Published in final edited form as:

Diam Relat Mater. 2011 February ; 20(2): 75–83. doi:10.1016/j.diamond.2010.11.003.

Improvements in the Formation of Boron-Doped Diamond Coatings on Platinum Wires Using the Novel Nucleation Process (NNP)

Mathew Phaner¹, Hong Zhao^{1,2}, Xiaochun Bian², James J. Galligan², and Greg M. Swain^{1,2}

¹Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322

²Department of Pharmacology and Toxicology, Michigan State University, East Lansing, MI 48824-1317

Abstract

In order to increase the initial nucleation density for the growth of boron-doped diamond on platinum wires, we employed the novel nucleation process (NNP) originally developed by Rotter et al. and discussed by others [1–3]. This pretreatment method involves (i) the initial formation of a thin carbon layer over the substrate followed by (ii) ultrasonic seeding of this “soft” carbon layer with nanoscale particles of diamond. This two-step pretreatment is followed by the deposition of boron-doped diamond by microwave plasma-assisted CVD. Both the diamond seed particles and sites on the carbon layer itself function as the initial nucleation zones for diamond growth from an H₂-rich source gas mixture. We report herein on the characterization of the pre-growth carbon layer formed on Pt as well as boron-doped films grown for 2, 4 and 6 h post NNP pretreatment. Results from scanning electron microscopy, Raman spectroscopy and electrochemical studies are reported. The NNP method increases the initial nucleation density on Pt and leads to the formation of a continuous diamond film in a shorter deposition time than is typical for wires pretreated by conventional ultrasonic seeding. The results indicate that the pregrowth layer itself consists of nanoscopic domains of diamond and functions well to enhance the initial nucleation of diamond without any diamond powder seeding.

Keywords

novel nucleation process; boron-doped diamond; microelectrodes; platinum wires and electrochemistry

Introduction

Our group has been utilizing diamond microelectrodes for *in vitro* electroanalytical measurements of neurosignaling molecules in the gastrointestinal tract [4–7] and vasculature [8–14]. These microelectrodes perform well in these measurements providing excellent response sensitivity, reproducibility and stability for several neurotransmitters: norepinephrine [8–14], serotonin [4,5,7] and nitric oxide [6]. They are prepared by coating sharpened Pt wires with a layer of boron-doped ultrananocrystalline diamond [10,13–15]. Pt

© 2010 Elsevier B.V. All rights reserved.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

is not typically used as a substrate for diamond growth, but it did receive significant attention back in the early 1990s when Tachibana et al. reported heteroepitaxial diamond growth on Pt (111) [16]. Our films are deposited on sharpened Pt wires (40 or 76 μm diam.) that are mounted horizontally in a conventional microwave CVD reactor (As Tex design). A challenge with coating Pt wires is the formation of a continuous diamond film over the wire surface in a short growth time. This is because the initial nucleation density on this material is quite low. Incompletely coated wires often result because of this low initial nucleation density even after pretreatment to enhance nucleation. For incompletely coated wires, solution can permeate the voids and cracks to contact the Pt. Since Pt exhibits a very distinctive voltammetric response, particularly in acid, it becomes straightforward to determine if the diamond film is continuously or discontinuously coated. In some electroanalytical measurements, exposed Pt would be undesirable for a number of reasons (*e.g.*, larger background current and reduced potential window). Therefore, a challenge with depositing diamond on Pt is proper pretreatment (*i.e.*, seeding) of the substrate.

Our past pretreatment protocol involved, first, (i) cleaning the wires ultrasonically in acetone followed by (ii) ultrasonic seeding of the cleaned wires in a nanodiamond powder (3–6 nm diam)/ethanol suspension. The latter step scratches and seeds the metal surface with diamond particles; both of which likely serve as the initial nucleation sites. The Pt metal is relatively hard though, so the embedded particle coverage after ultrasonic treatment is likely rather low and non-uniform. For this reason, the yield of completely coated wires after deposition times of up to 10 h can be less than 50%. An improved method for seeding the Pt wires is needed. This would increase the yield of fully coated wires during a deposition run and reduce the time needed to achieve complete coating.

Back in the mid 1990s, Rotter developed what has since become known as the novel nucleation process (NNP) [1–3]. NNP has been successfully used to pretreat a variety of substrate materials. The pretreatment involves the initial growth of an amorphous carbon layer on the substrate surface at elevated carbon levels (*e.g.*, 2–3% CH_4/H_2 source gas mixture). This is followed by ultrasonic seeding of the amorphous carbon-coated substrate in a nanodiamond powder/solvent suspension. The microstructure of the amorphous carbon layer is such that it can provide sites for the initial nucleation of diamond. Additionally, the “soft” texture of the layer allows for a relatively high number of diamond particles to be embedded during the seeding step. Clearly, the NNP is an attractive pretreatment for producing a high initial nucleation density on substrates for diamond growth.

We hypothesized that the NNP would be effective at increasing the initial nucleation density on the Pt wires; therefore, we conducted studies to evaluate its effectiveness in terms of improvements in film coverage and reductions in deposition time. The pre-growth carbon layer as well as the boron-doped diamond films were characterized by SEM, visible-Raman spectroscopy and electrochemical methods after deposition times of 2, 4 and 6 h. The results clearly demonstrate that the NNP is effective at increasing the initial nucleation density on Pt, leading to continuous films being formed in a shorter deposition time.

Experimental

Wire Preparation

Platinum wires (76 μm diam., Sigma Aldrich) were cut into 1.3-cm lengths. Each wire was then electrochemically etched in 1M KOH to form a conically-shaped tip. The etching was performed by lowering the end of a wire into the KOH solution and applying a 12 V AC relative to four carbon counter electrodes positioned equidistant from the Pt wire. The voltage was applied using a variable autotransformer (Staco Energy Products, Dayton, OH). The wire was etched until visible bubble evolution ceased (*ca.* 30 s). This process was then

applied to the other end of the wire. The sharpened wires were then ultrasonically cleaned in clean acetone for 30 min while suspended vertically in the solvent in order to avoid tip damage [10,13–15].

Pre-Growth Carbon Layer Formation and Diamond Deposition

The clean wires were then positioned horizontally on the reactor stage of a microwave CVD system (1.5 kW, formally AsTex Inc., now Seki Technotron, Japan). The wires were then exposed to a 2% CH₄/H₂ source gas mixture (4 sccm CH₄ and 196 sccm H₂) for 30 min at 600 W and 45 torr. The total gas flow was 200 sccm. At the end of this period, the plasma was extinguished and the wires were allowed to cool to room temperature under reduced pressure (no H₂ plasma cool down). The wires were then removed from the reactor and each one was seeded with nanoscale diamond particles by ultrasonication in a diamond powder (3–6 nm diam., Nanostructured and Amorphous Materials Inc., Los Alamos, NM)/ethanol suspension for 30 min. Each wire was suspended vertically during the seeding to avoid damage to the tip ends. This process embeds diamond particles into the relatively soft carbon layer and these particles, as well as sites on the carbon layer itself, serve as the initial nucleation zones for UNCD growth (see Figure 11).

Boron-Doped Diamond Film Growth

The seeded wires were placed back into the CVD reactor, mounted horizontally on the quartz stage and coated with boron-doped microcrystalline diamond. The diamond film was deposited from a 0.5% CH₄/H₂ source gas mixture with B₂H₆ added for boron-doping. The total gas flow was 200 sccm (197 sccm H₂, 1 sccm CH₄, 2 sccm B₂H₆). The microwave power and system pressure were 600 W and 45 torr, respectively. To study the effect of deposition time on the film properties, the wires were coated over the pregrowth carbon layer for 2-, 4- and 6-h periods. At the end of the deposition period, the CH₄ and B₂H₆ gas flows were stopped and the wires remained exposed to an H₂ plasma. Over a 30-min period, the plasma power and pressure were slowly reduced to cool the films to a temperature below *ca.* 400 °C in the presence of atomic hydrogen. The wires were then cooled to room temperature under reduced pressure prior to removal from the deposition chamber.

Raman Spectroscopy

Visible Raman spectroscopy was used to probe the film microstructure. Spectra were acquired at room temperature using a RAMAN 2000 spectrograph (Bruker Optics, Inc., Billerica, MA) that consisted of a diode pumped, frequency-doubled, continuous-wave Nd:YAG laser (500 mW at 532 nm, COHERENT), a Chromex 500 spectrometer (f/4, 600 grooves/mm holographic grating) and a thermoelectrically-cooled, 1024 × 256 element charge-coupled device (CCD) detector (ANDOR Tech., Ltd., South Windsor, CT). The spectrometer was calibrated (wavelength position) using 4-acetamidophenol (CH₃CONHC₆H₄OH) and a piece single crystal diamond grown by HPHT (first-order phonon position = 1332 cm⁻¹).

Scanning Electron Microscopy

Images of the film morphology were obtained using a JSM-6300F (field emission) scanning electron microscope (JEOL Ltd., Tokyo, Japan) housed at MSU's Center for Advanced Microscopy. The images were constructed from both secondary and backscattered electrons using an accelerating voltage of 10 kV.

Electrochemistry

Cyclic voltammetric measurements were made using a CHI650A potentiostat (CH Instruments, Austin, TX). Fe(CN)₆^{-3/-4} was a redox mediator employed to probe the

electrode activity. The analyte concentration was 100 μM and the supporting electrolyte was 1 M KCl. Measurements were made in a single-compartment glass cell with a platinum wire counter electrode and a no-leak Ag/AgCl reference electrode (EE009, Cypress Systems Inc., Chelmsford, MA) [17]. The diamond-coated wires were cut in half creating two electrodes from one substrate wire. Electrical connection was made to each by attaching a longer Cu wire to the uncoated portion of the Pt with silver epoxy. The contact was reinforced with super glue that was applied after the epoxy was fully cured. The microelectrode design is shown in Figure 1. No insulation was applied to these microelectrodes as is the normal protocol these days [7,10,13–15]. Prior to use, each electrode was cleaned by soaking in clean (distilled and stored over activated carbon) isopropyl alcohol for 30 min [18].

Results

Film Morphology

Figure 2A–C shows scanning electron micrographs of the pre-growth carbon layer on a sharpened Pt wire. The images presented in Figure 2A and B reveal that the cone tip is more or less continuously coated with a carbon film while the image in Figure 2C shows the side of the cone is only partially covered. This is a typical observation. The interesting finding is that at the 2% CH_4/H_2 source gas ratio used to deposit the pregrowth carbon layer in our CVD reactor, the carbon film is predominantly composed of nanoscopic crystals of diamond 100–500 nm in diameter. Higher magnification images of the (B) tip and (C) cone reveal the faceted nanocrystalline morphology. Raman spectroscopy (see Fig. 4) confirmed that the faceted particles are indeed diamond. The thickness of this layer is on the order of 1 μm , or so, based on cross sectional SEM image analysis (data not shown). In summary, three key findings are (i) diamond can readily nucleate on Pt as the pregrowth layer is essentially nanocrystalline diamond, and (ii) the pregrowth carbon layer thickness is near 1 μm on Pt instead of the typical 10's-nm thickness on other substrates as reported by Rotter [3], and (iii) the pregrowth carbon layer does not uniformly form over the Pt wire.

Figure 3A–C shows SEM images of wires coated with boron-doped diamond films grown over the pre-growth carbon layer for 2, 4 and 6-h periods. Figure 4A–C and 5A–C show higher magnification images of the tips and cones, respectively. Clearly, the diamond film is not continuous after the 2-h growth (Fig. 3A). The tip of the wire looks to be covered with a continuous faceted film (Fig. 4A), but the cone is only partially coated with diamond (Fig. 3A and 5A). The films deposited for 4- and 6-h do, however, appear continuous (Fig. 3C, 4C and 5C). Well faceted crystallites, micrometers in dimension, are seen for both films with a crystallite diameter that increases with growth time (Fig 5A–C). This is indicative of a van der Drift growth mechanism. The number of secondary growths appears to be minimal for these two films. The aspect ratio of the conically-shaped microelectrode is nicely visualized in Figure 3B, which reveals a tip diameter of 10 μm and a cone height of 115 μm .

Additional SEM images are presented in Figure 6A–D for the pre-growth carbon layer and diamond films grown over the pre-growth layer for 2-, 4- and 6- h periods of time. These provide additional evidence for the distinct morphological differences between the carbon coatings. Interestingly, the image for the pre-growth carbon layer (Fig. 6A) reveals a thick ($\sim 1 \mu\text{m}$), high surface area, and discontinuous coating.

Raman Spectroscopy

Figure 7A–D shows Raman spectra for the pre-growth carbon layer as well as for diamond films deposited over the pre-growth layer for 2-, 4- and 6-h periods. The spectrum for the pre-growth carbon layer looks like that typically seen for ultrananocrystalline diamond deposited from Arrich source gas mixtures (Fig. 7A) [19–24]. There are four peaks: a

relatively weak one at 1193 cm^{-1} , a strong one at 1333 cm^{-1} and moderately intense ones at 1493 and 1570 cm^{-1} . The peak at 1333 cm^{-1} is ascribed to the first-order phonon for cubic diamond. The full width at half maximum (FWHM) of this peak is 137 cm^{-1} . The large FWHM, compared to $2\text{--}4\text{ cm}^{-1}$ seen for single crystal diamond, indicates that carbon layer is nanocrystalline in morphology with a large number of phonon scattering centers, such as grain boundaries. This is completely consistent with the nanocrystalline morphology revealed in the SEM images. The peak at 1570 cm^{-1} is ascribed to the G-band well known for sp^2 -bonded carbon. This peak arises from the in-plane stretching modes of the sp^2 -bonded carbon in the grain boundaries of the nanocrystalline diamond and that comprise the pre-growth carbon layer. The peaks at 1193 and 1493 cm^{-1} are attributable to C–H bonds of the sp^2 -bonded carbon domains [19–24]. Birrell et al. showed that the intensity of these peaks correlates with the amounts of hydrogen using during the growth [21]. Furthermore, they showed that these peaks are absent in the spectrum using UV-Raman. The reduction in peak intensity with decreasing excitation wavelength is consistent with the assignment of these peaks to sp^2 carbon, although the exact nature of these bonds is yet unknown. Clearly, the pre-growth carbon layer is composed of small grains of diamond with a high volume of grain boundaries. The grain boundaries are composed of sp^2 -bonded carbon. Additionally, the presence of the 1570 cm^{-1} is consistent with the presence of a more amorphous sp^2 -bonded carbon layer at the interface between the Pt and the diamond nanocrystallites. For these reasons, the visible Raman spectrum is dominated by the scattering of sp^2 -bonded carbon as the scattering cross section is $50\times$ greater for sp^2 than for sp^3 -bonded carbon [25,26].

Spectra for the diamond films grown over the pre-growth layer are shown in Figure 7B–D. These spectra were recorded using a different integration time and spot size than were used to record Figure 7A so direct comparison so the spectral intensities is not possible. The spectra are all similarly shaped with an intense peak at 1333 cm^{-1} and a weaker but broad peak at 1560 cm^{-1} . The intensity of the diamond-phonon peak (1333 cm^{-1}) relative to the intensity of the sp^2 -bonded carbon peak (1560 cm^{-1}) increases with the deposition time. This is due to a thicker film with a larger crystallite size that results with increasing deposition time. The SEM images in Figure 3–5 reflect this.

Figure 8 shows a series of Raman spectra recorded along the length of a wire coated only with the pre-growth carbon layer. The spectra are quite similar in shape at the different wire positions. This suggests that the microstructure of the pre-growth carbon layer is uniform along the length of the wire. The intense diamond phonon peak is seen at 1332 cm^{-1} along with the broad scattering intensity in the $1500\text{--}1580\text{ cm}^{-1}$ region due to the sp^2 -bonded carbon that exists at the grain boundaries and the interface between the Pt and the diamond nanocrystals. The 1190 and 1490 cm^{-1} peaks are not as well resolved in these spectra as they are in Figure 7A.

Electrochemical Measurements

Figure 9 shows background cyclic voltammetric *i*-*E* curves for Pt wires coated with the pre-growth carbon layer (A) and with boron-doped diamond overlayers deposited for 2-, 4- and 6-h (B–D). The curves were all recorded at 100 mV/s in 1M KCl . Importantly, none of the curves shows any evidence for exposed Pt [15]. This observation is consistent with the void regions in the pre-growth layer (*i.e.*, regions where the diamond nanocrystallites do not exist, Figs. 3,4 and 6) consisting of a thin layer of amorphous sp^2 carbon. The curve for the wire with the pre-growth layer is featureless over the potential range, but the current is $10\text{--}50\times$ greater than the current for the diamond-coated wires (B–D). The large background current results from the (i) high surface area morphology of the pre-growth layer (see Figs. 2,3 and 6), (ii) the exposed amorphous sp^2 -bonded carbon, and (iii) the nanoscale roughness imparted to the wire during the formation of the pre-growth layer. The curves are featureless

within the potential range with no evidence for any electroactive surface carbon-oxygen functional groups [27–30]. There was no B₂H₆ added intentionally during the formation of the pre-growth carbon layer; however, the carbon possesses good electrical conductivity as evidenced by the flat, relatively symmetric *i*–*E* curve around the zero-current line. Films with significant ohmic resistance exhibit sloped and asymmetric voltammetric *i*–*E* curves about the zero current line. The electrical conductivity presumably arises from the sp² carbon domains in the grain boundaries as well as from some adventitious boron-doping from residual boron contamination in the reactor. It should be noted that the reactor used for coating the pre-growth carbon layer is routinely used for depositing boron-doped diamond films.

The background voltammetric *i*–*E* curves for the Pt wires after 2-, 4- and 6-h diamond growths all have much lower background currents than the wire coated with just the pre-growth carbon layer, for the reasons mentioned above. The curve for the 2-h film is somewhat sloped about the zero-current line consistent with there being some ohmic resistance within the film or between the film and the Pt. After the 4- and 6-h growths, the electrical resistance decreases as the curves become more symmetric about the zero-current line. The curves are largely featureless except for the anodic and cathodic peaks at ca. 0.8 V just prior to the onset of Cl₂ evolution. The faradaic reactions or surface processes responsible for these peaks are unknown; however, this curve shape is typical for diamond-coated Pt wires [10,13–15].

Figure 10 shows cyclic voltammetric *i*–*E* curves for the surface-sensitive redox mediator, Fe(CN)₆^{−3/−4}. Total current curves are shown as no background correction was applied. The currents for each of the microelectrodes cannot be directly compared because the area of each exposed to the solution was not controlled. Well defined oxidation and reduction peaks are seen for the pre-growth carbon electrode but they are somewhat buried within the large background current (Fig. 6A). The Δ*E*_p is 110 mV. By comparison, near-Nernstian behavior (Δ*E*_p = 60–70 mV) is typical for this redox system at clean glassy carbon and hydrogen-terminated diamond. Better defined redox peaks are seen for all three diamond-coated wires (Fig. 10B–D) as the background currents for each are substantially lower. The Δ*E*_p values are 90, 138 and 238 mV respectively, for the 2-, 4- and 6-h growths. Clearly, all the microelectrodes are responsive for the redox system. An interesting observation is the fact that Δ*E*_p (no iR correction) increases for the wires with increasing diamond deposition time (*i.e.*, more complete diamond coverage).

Discussion

Taken together, the results indicate that the novel nucleation process can be applied to Pt wires to enhance the initial nucleation density. Consistently (near 100 % success), continuous films were formed after 4–6 h on the NNP-treated wires as opposed to the normal 10-h depositions on the conventionally-seeded wires, which produces only about 50% fully coated wires. A key finding of this work is that diamond appears to readily nucleate on Pt; an observation that is consistent with that reported by Sakamoto et al. [31]. SEM and Raman data indicate that the pre-growth carbon layer, as grown using a 2% CH₄/H₂ gas mixture in our reactor, consists of 100–500 nm diameter, well faceted nanocrystals of diamond, as well as some sp²-bonded carbon. Although not presented herein, identical SEM, Raman and electrochemical data were found for diamond-coated wires (2, 4 and 6 h) without ultrasonic seeding of diamond seed particles. Therefore, it is understandable why the diamond overlayer readily forms on the pregrowth layer with or without any diamond powder seeding. This certainly simplifies the deposition as the wires never have to be removed from the reactor. Once the pregrowth layer is formed, the CH₄ and H₂ flows can be

adjusted to carry out the diamond deposition without ever extinguishing the plasma or removing the substrates. A diagram of the seeding and growth steps is shown in Figure 11.

There are three interesting observations to discuss. First, the evolution in the shapes of the background cyclic voltammetric *i*-*E* curves, as shown in Figure 9, is quite intriguing. The background current for the wire covered with only the pre-growth carbon layer is 10–50x greater across the potential range than is the background current for the 2-, 4- or 6-h diamond-coated wires. Even though the pre-growth carbon layer consists of nanocrystalline diamond particles, some of the exposed microstructure is a thin amorphous sp²-bonded carbon. Our attempts to visualize this amorphous carbon layer by SEM and TEM so have been unsuccessful. The background voltammetric *i*-*E* curves are quite sensitive to the presence of sp² and sp³ carbon [29,32,33]. The larger background results from two factors: (i) the high surface area of the pre-growth layer and the nanoscopic roughness imparted to the Pt wire during formation of the pre-growth layer; both of which lead to a electrode high surface area in contact with the supporting electrolyte, and (ii) the exposed amorphous sp² carbon. sp²-bonded carbon has a higher density of electronic states over the potential range (*i.e.*, higher C_{dl}) than does the diamond and there is often pseudocapacitance associated with redox-active and or ionizable surface carbon-oxygen functional groups [29,32,33].

Second, the diamond-coated wires, particularly the 4- and 6-h ones, have anomalous currents in the background voltammograms centered near 0.8 V. We have reported that the unusual currents are consistently present for boron-doped diamond films deposited on Pt [10,14,15]. They are, however, never seen for diamond films deposited on Si, for example. Therefore, the currents are somehow related to the Pt substrate. We previously proposed that the currents could be associated with the electrolysis of residuals from the polypropylene insulation [10,14,15]. The present wires were, however, not insulated so the currents cannot be due to the polymer. We also investigated the possibility that the currents are somehow associated with Pt nanoparticles that get incorporated near the film surface [34–36]. EDAX analysis and backscattered electron micrographs have revealed no presence of nanoscopic domains of Pt at the diamond film surface, where they could directly interact with the electrolyte solution. However, these measurements have indicated that the Pt is considerably roughened during the pre-growth carbon layer formation and that small domains of Pt are separated from the substrate and incorporated within the pre-growth carbon layer near the Pt/carbon interface. Therefore, the Pt is not directly contacting the electrolyte solution but it could be altering the electronic properties of the diamond overlayers. Even though, other researchers have demonstrated that diamond can nucleate directly on Pt, issues such as interfacial composition and roughening, Pt impurity incorporation within the diamond overlayer and the effect of these processed on the electrochemical properties of the diamond electrodes have not been addressed [16,31,37,38]. Future work will examine this issue more thoroughly.

Third, the cyclic voltammetric ΔE_p values for the Fe(CN)₆^{-3/-4} redox mediator progressively increase with increasing diamond deposition time. No studies were performed to determine if this is a reproducible trend; however, there are several possible reasons for the larger than expected ΔE_p values. One reason is the fact that the electron transfer for this redox systems is occurring at both the diamond and amorphous sp² carbon regions at the incompletely coated 2- and 4-h films. It could be that the amorphous carbon supports a higher rate of electron transfer than does the nanocrystalline diamond, so as the fraction of exposed amorphous carbon decreases, the overall kinetics decrease. The progressively increasing ΔE_p would be consistent with this.

The heterogeneous electron-transfer rate constant for Fe(CN)₆^{-3/-4} at carbon electrodes, including diamond, is extremely sensitive to the surface cleanliness and coverage of surface

carbon-oxygen functional groups [39–42]. For boron-doped diamond, the heterogeneous electron-transfer rate constant decreases (*i.e.*, ΔE_p increases) with increasing coverage of oxygen functional groups [39–42]. The increasing ΔE_p values could also be due to increasing surface oxygen coverage on the diamond films. No efforts were made to minimize the surface oxygen content.

Conclusions

The NNP is useful for enhancing the initial nucleation density for diamond deposition on Pt. Boron-doped microcrystalline diamond, deposited from H₂-rich source gas mixtures can readily nucleate on the Pt an on the pre-growth carbon layer with or without the any subsequent diamond powder seeding. This is because the pre-growth carbon layer consists of nanocrystals of diamond. Importantly, the application of the NNP increases the number of wires in a batch that get conformally coated with diamond. The nucleation density is increased with the pre-growth carbon layer and continuous films are achieved at reduced deposition times, as compared with the conventionally pretreated wires (simple ultrasonic seeding with diamond particles).

Research Highlights

- Nanocrystalline can readily nucleate on Pt, a unique feature of the metal.
- The pre-growth carbon layer (NNP layer) formed on Pt consists of nanocrystals of diamond mixed with amorphous sp² carbon.
- The pre-growth carbon layer functions to enhance the initial nucleation of microcrystalline diamond without any diamond powder seeding.
- The NNP method increases the initial nucleation density on Pt and leads to the formation of a continuous diamond film in a shorter deposition time than is typical for wires pretreated by conventional ultrasonic seeding.

Acknowledgments

This work was generously supported by the National Institutes of Health through the following grants: (R21 DK082967-AARA09; R21 HD056197 and P01 HL070687).

References

1. Field, JE. Properties of Natural and Synthetic Diamond. London: Academic Pres; 1992.
2. Derjaguin BV, Fedoshev DB, Lukyanovich VM, Spitsyn BV. J. Cryst. Growth. 1968; 2:380.
3. Rotter SZ, Madaleno JC. Chemical Vapor Deposition. 2009; 15:206.
4. Patel BA, Galligan JJ, Swain GM, Bian X. Neurogastroenterology & Motility. 2008; 20:1243. [PubMed: 18694441]
5. Bian X, Patel BA, Dai X, Galligan JJ, Swain GM. Gastroenterology. 2007; 132:2438. [PubMed: 17570217]
6. Patel BA, Galligan JJ, Swain GM, Bian XC. Neurogastroenterol Motil. 2008; 20:1243. [PubMed: 18694441]
7. Patel BA, Bian X, Quaiserova-Mocko V, Galligan JJ, Swain GM. Analyst. 2006; 131:41. [PubMed: 16365661]
8. Park J, Quaiserova-Mocko V, Patel BA, Novotny M, Liu A, Bian X, Galligan JJ, Swain GM. Analyst. 2008; 133:17. [PubMed: 18087609]
9. Park J, Galligan JJ, Fink GD, Swain GM. Autonom. Neurosci: Basic and Clinical. 2010; 152:11.
10. Dong H, Wang S, Liu A, Galligan JJ, Swain GM. J. Electroanal. Chem. 2009; 632:20.

11. Novotny M, Quaiserova-Mocko V, Wehrwein E, Kreulen DL, Swain GM. *J. Neurosci. Meth.* 2007; 163:52.
12. Park J, Galligan JJ, Fink GD, Swain GM. *J. Physiol.* 2007; 584.3:819. [PubMed: 17761778]
13. Park J, Galligan JJ, Fink GD, Swain GM. *Anal. Chem.* 2006; 78:6756. [PubMed: 17007494]
14. Park J, et al. *Diam. Rel. Mater.* 2006; 15:761.
15. Cvačka J, Quaiserova V, Park J, Show Y, Muck A Jr, Swain GM. *Anal. Chem.* 2003;2678. [PubMed: 12948136]
16. Tachibana T, Yokota Y, Miyata K, Onishi T. *Physical Review B.* 1997; 56:15967.
17. Granger MC, Witek M, Xu J, Wang J, Hupert M, Hanks A, Koppang MD, Butler JE, Lucazeau G, Mermoux M, Strojek JW, Swain GM. *Anal. Chem.* 2000; 72:3793. [PubMed: 10959965]
18. Ranganathan S, Kuo T-C, McCreery RL. *Anal. Chem.* 1999; 71:3574.
19. Ferrari, AC.; Robertson, J. *Nanostructured Carbon for Advanced Applications.* Amsterdam, The Netherlands: Kluwer Academic Publishers; 2001. p. 177
20. Ferrari AC, Robertson J. *Phys. Rev. B.* 2001; 63 121405-1.
21. Birrell J, Gerbi JE, Auciello O, Gibson JM, Johnson J, Carlisle JA. *Diam. Rel. Mater.* 2005; 14:86.
22. Wang S, Swope VM, Butler JE, Feygelson T, Swain GM. *Diam. Rel. Mater.* 2009; 18:669.
23. Hikavy A, Clauws P, Maes J, Moshchalkov VV, Butler JE, Feygelson T, Williams OA, Daenen M, Haenen K. *Physica Status Solidi a-Applications and Materials Science.* 2006; 203:3021.
24. Butler JE, Sumant AV. *Chem. Vap. Deposition.* 2008; 14:145.
25. Wagner J, Wild C, Koidl P. *Appl. Phys. Lett.* 1991; 59:779.
26. Knight DS, White WB. *J. Mater. Res.* 1989; 4:385.
27. Kinoshita K, Bett J. *Carbon.* 1973; 11:273.
28. Hu IF, Karweik DH, Kuwana T. *J. Electroanal. Chem.* 1985; 188:59.
29. Chen Q, Swain GM. *Langmuir.* 1998; 14:7017.
30. Kuo T-C, McCreery RL. *Anal. Chem.* 1999; 71:1553.
31. Sakamoto Y, Takaya M, Sugimura H, Takai O, Nakagiri N. *Diam. Rel. Mater.* 2009; 15:206.
32. Bennett JA, Wang J, Show Y, Swain GM. *J. Electrochem. Soc.* 2004; 151:E306.
33. Show Y, Swope VM, Swain GM. *Diam. Rel. Mater.* 2009; 18:1426.
34. Wang J, Swain GM, Tachibana T, Kobashi K. *Electrochem. Solid-State Lett.* 2000; 3:286.
35. Wang J, Swain GM. *Electrochem. Solid State Lett.* 2002; 5:E4.
36. Wang J, Swain GM. *J. Electrochem. Soc.* 2003; 149:E24.
37. Shintani Y. *J. Mater. Res.* 1996; 11:2953.
38. Tachibana T, Yokota Y, Nishimura K, Miyata K, Kobashi K, Shintani Y. *Diam. Rel. Mater.* 1996; 5:197.
39. Show Y, Witek MA, Sonthalia P, Swain GM. *Chem. Mater.* 2003; 15:879.
40. Granger MC, Swain GM. *J. Electrochem. Soc.* 1999; 146:4551.
41. Fischer A, Show Y, Swain GM. *Anal.Chem.* 2004; 76:2553. [PubMed: 15117197]
42. Yagi I, Notsu H, Kondo T, Tryk DA, Fujishima A. *J. Electroanal. Chem.* 1999; 473:173.

Figure 1.
Diagram of the diamond microelectrode architecture.

Figure 2. SEM images of the pre-growth carbon layer on an etched Pt wire. Images shown are for (A) the entire microelectrode and (B) the tip region and (C) the cone. The pre-growth carbon layer was deposited for 30 min using 2% CH_4/H_2 at 600 W and 45 torr.

Figure 3. SEM images of boron-doped diamond films grown over the pre-growth carbon layer for (A) 2-, (B) 4- and (C) 6-h. The diamond films were deposited using 0.5% CH₄/H₂ at 600 W and 45 torr.

Figure 4. SEM images of boron-doped diamond films grown over the pre-growth carbon layer for (A) 2-, (B) 4- and (C) 6-h. The images shown are for the tip region of each electrode. The diamond films were deposited using 0.5% CH_4/H_2 at 600 W and 45 torr.

Figure 5. SEM images of boron-doped diamond films grown over the pre-growth carbon layer for (A) 2-, (B) 4- and (C) 6-h. The images shown are for the cone region of each electrode. The diamond films were deposited using 0.5% CH_4/H_2 at 600 W and 45 torr.

Figure 6. SEM images of (A) the pre-growth carbon layer and boron-doped diamond films grown over the pre-growth carbon layer for (B) 2-, (C) 4- and (D) 6-h.

Figure 7. Visible Raman spectra for (A) the pre-growth carbon layer and boron-doped diamond films grown over the pre-growth carbon layer for (B) 2-, (C) 4- and (D) 6-h. Excitation = 532 nm. Integration time = 20 s.

Figure 8. Visible Raman spectra recorded at different points along a sharpened Pt wire coated with the pre-growth carbon layer.

Figure 9. Background cyclic voltammetric i - E curves for wires coated with (A) the pre-growth carbon layer, and boron-doped diamond for (B) 2-, (C) 4- and (D) 6-h. Electrolyte solution = 1 M KCl. Scan rate = 100 mV/s. Stable traces are shown for each electrode recorded after at least 10 cycles.

Figure 10.

Cyclic voltammetric *i-E* curves for 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at wires coated with (A) the pre-growth carbon layer, and boron-doped diamond for (B) 2-, (C) 4- and (D) 6-h. Electrolyte solution = 1 M KCl. Scan rate = 100 mV/s. Stable traces are shown for each electrode recorded after at least 10 cycles.

Figure 11.

Diagrams illustrating the steps involved in conventionally (top) seeding the Pt wires for diamond growth and the steps associated with the NNP pretreatment.