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Formation of oriented nanostructures in diamond using metallic nanoparticles

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Abstract
A simple, fast and cost-effective etching technique to create oriented nanostructures such as pyramidal and cylindrical shaped nanopores in diamond membranes by self-assembled metallic nanoparticles is proposed. In this process, a diamond film is annealed with thin metallic layers in a hydrogen atmosphere. Carbon from the diamond surface is dissolved into nanoparticles generated from the metal film, then evacuated in the form of hydrocarbons and, consequently, the nanoparticles enter the crystal volume. In order to understand and optimize the etching process, the role of different parameters such as type of catalyst (Ni, Co, Pt, and Au), hydrogen gas, temperature and time of annealing, and microstructure of diamond (polycrystalline and nanocrystalline) were investigated. With this technique, nanopores with lateral sizes in the range of 10–100 nm, and as deep as about 600 nm, in diamond membranes were produced without any need for a lithography process, which opens the opportunities for fabricating porous diamond membranes for chemical sensing applications.

1. Introduction
Diamond thin films are now easily produced on large areas with nanocrystalline or polycrystalline microstructures, and various applications are under development that take into account the exceptional properties of diamond [1–4]. Among them, chemical sensors are of particular interest, due to the bio-compatibility of diamond, its chemical inertness and wide potential window [5, 6]. In most cases, the device fabrication process involves an etching step which is performed almost exclusively by the reactive ion etching (RIE) technique with the help of lithographic processes [7–9]. However, in the case of sensors based on nanopores in a membrane [10–12], this etching technique fails to create narrow (10–50 nm in diameter) and long (typically longer than 300 nm) holes in the diamond membrane due to the limitation of lithographic resolution. Based on reported works [13, 14] on catalytic etching of diamond, we have developed a fast and simple etching method through the catalytic gasification of carbon by metallic nanoparticles in a hydrogen atmosphere. In this process, the etching of diamond proceeds with: (1) the formation of nanoparticles from the initially deposited metal film, (2) the carbon dissolution into nanoparticles through the breaking of crystallinity at the diamond–metal interface [15–17] and, finally, (3) the desorption of carbon with the assistance of a hydrogen atmosphere. Hydrogen gets catalytically dissociated into hydrogen atoms by metal nanoparticles and gasifies the dissolved carbon in the particles, and the amorphous carbon at the interface forms methane [18] or some CH\text{x} complex.

In this study, the key parameters of the etching process were investigated: type and thickness of the metallic layer; the annealing temperature; the hydrogen pressure; the diamond microstructure and the annealing time. We emphasized the etching of [100]-oriented diamond planes, since it is shown that metal-assisted diamond etching is slowest for [111]-oriented planes and that they act as stopping planes [13].

2. Methods and materials
The etching technique consists of two steps, (i) the deposition of thin metallic layers on a diamond substrate and (ii) the subsequent annealing in a hydrogen atmosphere. Metals (Ni,
Figure 1. SEM images of the (100) surface of polycrystalline diamond after 10 min of annealing with a 3 nm film of (a) Ni, (b) Co, (c) Pt and (d) Au (800 °C, 60 Torr H₂); the corresponding enlarged images show etch pits with flat sidewall faces and sharply defined edges for Ni, Co, Pt and finely dispersed nanoparticles for Au.

Co, Pt and Au) with thickness in the range of 1–10 nm were deposited on diamond substrates by e-beam evaporation, the thickness being measured by a quartz crystal oscillator. The annealing step was carried out in a hot-filament-assisted CVD diamond growth reactor at 750–900 °C in 60 Torr flowing hydrogen with 100 sccm (sccm denotes cubic centimeter per minute at STP) for between a few minutes to several hours. The base pressure of the furnace before annealing was <10⁻⁶ Torr. The temperature was increased at a rate of ~200 °C min⁻¹ and measured with an infrared pyrometer with a reading precision of ±10 °C. After the annealing step, the samples were cooled down for 30 min under a continuous hydrogen flow.

Two types of diamond films were used for these experiments, namely polycrystalline diamond with a grain size of typically 50 µm and nanocrystalline diamond (grain size 100 nm). Polycrystalline diamond was grown by Element Six (electrochemical grade and boron doped CVD diamond). Nanocrystalline diamond (undoped) with a thickness of about 1.5 µm was grown on silicon substrates in a microwave plasma CVD reactor (5200 Seki Technotron MPCVD reactor) using the bias-enhanced nucleation method [19] with following parameters: 900 °C temperature, 1000 W microwave power, 0.3% methane in hydrogen, and pressure of 30 Torr.

Annealed samples were characterized using a field emission gun scanning electron microscope (FEG-SEM; ZEISS Ultraplus) and Raman spectroscopy (HORIBA Scientific, Raman spectroscopy system T64000, 514 nm excitation).

3. Results and discussion

3.1. Effect of type and thickness of metallic layer

In order to study the effect of metal type on the etching process, Ni, Co, Pt, and Au with a thickness of 3 nm were evaporated on polycrystalline diamond and annealed at 800 °C for 10 min. Figure 1 shows the SEM images of the (100) surface of annealed polycrystalline diamond.

During annealing, nanoparticles were generated from the metallic layers, prior to etching, in order to minimize the surface energy. This effect is well known and relates to the melting point lowering effect of thin metal films and hydrogen diffusion into the metal [20–23]. From the SEM observation, we estimated the diameter of the resulting nanoparticles (Ni, Co and Pt) to be approximately fifteen times larger than the initially evaporated metal layer thickness.

Etching was observed for Ni, Co, and Pt, figures 1(a)–(c), forming etch pits with flat sidewall faces and sharply defined edges. In contrast, finely dispersed Au nanoparticles were formed, figure 1(d), and neither etch pits nor nano-channels were apparently found on the diamond surface. Ni nanoparticles showed higher etching activity than Co and Pt. The observed difference in etching behavior between the metals may be caused by the combined effect of the difference in the size and melting point of metallic nanoparticles as well as carbon solubility into the nanoparticles at the temperatures in our experiment. The solubilities of carbon into Ni, Co and Pt at 900 °C estimated from M–C, metal–carbon, phase diagrams are 1 at.%, 0.8 at.%, and 0.04 at.% respectively [24]. On the other hand, unlike the iron-group elements (Ni, Co), the carbon solubility of Au is extremely low (0.018 at.% at 800 °C in bulk phase) [25]. It has recently been reported that when the Au particle size becomes several tens of nanometers, it has carbon solubility depending on the nature of the substrate and source of carbon [26]. However, this model of carbon solubility in nanosized Au particles would not be similar to the uptake of carbon from diamond surface.

The observation also suggests that the size of the etched structures depends on the size of the initially formed metal nanoparticles. Moreover, the size can be adjusted to a certain extent by the metal layer thickness, as shown in figure 2. Nanoholes with a lateral size of 20 ± 5 nm, figure 2(a), and 150 ± 10 nm, figure 2(b), were achieved by etching nanocrystalline diamond with Ni particles that originated from 1.5 nm to 10 nm Ni films respectively.

3.2. Effect of annealing temperature

To understand the influence of annealing temperature on the etching process, polycrystalline diamond with a 3 nm film...
Figure 2. SEM images of etched nanocrystalline diamond after 30 min of annealing with (a) 1.5 and (b) 10 nm Ni films, (800 °C, 60 Torr H$_2$); the inset showing nanoholes with a lateral size of 20 ± 5 nm.

Figure 3. SEM images of a (100) surface of polycrystalline diamond after 30 min annealing at (a) 750 °C, (b) 800 °C, (c) 850 °C and (d) 900 °C, (3 nm Ni, 60 Torr H$_2$).

of Ni was annealed at 750, 800, 850 and 900°C in 60 Torr H$_2$ atmosphere. Figure 3 shows the SEM images of a (100) surface of polycrystalline diamond after 30 min of annealing.

The observation suggests that etching occurs typically in the range of 800–850°C. The absence of etching at 750°C, figure 3(a), could be due to the very low solubility of carbon into Ni at this temperature. On the other hand, the density of etched nanostructures decreased dramatically at 850°C, figure 3(c). It seems that, at this temperature, some of the particles are not active, in particular the smallest particles. The effect is even stronger at 900°C, where no etching was observed at all, instead particles started to form clusters, figure 3(d). We attribute this to the random nucleation and growth of carbon overlayers on the metal particles, poisoning them at higher temperatures, where the rate of carbon diffusion to the metal–gas interface was the highest. A high surface concentration of carbon enhances the probability of nucleation and the subsequent growth of an inactive carbon layer.

3.3. Effect of hydrogen pressure

Figure 4 shows SEM micrographs of a (100) surface of polycrystalline diamond annealed with a 3 nm Ni film for 10 min at 800 °C in vacuum, 60 Torr Ar, 60 Torr H$_2$, and 1 atm H$_2$.

Neither etch pits nor nano-channels were apparently found on the diamond surface when there was no hydrogen in the furnace, i.e. under vacuum, figure 4(a), and Ar atmosphere, figure 4(b). Moreover, in both cases Ni nanoparticles were covered by overlayers, as apparent in the SEM images observed by an in-lens energy and angle selective backscatter detector (EsB), right panels of figures 4(a) and (b). The overlayers were confirmed as carbon by energy dispersive x-ray analysis (EDX), and most likely could be amorphous carbon, since nickel carbides become unstable at temperatures as low as 350°C [27]. This observation indicates that when there is no hydrogen, and thereby no desorption, carbon absorbed by the Ni can lead to the nucleation and growth of inactive carbon layers that
eventually decrease the catalytic activity of the metal. So, hydrogen is instrumental in the etching process. Moreover, the higher the pressure of hydrogen gas in the furnace, the faster the diamond is etched, figure 4(d). We attributed this to the increased concentration of atomic hydrogen, generated catalytically, that, indeed, enhances the desorption rate.

3.4. Effect of diamond microstructure

Polycrystalline diamond and nanocrystalline diamond were annealed with a 3 nm Ni film at 800°C under 60 Torr hydrogen atmosphere. After 30 min of annealing, etching was observed on both microstructures of diamond. No particular effect related to the grain boundaries was observed. Etch pits with an inverted four-sided pyramid were formed on [100]-oriented planes of polycrystalline diamond, figure 5(a), whereas a mixture of pyramidal, hexagonal, and trigonal shaped etch pits were observed on nanocrystalline diamond, figure 5(b). Note that the nanocrystalline diamond sample exhibits a mixture of [111]-oriented and [100]-oriented planes, and the etching behavior is different depending on the crystallographic orientation.

The orientation dependence of diamond etching has been studied before using molten Ce [28], Fe particles [29], Co nanoparticles [30], and molten Ni [13], as catalysts. It has been shown that Ni-assisted diamond etching is slowest for the [111]-oriented diamond planes and that they act as stopping planes [13]. Since the uptake of carbon atoms from diamond by the metal nanoparticles occurs from the weakly bonded atoms, the carbon atoms of the closest packing plane, the [111] planes, are the most stable against the dissolution of carbon in nanoparticles, as compared to the other crystal planes [30]. As a result, etch pits walled with four [111] planes are formed on the [100] planes, whereas [111] show etching pits with equilateral triangles and hexagons [13].

3.5. Change in microstructure during etching

Two diamond samples, [100]-oriented single crystalline (CVD diamond plate, Element Six) and nanocrystalline diamond (1.5 μm thickness, 100 nm grain size), were annealed with 3 nm Ni for 10 min at 800°C. In order to detect an eventual change in microstructure, such as the appearance of graphitic phases on the surface, both samples were then characterized by Raman spectroscopy using 514 nm excitation, and the spectra were compared with those recorded before annealing.
Figure 5. SEM images of (a) (100) surface of polycrystalline diamond and (b) nanocrystalline diamond after 30 min annealing with 3 nm Ni film, (800°C, 60 Torr H₂), showing the formation of nanopores with no obvious dependence on the diamond microstructure.

Figure 6. Raman spectra of (a) single crystal diamond ([100]-oriented, CVD diamond, Element Six), (b) nanocrystalline diamond (1.5 µm thickness, 100 nm grain size), showing no change in the diamond structure after the catalytic etching by Ni nanoparticles, (3 nm Ni, 800°C, 10 min, 60 Torr H₂).

Figure 6(a) shows Raman spectra for a [100]-oriented diamond crystal recorded before (red curve) and after (blue curve) annealing. Both spectra show a similar characteristic diamond line at 1332.4 cm⁻¹, and no graphitic component is observed before or after treatment. On the other hand, D and G peaks, which lie at 1337 and 1590 cm⁻¹ respectively, were observed for the nanocrystalline diamond sample, figure 6(b). The band at 1337 cm⁻¹ is assigned to the sp³-bonded carbon in diamond (D band) and the broad peak around 1590 cm⁻¹ is attributed to the sp²-bonded carbon (G band). The peak intensity ratio of the D band to the G band (I_D/I_G) is a measure of the amount of graphitic impurities. The measured I_D/I_G values of the treated and untreated samples were 1.02 and 1.01 respectively. The observation suggests that the diamond structure was maintained for both samples (single crystalline and nanocrystalline diamond) after the catalytic etching by Ni nanoparticles.

3.6. Effect of annealing time

Nanocrystalline diamond with a thickness of about 1.5 µm was annealed with a 3 nm Ni film for 6 h at 800°C. After every 10 min, the cross section of the sample was observed in SEM and the depth of etch pits was roughly estimated from the observation, figure 7(a). Figure 7(b) shows the SEM micrograph of the cross section of the etched nanocrystalline diamond after 90 min of annealing, observed by an EsB detector. The white spots correspond to Ni nanoparticles.

According to figure 7(a), etching proceeded rapidly within first 60 min, then slowed down, and eventually was saturated after 90 min of annealing. After 6 h of annealing, the mean depth was estimated to be about 520 nm. The observed reduction and saturation of the etching rate for long processing times could be explained by the increase in the distance from the top surface down to the metal nanoparticle. As the Ni nanoparticle moves deeper into the diamond, away from the source of molecular hydrogen, the carbon desorption from the nanoparticle becomes less effective, eventually leading to the saturation of the catalyst with carbon.

4. Conclusion

The careful study of the process parameters shows that nanopores can be formed in diamond, whatever its microstructure. The process requires a catalyst with high carbon solubility, such as nickel, in a hydrogen atmosphere at a temperature of 800–850°C. The etching process is stopped for catalyst particles located deep inside the crystal volume, probably because of a limited gas exchange between the surface and the particle, leading to carbon saturation. After optimization of the process parameters, nanopores as long as 600 nm were formed in nanocrystalline diamond, which will allow the fabrication of porous diamond membranes for chemical sensor applications.
Figure 7. (a) Variation of etch depth with annealing time measured for nanocrystalline diamond after 6 h of annealing with 3 nm Ni film, (800 °C, 60 Torr H$_2$). Bottom and top line of the box represent the 25th and 75th percentile of each data set. The band and square inside refer to the median and mean respectively; minimum and maximum values are indicated by the cross. Whiskers refer to mean ± standard deviation. After every 10 min the cross section of the etched sample was observed by SEM and pore depth was estimated roughly from the SEM image. Note that the Ni particles that were present on the diamond surface after annealing were excluded from the depth measurement. (b) Corresponding SEM image recorded by using an EsB detector after 90 min, revealing Ni nanoparticles embedded into the crystal volume.

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