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FLUOROALKYL IODIDE PHOTODECOMPOSITION ON DIAMOND (100) - AN EFFICIENT ROUTE TO THE FLUORINATION OF DIAMOND SURFACES

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ABSTRACT

The photodecomposition of CF_3I and C_4F_9I overlayers at 119 K on diamond (100) surfaces has been shown to be an efficient route to fluorination of the diamond surface. X-ray photoelectron spectroscopy (XPS) has been used for photoactivation as well as for studies of the following processes: the photodecomposition of the fluoroalkyl iodide molecules; the attachment of the photofragments to the diamond surface; and the thermal decomposition of the fluoroalkyl ligands. Chemisorbed CF_3 groups on diamond (100) decompose by 300 K whereas C_4F_9 groups decompose over the temperature range of 300 K to ~ 700 K. Both of these thermal decomposition processes produce surface C-F bonds on the diamond surface which thermally decompose over a wide temperature range extending up to 1500 K. Hydrogen passivation of the diamond surface is ineffective in preventing free radical attack from the photodissociated products of the fluoroalkyl iodides. The use of photoactivation of fluoroalkyl iodides for the fluorination of diamond surfaces provides a convenient route compared to other methods involving the direct production of atomic F, molecular fluorine, XeF_2, and F containing plasmas.

INTRODUCTION

Due to recent advances in the growth of high quality diamond films [1,2] and the unique physical properties of diamond [2,3], numerous applications of diamond films have been proposed [4]. For many of these applications, it would be desirable to functionalize the diamond surface with adsorbates. Unfortunately, the diamond surface is rather unreactive and to date, no one has been able to successfully anchor a long chain organic molecule directly to the surface of diamond [5].

One candidate for functionalization of the diamond surface is fluorine [6]. It has been demonstrated that strong C-F bonds [7] on diamond provide enhanced lubricity [8] and enhanced stability with respect to oxidation at high temperatures [9]. Others have used F_2 [9], atomic F [10], XeF_2 [8,11], and fluorine-containing plasmas [12] to fluorinate the surface of diamond. These fluorination routes require handling corrosive gases under harsh conditions and therefore are not feasible for practical applications. In addition, the fluorine coverage obtained using these methods has been low (less than 1 surface F atom/surface diamond atom) [8-12].

In this report, we will show that perfluorinated alkyl iodides ($C_xF_{2x+1}I$) may be condensed onto a diamond (100) surface at ~ 119 K. Following X-ray irradiation and heating to ~ 300 K (to desorb the undecomposed molecular species), fluorination of the diamond surface is obtained. This method does not require handling of corrosive gases, is performed under ultra-high vacuum (UHV) conditions (chamber pressure < 1 x 10^{-10} Torr), and is feasible for practical applications. It will be shown that fluorination, via this route, is capable of depositing more than one F atom/surface diamond atom. Spectroscopic evidence is obtained for the successful anchoring of a long chain perfluoroalkyl ligand [$CF_3(CF_2)_3$-] to the diamond (100) surface. The thermal stability of the various fluorinated layers will be reported. A detailed account of this work is presented elsewhere [13,14].

EXPERIMENTAL

The preparation, mounting, heating (under UHV), and temperature measurements of the type II A natural diamond (100) crystals (6 mm x 6mm x 0.5 mm) are described in detail elsewhere [15,16]. Two W5%Re vs. W26%Re thermocouples were placed inside laser drilled

holes in opposing edges of the diamond (100) substrates. while a third thermocouple was spot welded to the side of the Mo can which contains a thermionic emitter and supports the diamond crystal [15.16]. By simultaneously monitoring all three thermocouples. we have been able to show that the temperature measured inside the diamond (100) crystal is accurate to within 15 K at ~1450 K, while the temperature of the Mo can is a few hundred degrees higher [15]. Upon insertion into the UHV chamber, the diamond crystals were conditioned using cycles of atomic D exposure and heating to 1450 K [16]. Failure to condition the diamond using this procedure resulted in X-ray photoelectron (XP) spectra which provided irreproducible values for both the C(1s) binding energy and peak full width at half maximum (FWHM) [16].

This work was performed in a UHV chamber which is described in detail elsewhere [16]. Accurate gas exposures were achieved using a beam doser [17] which had a square orifice (5 mm x 5 mm) which could be reproducibly positioned 4 mm from the front face of the diamond (100) single crystal. as shown in Figure 1. Using this geometry, the maximum pressure rise in the chamber during dosing was less than 8×10^{-10} Torr. The effusion rate for this doser was checked periodically (over a four year interval) and remained constant to within 3% [14]. A Leybold Heraeus dual X-ray anode was used for X-ray irradiation (Mg Kα. 1253.6 eV, 300 W) and XPS measurements. A Leybold Heraeus EA-11 pre-retarding hemispherical electron energy analyzer was used for XPS measurements.
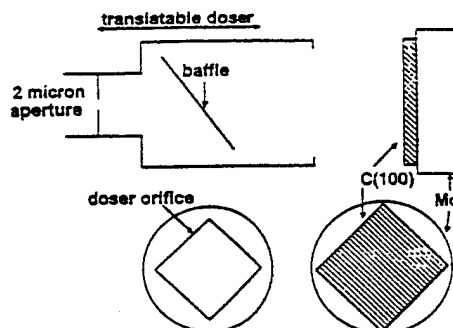

Figure 1. Gas doser used for adsorption onto the diamond (100) surface.

RESULTS AND DISCUSSION

Exposure of the diamond (100) surface to perfluorinated alkyl iodide species at a diamond surface temperature of 150 K < T < 900 K did not result in dissociative chemisorption. Condensation of the perfluorinated alkyl iodide onto the diamond (100) surface at 119 K, followed by heating to 300 K, also did not induce dissociative chemisorption. Dissociative chemisorption (fluorination) was only observed when the condensed perfluorinated alkyl iodide was X-ray irradiated at 119 K, then heated to 300 K to desorb the undecomposed species. Figure 2 illustrates that as the X-ray irradiation time is increased, the degree of fluorination increased. For each data point in Figure 2, a clean diamond surface was obtained. In order to reduce systematic errors, the data of Figure 2 were obtained in random order. The open data point was obtained with a -200 V bias on the diamond surface during X-ray irradiation and served as a control experiment which demonstrated that these effects were not induced by stray electrons originating in the X-ray source. For all of the experiments reported below. the C_4F_9I exposure was 5×10^{16} cm^{-2}, and the X-ray irradiation time was 180 minutes.

The top panel of Figure 3 shows XP spectra of the C(1s), I(3d) and F(1s) regions of a thick C_4F_9I layer condensed onto the clean diamond (100) surface at 119 K. The C(1s) emission from the diamond substrate at a binding energy of 284.0 eV is almost completely suppressed by the thick overlayer. Additional C(1s) features, corresponding to the CF_2 and CF_3 groups of the C_4F_9I molecule, are observed at 289.7 eV and 291.9 eV [12,18]. X-ray irradiation, followed by heating to 300 K to desorb the excess (non-dissociated) C_4F_9I, causes the C(1s) intensity from the diamond substrate to increase - as shown in the lower panel of Figure 3. The lower spectra of Figure 3 also reveal chemically bound surface I and F. C(1s) features corresponding to the CF_2 and CF_3 groups of adsorbed $CF_3(CF_2)_3-$ species on the diamond surface are observed. The ratio of C(1s) integrated intensities of these two features is 2.8 ± 0.1, as expected for the $CF_3(CF_2)_3-$ species if self-screening effects are essentially absent.
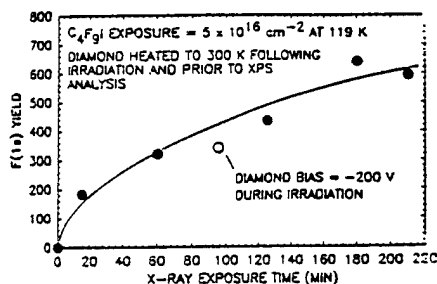
Figure 2. Plot of F(1s) yield as a function of X-ray exposure time for C_4F_9I on diamond (100) at 119 K.
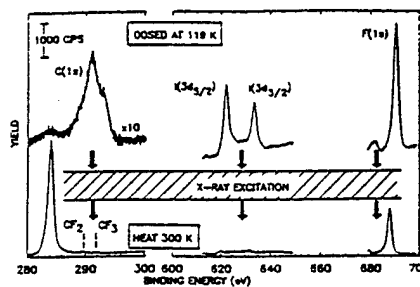

Figure 3. (Top): XP spectra of a C_4F_9I condensed overlayer on diamond (100). (Bottom): Following 180 minutes X-ray irradiation at 119 K and heating to 300 K to desorb excess C_4F_9I.

The thermal behavior of the anchored $CF_3(CF_2)_3-$ groups on the diamond surface is shown in Figure 4. Here, the crystal was momentarily heated to the various temperatures, then cooled to 300 K prior to XPS analysis. It may be seen that the ratio of the two C(1s) intensities remained approximately constant as the C_4F_9- groups on the diamond surface decomposed above 300 K.
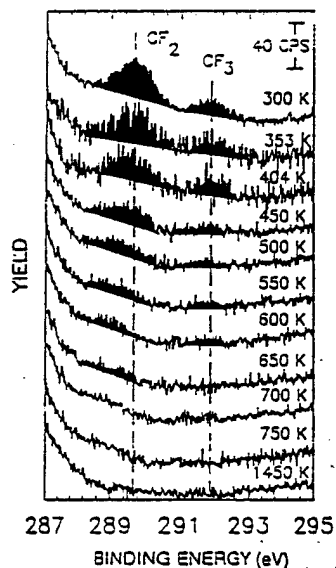

Figure 4. C(1s) XP spectra illustrating the thermal decomposition of CF_3 and CF_2 species of anchored $CF_3(CF_2)_3-$ groups on diamond (100).
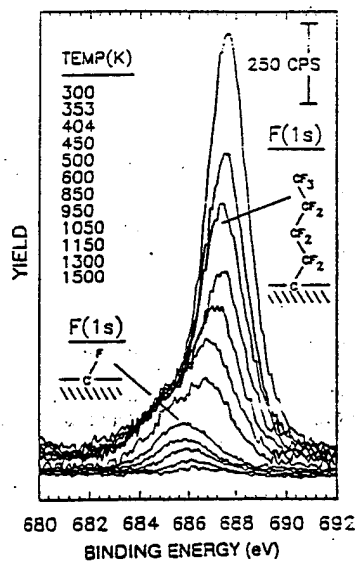

Figure 5. F(1s) XP spectra showing the thermal decomposition of anchored C_4F_9- groups which produces surface C-F groups which cover the diamond (100) surface.

The decomposition of the C_4F_9- groups on the diamond surface was also monitored via the thermal behavior of the F(1s) intensity, as shown in Figure 5. Figure 5 shows that two F(1s) features are observed. The first, at a binding energy of 687.6 eV, corresponds to the F(1s) emission characteristic of both the CF_2 and CF_3 groups of the anchored $CF_3(CF_2)_3$- species. Following heating to ~950 K, all evidence for these XPS features has disappeared and a F(1s) emission feature near 686 eV is observed, corresponding to F atoms bound directly to the diamond surface. Chemisorbed surface fluorine persists up to ~ 1500 K. Ab-initio theoretical calculations support the assignment of these two F(1s) XPS features [14].

Figure 6 is a plot of the diamond-C(1s), F(1s), and I(3d) XPS integrated intensities obtained at various heating temperatures. Here the initial desorption of non-decomposed molecular C_4F_9I is observed upon heating from 119 K to 300 K. Following heating to 350 K, surface I is no longer detected. The F(1s) integrated intensity decreases in two stages. The first stage of F(1s) integrated intensity depletion occurs, slowly, in the temperature range of 300 K to 900 K and correlates with the thermal decomposition of C_4F_9- surface species. The thermal decomposition of the C_4F_9- surface species produces surface C-F species which desorb from the diamond surface in the temperature range of 900 K to 1500 K (cf Figure 5).

Experiments were also performed using CF_3I as the fluorinating agent [14]. For CF_3I, C(1s) emission from CF_2 and CF_3 species were not detected using high S/N data acquisition. In addition, only a single F(1s) feature was observed at a binding energy of 686 eV, corresponding to F atoms bound directly to the diamond surface [14].
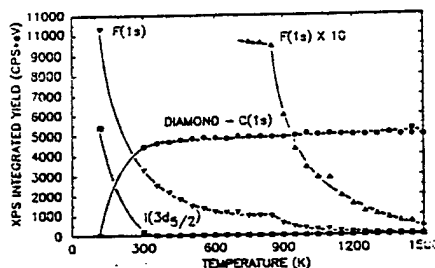

Figure 6. Thermal stability of C_4F_9I derived species on diamond (100).
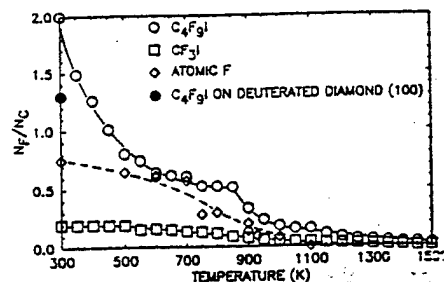
Figure 7. Comparison of the fluorine coverage and thermal stability of fluorine layers prepared via different routes.

The coverage of fluorine on diamond (100) was obtained using an electron mean free path of $\lambda = 14$ Å [19] for C(1s) electrons and XPS relative sensitivity factors of $S_C = 0.2$ and $S_F = 1.0$ [20]. For the anchored C_4F_9- layer produced by heating to 300 K, $N_F/N_C = 2.0$ (where N_F is the number of surface F atoms and N_C is the number of surface carbon atoms on the diamond surface). Following almost complete decomposition of the anchored C_4F_9- species, by heating to 700 K, $N_F/N_C = 0.6$. For similar experiments performed using CF_3I, $N_F/N_C \sim 0.2$ at 300 K. The use of a longer chain perfluoroalkyl iodide species therefore drives the fluorination of the diamond surface to higher levels.

In Figure 7 we plot the surface coverage of F , as a function of heating temperature, following fluorination of diamond (100) with C_4F_9I, CF_3I, and atomic F [10]. The atomic F results were obtained in another laboratory [10]. For saturation at 300 K, the surface coverage of atomic F was reported to be about 3/4 of a monolayer [10]. It is noted that the thermal stability of F is similar in all three cases, even though the atomic F work was performed on a diamond (100) surface which exhibited a (1x1) LEED pattern, indicating that the diamond surface was dihydride terminated [10].

The above experiments were performed on an atomically clean diamond surface in order to study the inherent reactivity of the diamond surface. However it is well known that natural

diamond surfaces are passivated by the presence of surface C-H bonds, and this passivation may be expected to make the method described above impractical in most technological cases. Recently, it has been shown that diamond films are monohydride terminated when removed from the growth chamber [21]. We therefore repeated the fluorination experiments on a deuterium passivated (monohydride) diamond (100) surface finding XPS evidence for the production of DI species at 119 K and for the subsequent fluorination of the diamond (100) surface [14]. Apparently, the free radical species produced by radiation induced decomposition of the C-I bond in C_4F_9I molecules are able to abstract D atoms from C-D bonds on the diamond surface leading to DI formation and fluorination of the diamond surface [14]. The surface F coverage for C_4F_9I on deuterium passivated diamond (100) following X-ray exposure and heating to 300 K is shown by the filled circle point in Figure 7. These observations indicate that the radiation-induced fluorination of technologically useful hydrogen-terminated diamond surfaces can be achieved by the methods described above.

The radiation-induced mechanism for the fluorination of diamond was not investigated. A variety of radiation-induced processes could be responsible, including direct photoionization by X-rays and electron stimulated dissociation due to secondary electron emission from the irradiated substrate [22]. We have shown (cf Figure 2) that stray electrons produced in the X-ray source are not responsible for this effect. It is well known that the weak C-I bond in C_4F_9I ($D^0 = 2.05$ eV) [7,23], can be easily photolyzed and this route is commonly used to induce free radical chemistry in homogeneous phases [24].

SUMMARY

We have developed a new method for the fluorination of diamond surfaces using radiation-induced activation of perfluoroalkyl iodide molecules adsorbed on the diamond surface. For C_4F_9I. C_4F_9- species are spectroscopically observed to anchor to the diamond surface and provide an easily controlled source of fluorine for the production of chemisorbed fluorine on the diamond surface. The thermal stability of the fluorinated diamond surface is high; chemisorbed surface F is still detected following heating to 1500 K for ~ 10 minutes. The presence of passivating surface C-H groups on the diamond does not inhibit fluorination by this method.

ACKNOWLEDGMENTS

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