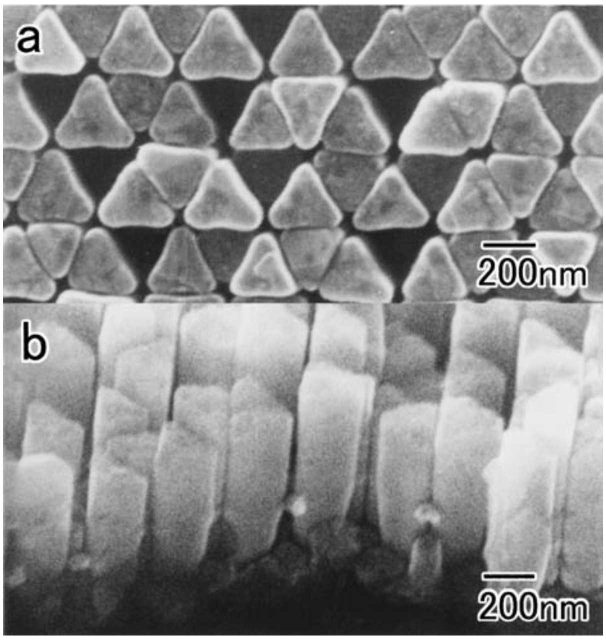

Figure 3. SEM micrograph of the array of diamond cylinders with a triangular cross section: (a) surface view and (b) oblique view. CVD time was 300 min. The SEM observation angle was 45 degrees to the surface.

Each diamond cylinder was formed independently, although the bottom part of cylinders was joined together partially. The obtained diamond cylinders could be isolated through the mechanical grinding of the samples after the removal of the alumina template in concentrated phosphoric acid. Figure 4 shows one example of the isolated diamond nanocylinders (particles) with a triangular cross section. In the case of the sample in Figure 4, the height of the cylinders was adjusted to 300 nm by controlling the period of CVD synthesis. From Figure 4, it was confirmed that the shape and size control of the diamond nanocylinders (particles) was achieved through isolation.

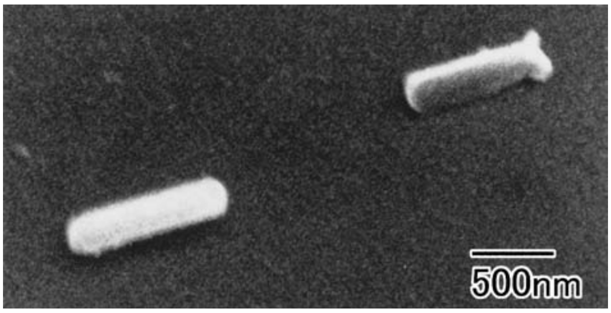

Figure 4. SEM micrograph of isolated diamond cylinders. The CVD time was 240 min.

In conclusion, ordered arrays of diamond nanocylinder with square and triangular cross sections were prepared by CVD synthesis using anodic alumina templates with modified hole shapes. The present process has the advantage of high controllability of the shape and size of the diamond nanocylinders. The obtained array of shape-controlled diamond nanocylinders can be applied to the fabrication of several kinds of nanodevices which require morphologically controlled diamond. In addition, the uniformly shaped particles obtained through the isolation of the cylinders will also be useful as the starting materials for several kinds of nanostructures.

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