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Photochemical Functionalization of Diamond Films

Todd Strother,[†] Tanya Knickerbocker,[†] John N. Russell, Jr.,[‡] James E. Butler,[‡] Lloyd M. Smith,[†] and Robert J. Hamers*,[†]

Department of Chemistry, 1101 University Avenue, University of Wisconsin, Madison, Wisconsin 53706-1396, and Chemistry Division, Naval Research Laboratory, Washington D.C. 20375-5342

We report a new scheme for attachment of functionalized organic molecules to polycrystalline diamond films. In this scheme, ultraviolet light is used to cause a local reaction between a hydrogen-terminated diamond surface and organic molecules present as a thin overlayer liquid film. Comparison of functionalized alkenes and alkanes shows that alkenes attach more efficiently. By attaching organic molecules with suitable protecting groups and then deprotecting after attachment to the surface, it is possible to prepare diamond surfaces terminated with carboxylic acid groups or with primary amine groups. These functional groups may serve as an attractive starting point for further chemical modification of diamond surfaces.

Recent developments in biotechnology and molecular electronics have fueled increased interest in chemical modification of surfaces. Modification of semiconductor materials, particularly silicon, has attracted widespread attention because of the importance of silicon in microelectronics. However, hydrolysis reactions may limit the overall stability of functionalized silicon surfaces in aqueous solutions.[1-5] Diamond has been widely studied because of its unusual electrical, thermal, and mechanical properties.[6] The high strength of C−C bonds and the well-established biocompatibility of diamond also make it a particularly attractive substrate for robust chemical and biochemical modification for sensor applications.[7-11]

Under ultrahigh vacuum conditions, hydrogen-free diamond[12] and silicon[13,14] surfaces are known to react with unsaturated C=C bonds of organic alkenes. Recent studies of silicon have shown that this idea can be extended to wet-chemical functionalization under ambient conditions by first passivating the Si surface with hydrogen[3,4] or iodine[15] and then locally initiating a self-terminating reaction with a superimposed thin layer of alkenes, producing a functionalized monolayer. In comparison, chemical modification of diamond under ambient conditions is much less advanced. Fluorine- and chlorine-terminated diamond surfaces have been prepared via photochemical modification of hydrogen-terminated diamond,[16] and the subsequent transformation to amines and thiol groups has been reported.[17] Organic layers have also been formed via the photochemical reaction of perfluorobutyl iodide multilayers with hydrogen-terminated diamond surfaces[18] and by the electrochemical reduction of phenyl diazonium salts on diamond electrodes.[19] However, there has not been a general method for attachment of organic molecules bearing specific reactive groups, such as primary amine groups or carboxylic acids, to diamond surfaces.

Here, we show that chemically modified diamond surfaces can be produced via ultraviolet irradiation of hydrogen-terminated diamond covered with liquid films of appropriate functionalized alkenes.

High-quality polycrystalline free-standing diamond films were deposited in a microwave plasma reactor using 1% CH_4 in H_2. The 1 mm thick films were cut into 5 mm × 10 mm samples, subjected to a series of acid baths to remove surface contaminants, and then heated at 800 °C in a 13.56 MHz inductively coupled hydrogen plasma (50 Torr H_2) for 1 h and cooled to 300 K before extinguishing the plasma.[20,21] Previous studies have established that this treatment removes sp^2 hybridized carbon from the surface, smoothing the crystal surface and terminating the surface with hydrogen.[20-25] The H-terminated samples were then placed in a nitrogen-purged Teflon reaction chamber. Chemical functionalization was accomplished

* Corresponding author. E-mail: rjhamers@facstaff.wisc.edu.
† University of Wisconsin.
‡ Naval Research Laboratory.

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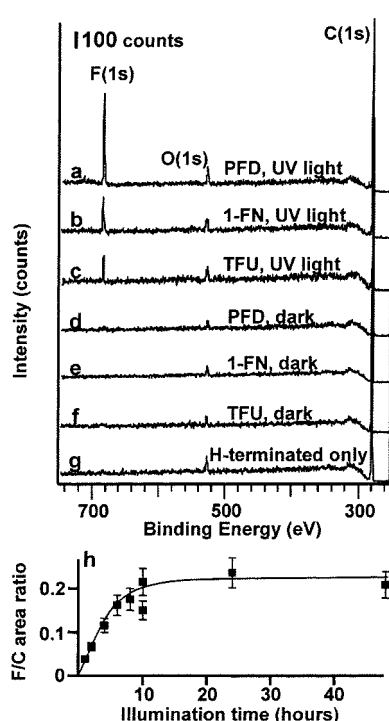(25) Küttel, O. M.; Diederich, L.; Schaller, E.; Carnal, O.; Schlapbach, L. *Surf. Sci.* **1995**, *337*, L812.

Figure 1. XPS survey spectra after hydrogen-terminated diamond samples were exposed to PFD (a), 1-FN (b), and TFU (c), with UV exposure for 2 h. Also shown are control experiments using the same molecules, but without exposure to light (d–f). For comparison, (g) shows the XPS spectrum of a freshly hydrogen-terminated diamond surface. In each spectrum, the C(1s) signal has been normalized to a total intensity of 1000, to facilitate comparison of the spectra. The plot in (h) shows the F(1s) signal as a function of illumination time for TFU.

by placing a small volume of long-chain organic compound on each sample to form a thin liquid film over the entire surface, sealing the chamber with a quartz window, and then irradiating with UV light from a low-pressure mercury vapor quartz grid lamp (254 nm) under dry nitrogen. Experiments were conducted over a range of exposure times; most samples reported here were characterized after 2 h of illumination.

The extent of reaction was monitored using an ultrahigh vacuum X-ray photoelectron spectroscopy (XPS) system ($P < 6 \times 10^{-10}$ Torr) with a monochromatized Al Kα source (1486.6 eV). The bulk diamond C(1s) peak at 284.5 eV binding energy was used as an internal standard. The experiments reported here were performed using molecules containing one or more fluorine atoms, because the F(1s) line is a convenient marker in XPS; however, other experiments on nonfluorinated molecules indicate that similar reactions occur with nonfluorinated compounds. The fluorinated alkene, perfluorodecene (3,3,4,4,5,5,6,6,-7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decene) (Aldrich), and a fluorinated alkane, 1-fluorononane (Aldrich), were purchased and used without further purification. The trifluoroethyl ester of ω-undecenoic acid (TFU), the trifluoroethyl ester of undecanoic acid (i.e., the saturated analogue of TFU), the trifluoroacetamide-protected 10-aminodec-1-ene (TFA-amine), and the *t*-BOC-protected 10-aminodec-1-ene (*t*-BOC amine) were synthesized and purified as described previously.[3,4] All reactants were stored over molecular sieves, purged with nitrogen before use, and applied to the hydrogen-terminated diamond as the pure liquids.

Figure 1 shows XPS survey spectra of hydrogen-terminated diamond surfaces that were exposed to per-fluorodecene (PFD), 1-fluorononane (1-FN), or TFU as

described above. For each molecule, Figure 1 shows results from two samples that were prepared identically, except that one sample was illuminated with UV light for 2 h while the other sample was kept in the dark. All samples were rinsed in chloroform and then in methanol (10 min each), before being introduced into the XPS system. Each of the three samples that were exposed to UV light shows a strong fluorine peak with a binding energy of 689 eV. In contrast, no fluorine signal is observed for the dark control experiments. From these experiments, we conclude that UV light initiates the attachment of each of the three molecules to the hydrogen-terminated diamond surface. While the results in Figure 1 suggest that there may be some attachment even in the absence of a C=C double bond, we directly compared the F(1s) signal from TFU with that from the trifluoroethyl ester of ω-undecanoic acid. These two molecules differ only in whether the terminal C–C bond is a single (alkane) bond or a double (alkene) bond. After identical attachment procedures, the ω-unsaturated molecule yielded a F(1s) signal ~10 times that of the corresponding saturated molecule. Since the alkene group significantly increases the attachment efficiency and is chemically isolated from other reactive groups of these molecules, we conclude that the C=C group is likely directly involved in attachment to the surface. While we do see some weak attachment for alkanes, the attachment efficiency of alkenes is always significantly higher.

Figure 1h shows the ratio of the area of the F(1s) XPS signal to that of the total C(1s) signal as a function of illumination time. The ratio of the F(1s) peak area to the C(1s) area reaches a limiting value of 0.22 at long times. When corrected for the different sensitivity factors[26] of C (0.30) and F (1.00) and the electron escape depth, this corresponds to a F coverage of ~0.3 monolayer, or approximately 1 TFU molecule per 10 C atoms at the surface. In contrast, a $C_{13}F_3$ polymer should yield a F(1s)/C(1s) area ratio of 0.8. Thus, the XPS data show that the F(1s) intensity is not consistent with the value expected from a polymerized film but *is* consistent with that expected from a monolayer of TFU molecules linked to the surface.

Thermal stability studies were conducted on TFU and the perfluorinated alkene. A comparison of the high-resolution spectra before and after heating to 200 °C for 15 min in the ultrahigh vacuum chamber showed no measurable change in the F(1s) and N(1s) experimental uncertainty of ~15%. Further heating to 400 °C for another 15 min again produced peaks that were, within statistical error, not different in area or width from those measured on the initial surface. Similar results were obtained on the perfluorinated alkene. This stability to heating is similar to that reported previously for perfluoroalkyl chains covalently bonded to diamond(110) surfaces[18] and, likewise, suggests that the layers produced here are also likely covalently linked to the surface.

Carboxylic acids and primary amines are particularly useful functional groups for further chemical attachment or modification beyond the first layer, such as attachment of biomolecules to the functionalized surfaces. In previous studies on silicon, we found that attempts to prepare surfaces terminated with carboxylic acid groups were hampered by the direct reaction of the carboxylic acid groups with the silicon surface but that acid-terminated surfaces could be prepared by first linking an ester to the

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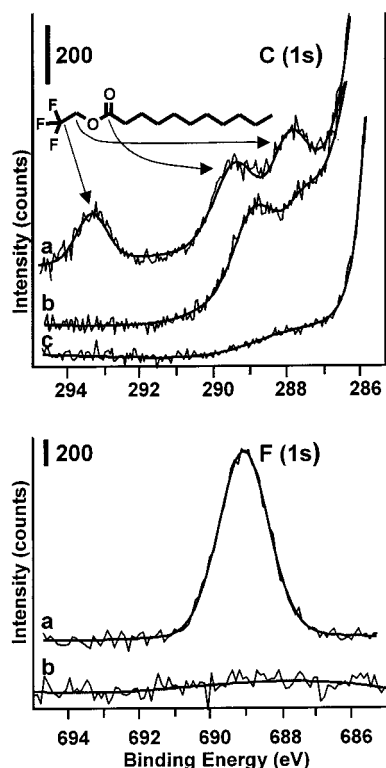
Figure 2. Carbon 1s (top panel) and fluorine 1s (bottom panel) XPS spectra of the trifluoroethyl ester of undecenoic acid (a) and the same surface after hydrolysis with potassium *tert*-butoxide (b). A carbon 1s spectrum of a freshly hydrogen-terminated diamond is included for comparison (c).

surface and then hydrolyzing the ester to the acid.[3] Figure 2 shows high-resolution XPS spectra of a H-terminated diamond sample after photochemical attachment of TFU (curve a, top and bottom panels) and the same sample after it was subsequently hydrolyzed in a 0.25 M solution of potassium *tert*-butoxide in DMSO (7 min) and then rinsed in 0.1 M HCl for 10 min and then deionized water for 5 min (curve b, top and bottom panels). For comparison, Figure 2 also shows (curve c, top panel only) the C(1s) XPS spectrum of a clean, H-terminated diamond surface that has not undergone any reaction. In the C(1s) spectra, the intense bulk C peak at 284.5 eV is not shown. After photochemical attachment of the TFU, the XPS spectrum shows new peaks at 287.8, 289.5, and 293.3 eV. Since fluorine is strongly electron-withdrawing, we attribute the peak at 293.3 eV to the C atom in the CF_3 group, the peak at 287.8 eV to the C atom of the ester CH_2, and the peak at 289.5 eV to the carbonyl (C=O) carbon atom.[3] Curves b in the top and bottom panels show the same sample after hydrolysis; the carbon XPS spectrum now shows only a single peak at 289.2 eV, which we attribute to the C atom in the carboxylic acid group. The effectiveness of the attachment and the subsequent deprotection are also shown in the F(1s) spectra (bottom panel). While the photoattached TFU shows a large, sharp F(1s) signal at 689.1 eV from the CF_3 group (curve a), after hydrolysis the F(1s) peak is completely gone (curve b). The loss of the F(1s) signal and the changes in the C(1s) spectrum both demonstrate nearly complete conversion of the ester group to the carboxylic acid.

Primary amine groups are also an attractive starting point for further chemical modification of diamond surfaces. Attempts to directly attach the ω-unsaturated aminoalkane (10-aminodec-1-ene) to diamond using the above method yielded XPS showing a very low density of amine groups on the surface. In previous studies on silicon,
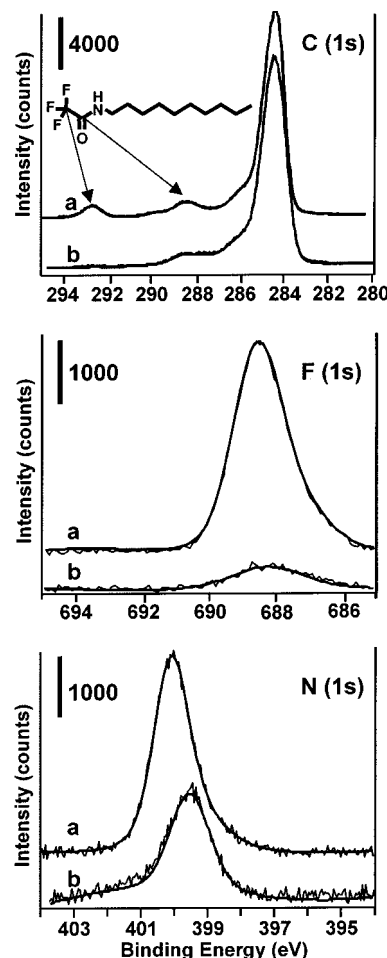

Figure 3. XPS spectra of a diamond sample after photochemical attachment of TFA-protected 10-aminodec-1-ene (curves a) and after deprotection (curves b). The top panel shows the C(1s) spectrum, while the middle and lower panels show the F(1s) and N(1s) spectra.

we found similar behavior, and we found that attaching a *protected* amine and then deprotecting led to improved amine termination.[4,5] Consequently, we prepared a modified 10-aminodec-1-ene in which the amine group was protected using the trifluoroacetyl (TFA) group. Figure 3 shows the carbon, fluorine, and nitrogen (1s) XPS spectra of a diamond sample that was photochemically bonded to TFA (curve a) and the same sample after deprotection (curves b) by refluxing in methanol/water (2:5 by volume) solution with 7% K_2CO_3 for 3.5 h.[27]

Immediately after attachment of the TFA-protected amine, the C(1s) spectrum shows peaks at 292.9 and 288.5 eV and the large bulk peak at 284.5 eV. The peaks at 292.9 and 288.5 eV are attributed to the carbon atoms in the CF_3 group and in the C=O group, respectively. The F(1s) spectrum shows a single, intense peak at 688.6 eV from the F atoms in the TFA protecting group, and the N(1s) spectrum shows a single peak at 400.1 eV from the protected amine group. After deprotection, the C(1s) spectrum shows only a broadened peak near 288.4 eV, the F(1s) spectrum shows nearly complete ($\sim$90%) loss of the fluorine atoms, and the N(1s) spectrum shows a slightly broadened peak centered at 399.6 eV, with a 40% decrease in area. Comparing the spectra before (curves a) and after (curves b) deprotection, the loss of the C(1s) peak at 292.9 eV and the F(1s) peak at 688.6 eV indicates that the TFA

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group is almost completely removed. However, the decrease in N(1s) intensity shows that the layer is also partially removed during the deprotection step. Initial experiments were also performed using amines protected with the *tert*-butoxycarbonyl (*t*-BOC) group. *t*-BOC-protected amines were successfully attached and deprotected. However, the initial attachment yielded a lower density of amine groups than TFA-protected amines, probably due to steric effects associated with the more bulky *t*-BOC group.

These experiments show that H-terminated diamond surfaces can be chemically modified through a UV-mediated reaction with functionalized alkenes. While the exact mechanism on diamond surfaces has not yet been determined, we note that recent studies of iodine-terminated Si surfaces have shown that photoattachment reactions can be initiated via photoexcitation of electrons and holes in the subsurface space-charge region, followed by nucleophilic attack by an alkene at the surface.[15] Although the bulk band gap of pure diamond (5.5 eV) is greater than the 4.9 eV energy of a 254-nm photon, synthetic diamond samples normally show strong absorption at wavelengths shorter than ~400 nm due to residual π-bonded carbon and to nitrogen impurities.[28]

The above results demonstrate that it is possible to prepare diamond surfaces terminated with organic molecules bearing primary amine groups and carboxylic acid groups. These functional groups are an attractive starting point for attachment of more complex molecules (such as DNA or proteins) to diamond surfaces. Diamond may prove to be a superior substrate for such attachment because the high strength of the C−C covalent linkage may make functionalized diamond surfaces more robust than those on alternative substrates such as silicon, gold, or glass.

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