

Fabrication of Ordered Diamond/metal Nanocomposite Structures

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Highly ordered diamond/Au nanocomposite structures were fabricated by preparing a honeycomb structured diamond film and subsequent Au deposition into holes by vacuum deposition. The cross-sectional SEM image of the composite film showed Au nanodots at the bottom of the holes. The optical absorption spectrum of the composite film showed a characteristic absorption due to the surface plasmon resonance at the wavelength of ~520 nm, indicating the possible application of honeycomb diamond in optoelectronics.

The unique properties, such as exceptional hardness, wide band gap, high thermal conductivity, high refractive index and high optical transparency have made diamond a highly promising material for various applications in optical and electronic devices.¹⁻³ Control of geometrical structures of diamond is necessary to realize its practical applications. Fabrication of nanocomposite structure with fine and controlled structure makes diamond more useful for advanced applications such as optical functional devices, sensors and electrodes. Recently, we demonstrated the fabrication of nanohoneycomb diamond film with highly ordered array of holes by oxygen plasma etching, using an anodic porous alumina as a mask.⁴ The advantage of this technique is that it overcomes the problems associated with conventional lithographic techniques, where the resolution using these techniques was only on the order of submicrometers. In addition, high resistance to oxygen plasma etching of anodic porous alumina yields the hole arrays with high aspect feature. Use of this technique to make diamond/metal composite structures is interesting because it produces well defined straight holes which makes it easy to deposit metal controllably at bottom of the each.

Composite structures consisting of small metal particles embedded in diamond matrix are interesting for several types of functional devices, such as optical devices⁵⁻⁸ and functional electrodes.⁹ For the optical devices based on the optical nonlinearity of the dielectric/metal small particles composites, the uniformity of the size and ordering of metal particles in the composite structure are very important. In addition, the composite structures of diamond/embedded metal particles are promising for the preparation of functional electrodes where metal small particles act as catalyst for electrolysis. The composite structure is effective for the fixation of the small metal particles on the diamond surface which is difficult to ensure due to the low adherence of metal on diamond surface. In the present letter, for the first time, we report the fabrication of diamond/Au nanocomposite films, which consist of Au small particles in the highly ordered hole arrays of diamond, and describe their optical properties.

Diamond thin films were grown by CVD method using a microwave plasma reactor (ASTEX).⁴ The as-grown films

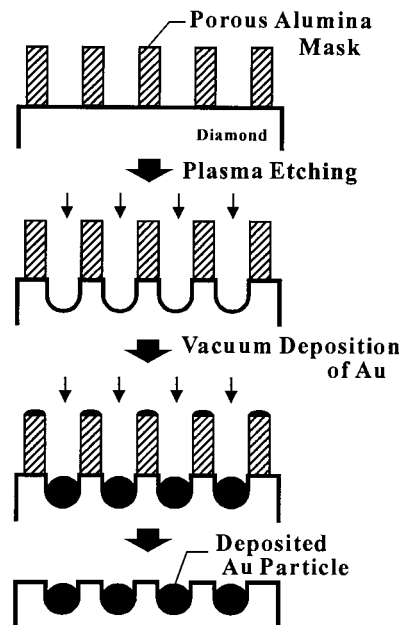


Figure 1. Fabrication process of diamond/Au nanocomposite structure

were polished to obtain smooth surfaces. Freestanding films were obtained after etching the Si substrates in a mixture of HF and HNO₃. Figure 1 shows the schematic diagram for the fabrication of diamond/Au nanocomposite structure. Prior to metal deposition, nanohoneycomb structure with an ordered hole array was prepared by oxygen plasma etching using an anodic alumina mask. The preparation of porous alumina mask and oxygen plasma etching procedure has been described previously.⁴ In the present work, oxygen plasma etching was carried out for 4 min in a plasma etching apparatus (SAMCO BP-1). The operating pressure of oxygen was 20 Pa, and the plasma power was 150 W.

Vacuum deposition of Au was subsequently carried out through the alumina mask at a pressure of 2.7×10^{-3} Pa using a vacuum deposition unit (ULVAC EBH-6). Nominal thickness measured by a quartz crystal film thickness monitor of Au was 70 nm. After the alumina mask was etched by 1 M NaOH solution, red color diamond/Au composite films were obtained by the above process.

Figure 2 shows the SEM image in the top view of a typical diamond/Au nanocomposite film which was fabricated using a freestanding polished diamond film. Uniform and well ordered holes are clearly seen in the figure. The average diameter of the holes was found to be 70 nm with an inter hole spacing of 100

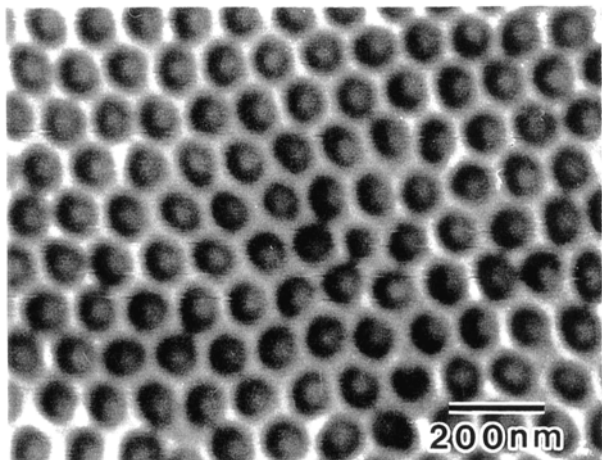


Figure 2. The top view of a typical diamond/Au nanocomposite film

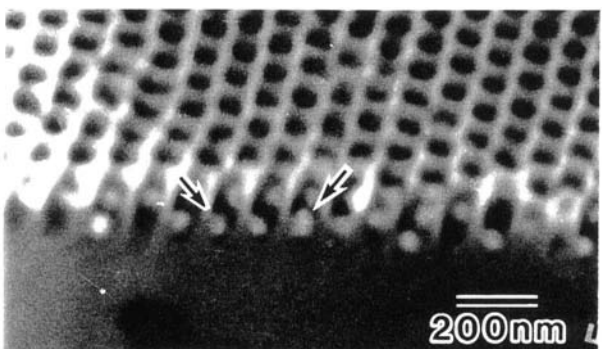


Figure 3. The cross-sectional view of the composite film

nm. The white spots in the holes represent the Au particles deposited in the holes.

Figure 3 shows the cross-sectional view of the composite film. This figure clearly shows that the Au particles are located at the bottom of the holes as indicated by arrows. As the deposition seems to proceed from the bottom of the hole, it is possible to control the size of the particles by changing the deposition time.

Figure 4 shows the optical absorption spectra obtained for the diamond/Au composite films. The absorption peak due to the surface plasmon from the Au particles is clearly seen at the wavelength of 520 nm in addition to the absorption at the shorter wavelength which is attributed to the interband transition ($5d \rightarrow 6s$) of Au.¹⁰ This absorption peak showed good agreement with the previously reported value.^{7,11} It is known that small metal particles embedded into a dielectric matrix show characteristic colors due to the dielectric anomaly between the metal and dielectric.⁵ Several methods were developed for fabrication of metal dispersed composite structures to study nonlinear optical properties.⁵⁻⁸ However, the deposition of metal particles is very random, and the size and distribution of the particles can not be controlled in those films. Our present technique offers highly ordered distribution of metal particles with uniform distribution.

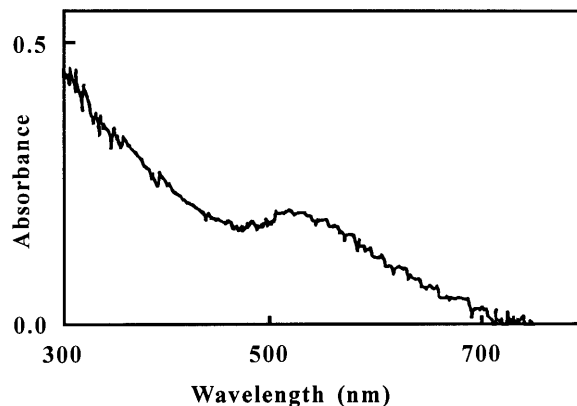


Figure 4. Optical absorption spectra measured for the diamond/Au composite films

In conclusion, for the first time, we have fabricated diamond/metal nanocomposite films by oxygen plasma etching using an anodic porous alumina mask to obtain a honeycomb structured diamond, and subsequent deposition of metal into the holes of diamond. The present technique is very common and is useful to obtain composite films with well dispersed and highly ordered metal particles having uniform size distribution.

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