Electrochemical Modification of Boron-Doped Chemical Vapor Deposited Diamond Surfaces with Covalently Bonded Monolayers

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Electrochemical reduction of phenyl diazonium salts in acetonitrile at boron-doped diamond electrodes yielded covalent bonding of aromatic groups to the sp^3 carbon surface. Diamond surfaces modified with nitrophenyl, trifluoromethylphenyl, and nitroazobenzene showed strong X-ray photoelectron spectroscopy (XPS) signals for surface nitrogen or fluorine, which were stable to exposure to air or solvents. Raman spectra of chemisorbed nitroazobenzene on boron-doped diamond were obtained, and were similar to those observed for derivatized glassy carbon. Estimated surface coverages of 50-70% of a compact monolayer were calculated from XPS spectra, indicating that the coverage is too high to be attributed solely to modification of sp^2 carbon impurities or boron dopant. The high coverages of covalently bonded molecules on diamond achievable by diazonium reduction imply that a variety of surface functionalities may be introduced on the normally unreactive diamond surface.
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The combination of boron doping and chemical vapor deposition (CVD)[1] has permitted the examination of conducting diamond films for electrochemical applications.[2-10] With sufficiently high boron doping levels (>10^{19} cm^{-3}), the resistivity of CVD diamond decreases to <0.1 Ω cm, and the material may be used for electrochemical applications requiring low background current, wide potential window, and excellent stability. Doped diamond exhibits facile electron transfer to outer sphere redox systems such as $Fe(CN)_6^{-3/-4}$ and $Ru(NH_3)_6^{+3/+2}$, but slow electron transfer to systems which involve chemisorption, such as O_2 reduction and halide oxidation.[6,8,10]

Several attempts have been made to chemically modify diamond electrode surfaces, in order to introduce specific sites into an otherwise unreactive surface. One route is based on surface chlorination with photochemically generated chlorine atoms, followed by subsequent reaction with H_2O, NH_3, CHF_3, pyridine, etc.[12-18] The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and temperature programmed desorption, and showed quite low surface coverage (~1%) of modifier. Fluorinated diamond surfaces are stable even at relatively high temperature,[19-21] but the C-F bond is not amenable to further modification with more reactive species.

We report here a successful modification of boron-doped diamond by electrochemical generation of aryl radicals via a route previously applied to sp^2 carbon based materials and silicon.[22-28] The general approach of this method is electrochemical reduction of a diazonium ion to form an aryl radical and a nitrogen molecule, followed by covalent bonding of the radical to the electrode surface. On glassy carbon and graphite, the diazonium reduction has been shown to yield a stable, compact monolayer with high stability, and the electrochemical behavior of the surface was varied significantly by the identity of the derivatizing agent.[23,27-29] We demonstrate here the diazonium modification on a boron-doped diamond surface followed by characterization with XPS and Raman spectroscopy. To our knowledge, this is the first electrochemical derivatization of diamond surfaces and the first Raman spectroscopic measurement of a monolayer on diamond surfaces.

Experimental

The boron-doped CVD diamond films were grown on p-type Si(100) substrates with resistivity < 0.025 Ω cm using a previously reported procedure.[8] The typical resistivity of the diamond film was 0.068 Ω cm measured with a four-point probe. Following sonication in acetone, isopropyl alcohol, and acetonitrile in order for 10 min each, diamond samples were placed in a solution of 1 mM diazonium salt in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate. A potential of 0.4 V negative of the reduction peak potential of the diazonium ions was applied for 10 min. We use the term

"derivatized" to indicate a surface which has undergone electrochemical reduction in diazonium solution. To produce a "physisorbed" surface, the diamond samples were immersed in the same solution used for electrochemical modification for 10 min with the electrode at open circuit, then rinsed and sonicated in CH_3CN for 10 min. The samples were then rinsed again with acetonitrile and dried with argon for further measurements.

X-ray photoelectron spectra were acquired with a VG Scientific ESCALAB MKII spectrometer coupled with a Mg X-ray source aligned 45° to the sample while the detector was oriented along the surface normal. All atomic ratios were calculated from the ratio of the areas under the respective peaks, followed by correction with their sensitivity factors. The theoretical coverage for a close packed monolayer was estimated from the area of an edge-bonded phenyl ring, including the van der Waals radii of carbon and hydrogen,[30] divided into 1 cm^2. This estimate assumes perfect packing on a flat surface, and equals 670 pmol/cm^2. Correlation of the observed N/C atomic ratios from XPS with the surface coverage of modifier is complicated by uncertainties of sampling depth, carbon atom density on diamond and graphite surfaces, and the effect of the phenyl group carbons. For a given XPS sampling depth, the number of carbon atoms sampled is higher for diamond than for graphite. A conservative estimate of coverage is provided by the product of the observed N/C ratio and the carbon surface density for graphite (7.3 x 10^{-9} mol/cm^2). This estimate predicts that 670 pmol/cm^2 of nitrophenyl groups yields an observed N/C ratio of 9.2%, and the same coverage of nitroazobenzene yields 27.5% N/C. For the trifluoromethylphenyl monolayer, 670 pmol/cm^2 corresponds to a F/C ratio of 27.5%.

Raman spectra were taken with a 514.5 nm laser, a f/1.5 spectrograph (Kaiser, model HoloSpec f/1.8i) with a holographic grating in 180° backscattered geometry.[23] 4-(4-nitrophenylazo)aniline, 4-nitrobenzenediazonium tetrafluoroborate, and tetrabutylammonium tetrafluoroborate were obtained from Aldrich Chemical Co. The synthesis of 4-nitroazobenzene-4´-diazonium tetrafluoroborate (NABDS) is described elsewhere.[23,25]

Results and Discussion

The O/C ratio for unmodified diamond surfaces was 5.3 ± 0.9% (after sensitivity correction), somewhat lower than the 8-15% typically observed for polished glassy carbon[7,34] but higher than the 2-4% observed for other diamond samples.[8] XPS is less sensitive to boron (at 190 eV) than to carbon by a factor of about six, but in no case was a boron XPS signal observed. For all diamond samples examined, the XPS signal near 190 eV showed only noise. Figure 1 shows XPS spectra before and after electrochemical reduction of three diazonium ions and subsequent rinsing as described in the experimental section. Initial nitrogen coverage was negligible, while the nitrophenyl derivatized surface exhibited an 8.6 ± 0.4% N/C ratio (Table I). The N_{1s}
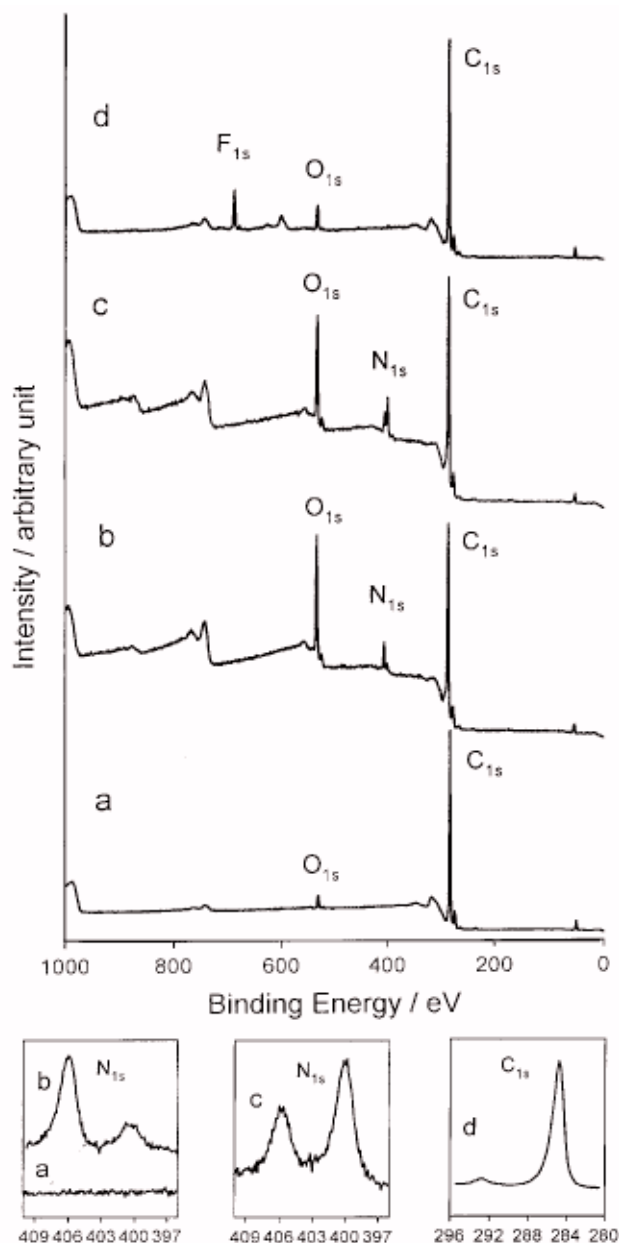
Figure 1. Survey XPS spectra of boron doped CVD diamond before and after electrochemical reduction in acetonitrile containing 0.1 M TBABF$_4$ and 1 mM diazonium ion. Insets show high resolution XPS scan of N$_{1s}$ and C$_{1s}$ regions. Spectrum a, boron-doped diamond surface; b, after 10 min electrochemical reduction in nitrophenyl diazonium solution at -0.6 V vs. Ag/Ag$^+$; c, fresh diamond electrode after 10 min in nitroazobenzene diazonium solution at -0.5 V vs. Ag/Ag$^+$; d, fresh diamond electrode after 10 min at -0.6 V vs. Ag/Ag$^+$ in trifluoromethyl phenyl diazonium solution.

Table I. XPS results for modified boron-doped diamond surfaces.

Sample[a]	N/C	F/C	O/C	Estimated coverage, (pmol cm^{-2})
Clean diamond	0	0	5.3 ± 0.9b	
Nitrophenyl				
derivatized[a]	8.6 ± 0.4[b,c]	0	20.1 ± 1.2[b]	470[c]
derivatized, then extensive sonication	8.6	0	20.7	470
physisorbed	0	0	8.4	0
Nitroazobenzene				
derivatized	14.9	0	17.0	363[d]
physisorbed	1.36	0	9.52	20[e]
Trifluoromethylphenyl				
derivatized nondegassed	0.9	5.6	5.9	136
derivatized degassed	0.8	14.3	5.1	347[f]
physisorbed	0	0	5.9	0

[a] "Derivatized" indicates potential was applied in diazonium solution. "Physisorbed" means the sample was immersed in diazonium solution at open circuit.
[b] Mean ± standard deviation for three to five determinations.
[c] 6.5% for 406 peak, 2.1% for 400 peak, coverage calculated from 406 eV peak.
[d] Coverage calculated from sum of 406 eV and 400 eV N$_{1s}$ peaks divided by 3.
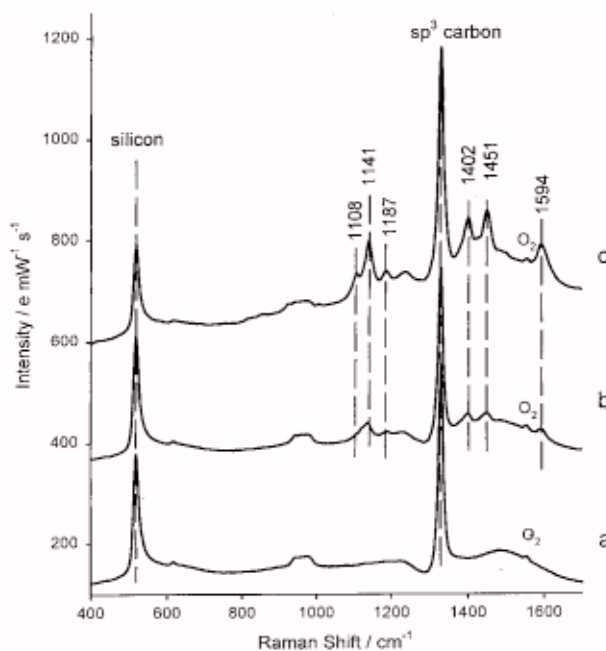[e] Coverage calculated from sum of 406 eV and 400 eV N$_{1s}$S peaks divided by 5.
[f] Calculated from F/C ratio divided by 3.

the observed N/C ratio. A physisorbed surface, prepared by exposing the diamond to the derivatization solution without an applied potential, showed negligible surface nitrogen, even when the nitrophenyl diazonium concentration was increased by 100 times.

XPS results for electrochemical reduction of nitroazobenzene diazonium salt (NABDS) and trifluoromethylphenyl diazonium (TFMB) are also shown in Fig. 1, and listed in Table I. NABDS showed some physisorption, and was not completely removed by acetonitrile sonication. The N$_{1s}$ region of diamond derivatized with nitroazobenzene showed both the NO$_2$ nitrogen (406 eV) and azo nitrogen (400 eV) with a total N/C ratio of 14.9% compared to 1.4% for physisorbed NABDS. For calculation of the surface coverages listed in Table I, the chemisorbed N/C ratio was divided by three (one nitro and two azo nitrogens), and the physisorbed N/C by five (one nitro and four azo nitrogens). The derivatization by trifluoromethylphenyl radical was found to be sensitive to oxygen, with higher coverage observed for argon saturated derivatization solution. The high resolution C$_{1s}$ spectrum of TFMB derivatized diamond shows a CF$_3$ carbon feature at 293 eV (Fig. 1d).

Previous reports from our laboratory have demonstrated the ability to obtain Raman spectra of a chemisorbed monolayer such as nitrophenyl on glassy carbon.[23,25] The nitrophenyl features were not observed by Raman on nitrophenyl/diamond surfaces because of a relatively large background. Nitroazobenzene (NAB) has a significantly larger cross section than nitrophenyl, and Raman spectra of the NAB on the derivatized surface were obtained. Figure 2a shows the initial diamond spectrum, plus that after physisorption of nitroazobenzene diazonium salt (spectrum 2b), and after electrochemical reduction (2c). The derivatized diamond has higher NAB intensity than the physisorbed surface, by a factor of ~3.2, after adjusting each spectrum for laser power and integration time. Subtraction of the substrate spectrum and close inspection reveals some qualitative differences between the chemisorbed and physisorbed spectra. The 1108 and 1141 cm^{-1} bands are resolved in the chemisorbed case, and the 1401 and 1451 cm^{-1} bands show different lineshapes upon diazonium derivatization. The NAB bands are similar to those observed on glassy carbon.[25]

With the exception of the nitroazobenzene case, the possibility that the observed XPS signal on derivatized diamond results from

region is magnified in the inset of Fig. 1, with the 406 eV peak attributable to NO$_2$ nitrogen. The ~400 eV N$_{1s}$ peak implies some reduced nitrogen (possibly from NO$_2$ group reduction) and has been observed for nitrophenyl derivatized glassy carbon.[22,23,28] Extensive sonication in acetonitrile (40 min) did not reduce the N/C ratio for the derivatized nitrophenyl/diamond surface. In addition, the derivatized nitrophenyl/diamond surface appeared to be stable in air, with no observable change in the XPS N/C ratio after 80 days of air exposure. The N/C ratio estimated for a monolayer of nitrophenyl groups is 9.2% (see Experimental section), so the observed ratio of 6.5% for the 406 eV nitro peak of the derivatized surface corresponds to approximately 70% of a close packed monolayer. Surface roughness will increase the coverage on a rough diamond surface, but will have little effect on

Figure 2. Raman spectra of (a) boron doped diamond before treatment, (b) after NABDS physisorption, and (c) after NAB derivatization. Power at sample was 5 mW, and 60 15 s integrations were averaged. Observed intensities were divided by laser power and integration time.

physisorption is clearly ruled out. The chemisorption resulting from electrochemical diazonium reduction is stable to solvent, while the physisorbed species are not. For the TFMB and nitrophenyl surfaces, the control experiment of exposure without reduction yields no observable surface coverage of fluorine or nitrogen. Nitroazobenzene diazonium ion does physisorb strongly enough to diamond to resist removal by acetonitrile, but the physisorbed concentration is significantly lower than that resulting from chemisorption. Based on the results in Table I, all three aryl radicals chemisorb to boron doped diamond at levels equal to a significant fraction of a monolayer. Based on the coverage calculated geometrically from the molecular dimensions, the coverages for chemisorbed nitrophenyl, TFMB, and nitroazobenzene are approximately 70, 52, and 54% of a compact monolayer, respectively.

Since CVD diamond contains a small amount of sp^2 carbon, the possibility that the aryl radicals bind to residual sp^2 carbon should be considered. Covalent bonding between the three radicals investigated and sp^2 carbon are well established,[23-27] and it is possible that the chemisorption observed for diamond is in fact occurring at such sp^2 impurities. However, Raman examinations of boron doped CVD diamond indicate that the sp^2 impurity level is low, equaling less than 1%.[8] Furthermore, the electrochemical behavior of boron doped diamond is qualitatively different from that of sp^2 carbon surfaces, by a variety of measures. Even if such sp^2 impurities were saturated with chemisorbed species, it is hard to envision an observed coverage of 50-70%. It does appear that the coverage on diamond is lower than that on GC, by 30-50%, but is much greater than predicted for chemisorption to sp^2 carbon impurities. It is remotely possible that sp^2 carbon impurities segregate on the diamond surface, thus leading to higher coverage from bonding to sp^2 carbon than expected from the bulk sp^2 carbon content. However, there is no evidence for such segregation of sp^2 carbon. A quite different possibility worth considering is binding of the aryl radical to boron sites rather than sp^3 carbon. Such sites would be too low in concentration (<1%) to account for the observed coverage (50-70%) unless the boron had somehow segregated onto the surface. If that were the case, the boron XPS signal would be visible in Fig. 1 (spectra b-d). The binding mechanism is currently under investigation, but presumably involves hydrogen abstraction from an sp^3 surface site followed by radical-radical coupling with a second aryl radical, as has been proposed for aryl radical binding to silicon[28] and hydrogenerated glassy carbon.[31]

Conclusion

Reduction of aromatic diazonium salts leads to a covalently bonded monolayer on boron-doped CVD diamond films. The surface layer was observed by XPS for nitrophenyl and trifluoromethylphenyl modified surfaces, and by XPS and Raman spectroscopy for the nitroazobenzene derivative. The coverage of chemisorbed species was approximately 50-70% of a monolayer, and was stable to solvent sonication and prolonged exposure to air. The coverages obtained with electrochemical derivatization are too high to be explained by bonding to sp^2 carbon or boron, and are much higher than the coverages observed following diamond derivatization by reactive plasmas, or photochemistry.[17-21] The possibility of introducing reactive sites into the diamond surface by electrochemical reduction is currently under investigation. The results reported here may provide a means to selectively enhance the reactivity of a normally unreactive diamond electrode surface.

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