Preparation of Periodic Microstructured Diamond Surfaces

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Two types of periodic surfaces were fabricated by utilizing two-dimensionally ordered arrays, in one case as a template and in another as a mask. In the first case, a bulb-like microstructured surface was formed, and, in the second, a cylinder-like microstructure. The Raman spectra of these films indicate that they consist mostly of diamond and therefore have a high refractive index as well as other well-known properties of diamond, making them attractive for photonic, electronic, and electrochemical applications.

Microporous materials have recently attracted much attention due to their various applications in electronic,[1] electrochemical,[2,3] and photocatalytic[4] systems. Many efforts have been made to prepare microporous materials with textured surfaces of controlled periodicity.[5,6] Diamond is a material that is difficult to prepare in such forms; however, its unique properties, e.g., hardness, high refractive index,[7] extreme chemical stability and inertness, and wide electrochemical potential window[8,9] make it attractive. Thus, diamond films with periodic microporous textured surfaces are expected to be used, for example, as electrodes for high-sensitivity sensors,[8] as photonic crystals[5] and so on.

In this letter, we report two types of porous diamond films with periodic surface structures, which we have called bulb-like and cylinder-like structures. The preparation processes utilize the intrinsic microstructures of two-dimensionally ordered arrays.[10] We selected SiO_2 particles as a template, because they are stable throughout the processing.[11] The SiO_2 particles (diameter, 1 μm) were obtained from Nihon Syokubai, Japan (Seahostar KE-P). The schematic processes are shown in Figure 1.

In the preparation of the bulb-type surface, at first, SiO_2 particle arrays were prepared on a Si (100) wafer using capillary forces and water evaporation.[10] The arrays were sintered at 600 °C for 1 h in an electric furnace (KFD 75, Den-ken, Japan). On this array, polycrystalline diamond was grown (1.2×10^4 Pa for 9 h at 117 °C) by microwave-assisted plasma chemical vapor deposition (CVD) with a commercial microwave plasma reactor (ASTeX Corp., Woburn, MA).[8] Finally, the Si plate and SiO_2 particles were removed from the diamond film using 47% HF solution. In the preparation of the cylinder-type surface, the SiO_2 particle arrays were prepared on the diamond film. Subsequently, oxygen plasma etching was carried out for 5–120 minutes at 150 W in a plasma etching apparatus (SAMCO, BP-1). The operating oxygen pressure was 20 Pa, and the plasma power was 150 W. Finally, the SiO_2 particles were removed from the diamond film by etching in 47% HF solution. These completed films were opalescent because of the periodic structures.

The morphologies of the diamond films thus prepared were examined with a scanning electronic microscope (SEM, S-4200, Hitachi, Ltd., Japan). Figure 2 shows SEM images of a film prepared in such a way as to exhibit a bulb-type surface texture. The images indicate that hollow spheres (white circles in Figure 2a) are hexagonally close-packed, reflecting the structure of the SiO_2 particle arrays. Most of these spheres contain a small hole at the top, with a diameter of 180–200 nm (Figure 2b). There were also several hollow sphere-like structures without holes at the top. In these cases, it may be said that the deposited diamond has intruded between the SiO_2 particles and the Si plate.

Figure 3 shows SEM images of a film prepared in such a way as to exhibit a cylinder-type surface texture. The film has

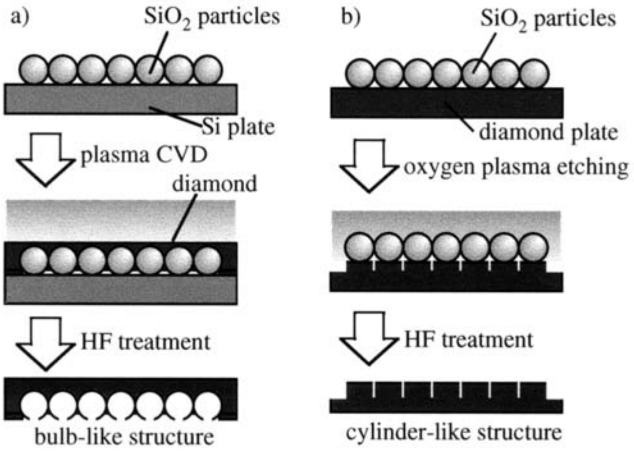

Figure 1. Schematic diagrams showing the preparation procedures for a) bulb-like and b) cylinder-like microstructured diamond films.

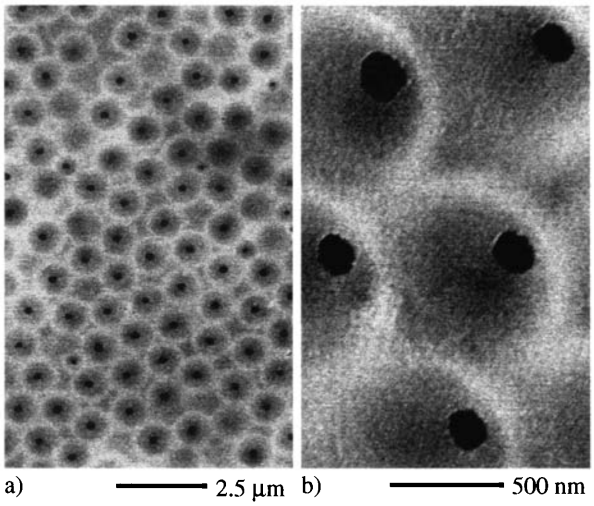

Figure 2. SEM images of bulb-like surfaces observed at tilt angles of a) 0° and b) 45°.

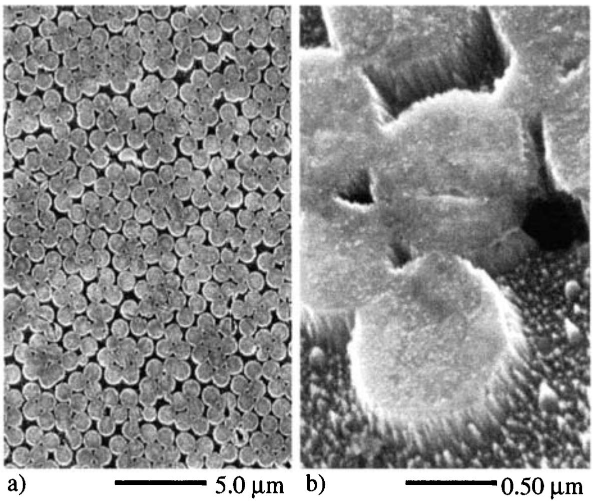

Figure 3. SEM images of cylinder-like surfaces observed at tilt angles of a) 0° and b) 30°.

a hexagonally close-packed array of cylinder-like structures on the surface. The cylinders form a projection of the original SiO_2 particle array. The diameters of the cylinders are approximately 1 µm. The domain size of the cylinder-type was smaller than that of the bulb-type. The diamond surface contains many grooves. If the surface is polished, it will be easier to make wide-domain SiO_2 arrays on the surface. When oxygen plasma etching was carried out for 5 min, the heights of the cylinders were about 0.35 µm. In a similar fashion, the etching was carried out for 10–120 min. The height reached the maximum after etching for approximately 90 min (maximum aspect ratio = 6). The duration of the oxygen plasma etching can be used to control the heights of the cylinders. Thus, we may be able to control the aspect ratio of the cylinders by varying the etching time and the SiO_2 particle diameters.

Raman spectra of the diamond surfaces are shown in Figure 4. In both spectra, the characteristic peak for crystalline diamond at 1332 cm^{-1} is clearly observed, and broad, low-intensity peaks at 1350 and 1600 cm^{-1} (sp^2 carbon) are also visible. Based on the known high sensitivity of Raman for sp^2 carbon vs. sp^3 carbon, these data indicate that diamond, together with smaller amounts of sp^2 carbon, both exist on these microstructured surfaces.[12] The percentage of sp^2 carbon on the bulb-type surface is larger than that on the cylinder-type. The reason for this is that the plasma conditions within the small enclosed space between the microspheres and the substrate may not be optimal for diamond growth. The oxygen plasma treatment may reduce the quantity of sp^2 carbon, because sp^2 carbon is known to be etched faster than sp^3. However, we could not find differences between the Raman spectra measured before and after oxygen plasma etching.

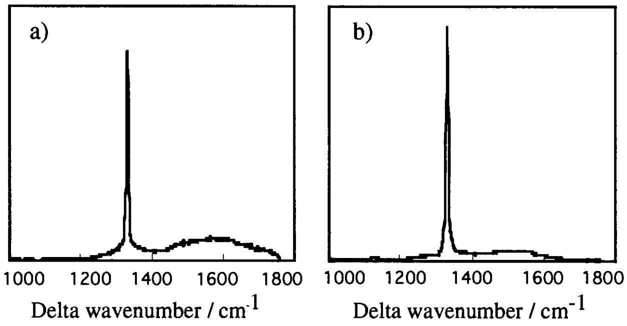

Figure 4. Raman spectra of a) bulb-like and b) cylinder-like microstructured diamond films.

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