

**Fluorination of the diamond surface by photoinduced dissociation of C<sub>60</sub>F<sub>48</sub>**K. J. Rietwyk,<sup>1</sup> M. Wanke,<sup>1</sup> H. M. Vulling,<sup>1</sup> M. T. Edmonds,<sup>1</sup> P. L. Sharp,<sup>2</sup> Y. Smets,<sup>1</sup> Q.-H. Wu,<sup>1</sup> A. Tadich,<sup>1,3</sup> S. Rubanov,<sup>4</sup> P. J. Moriarty,<sup>2</sup> L. Ley,<sup>5</sup> and C. I. Pakes<sup>1,\*</sup><sup>1</sup>*Department of Physics, La Trobe University, Victoria 3086, Australia*<sup>2</sup>*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*<sup>3</sup>*Australian Synchrotron, Clayton, Victoria 3168, Australia*<sup>4</sup>*Bio 21 Institute, University of Melbourne, Melbourne, Victoria 3010, Australia*<sup>5</sup>*Institut für Technische Physik, Universität Erlangen, Erwin-Rommel-strasse 1, 91058 Erlangen, Germany*

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The effect of synchrotron beam irradiation on C<sub>60</sub>F<sub>48</sub> adlayers absorbed on the hydrogen-terminated C(100) diamond surface has been examined using core level photoelectron spectroscopy. Irradiation causes the dissociation of fluorine from the C<sub>60</sub>F<sub>48</sub> and the formation of a fluorine-terminated surface with a (2×1) surface reconstruction. This is accompanied by a loss in the C<sub>60</sub>F<sub>48</sub>-induced surface transfer doping of the diamond substrate. The simplicity of this process makes it highly applicable to monofluoride surface patterning for nanoelectronic and surface functionalization applications of diamond.

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**I. INTRODUCTION**

The hydrogen-terminated surface of diamond has two unique properties not shared by any other semiconductor: an exceedingly high secondary-electron emission yield,<sup>1</sup> and a subsurface hole accumulation layer which gives rise to a *p*-type surface conductivity when the surface is exposed to air or fullerenes.<sup>2,3</sup> Both are due to the C<sup>δ−</sup>-H<sup>δ+</sup> surface dipole layer which lowers the vacuum level by up to 1.3 eV compared to the unterminated surface.<sup>4</sup> The result is a negative electron affinity (EA) which removes the energy barrier for electron emission and lowers the ionization potential sufficiently to allow the transfer of electrons from diamond to surface acceptors of suitably high EA. In contrast, the O- and F-terminated surfaces raise the intrinsically positive EA of diamond because they form dipoles of opposite sign. Hence, these surfaces do not give rise to *p*-type surface conductivity<sup>5,6</sup> and have a secondary-electron emission yield close to 1. Control of the surface termination can therefore be utilized to introduce contrasting surface electronic properties which can be of use, for example, in engineering Schottky barriers of different height with the same metal,<sup>5</sup> or defining nanometer-size conducting channels for a variety of applications.<sup>7</sup>

As an alternative to O termination, F termination may offer the same electronic properties with additional functionalities such as the possibility to prepare micropatterned arrays of DNA.<sup>8</sup> The carbon monofluoride is superhydrophobic and the strong C-F bonds yield enhanced stability under oxidizing conditions and at elevated temperatures. In addition, F-terminated diamond coatings are useful for low-friction tribological applications.<sup>9</sup> Methods of fluorination, based upon exposure of surfaces to elemental and molecular fluorine-based gases,<sup>10,11</sup> and plasmas<sup>8</sup> have been reported. Complications in processing and the aggressive nature of these surface treatments have so far limited their application to surface electronics. Fluorination of the diamond (100) surface via the irradiation of C<sub>4</sub>F<sub>9</sub>I has been demonstrated as an interesting alternative.<sup>9,12</sup> However, this process must be performed at cryogenic temperatures for which C<sub>4</sub>F<sub>9</sub>I condenses onto the surface. Here, we demonstrate that the photodissociation of C<sub>60</sub>F<sub>48</sub> adlayers on the H:C(100)-

2×1 diamond surface, via exposure to soft x-ray synchrotron radiation at room temperature, leads to the formation of a stable monofluoride-terminated surface. The method used is core level photoelectron spectroscopy (PES) using synchrotron radiation.

**II. EXPERIMENTAL DETAILS**

Experiments were performed using a synthetic, type-IIb, (100)-oriented diamond single crystal with a boron concentration in the range  $5 \times 10^{18} - 5 \times 10^{19} \text{ cm}^{-3}$ .<sup>13</sup> The sample was cleaned by boiling in acid (H<sub>2</sub>SO<sub>4</sub>/HClO<sub>4</sub>/HNO<sub>3</sub>; 1:1:1) in order to remove metallic contamination and nondiamond carbon phases. H termination was performed in a microwave H plasma at a sample temperature of 800 °C for 45 min. The sample was exposed to air before being transferred to ultrahigh vacuum (10<sup>−10</sup> mbar) at the soft x-ray spectroscopy beamline of the Australian Synchrotron, where subsequent processing and PES measurements were performed. The sample was mounted using Ta foil onto a Mo sample holder with an underlying heater for sample annealing. The sample temperature was determined by monitoring the temperature of the Ta foil using both an optical pyrometer and a thermocouple. The H-terminated surface of diamond is robust in air, with the exception of the formation of physisorbed hydrocarbon contamination, which was removed prior to the PES measurements by annealing in vacuum for 45 min at a temperature of 600 °C that is well below the hydrogen desorption temperature of about 1000 °C.<sup>14</sup> Subsequent low-energy electron diffraction (LEED) measurements revealed a clear (2×1) LEED pattern, as expected for the H:C(100)-2×1 surface.

PES data from the C 1s and F 1s core levels were obtained using photon energies  $\hbar\omega$  of 330 and 730 eV, respectively, to give high surface sensitivity with a detected electron kinetic energy of approximately 45 eV. The sample was oriented such that photoelectrons were collected at normal emission, at an angle of 57° with respect to the incident photon beam. The incident photon flux was approximately  $5 \times 10^{11}$  photons/s and the spectra were recorded with an overall energy resolution of approximately 0.1 and 0.3 eV at photon energies of 330

and 730 eV, respectively. The binding energies (BEs) of all spectra were calibrated using the Au  $4f_{7/2}$  core level at a BE of 84.0 eV observed for a freshly sputtered Au sample in electrical contact with the diamond.  $C_{60}F_{48}$  adlayers were deposited by sublimation from a quartz crucible at a deposition rate of 0.01 monolayer (ML)/minute determined using a quartz-crystal microbalance. Photoemission measurements were performed on the pristine H:C(100) surface and with  $C_{60}F_{48}$  coverages in the range 0 to 1.0 ML. Each spectrum took 150 s to collect, and 60 repeated spectra were recorded after each deposition to investigate the effect of beam irradiation. After the spectra for each coverage were taken, the sample was annealed at 550 °C for 30 min to remove the irradiated adlayer prior to a subsequent deposition. The sample was divided into four separate beam target regions, indicated in Fig. 4(a):  $R_1$ , from which all the PES data were obtained was exposed to the synchrotron beam for a total of 473 min;  $R_2$  and  $R_3$ , which were irradiated for only 13 and 25 min, respectively;  $R_4$  which was not exposed to the synchrotron beam. Secondary-electron emission (SEE) yield measurements of the four regions were carried out in a different vacuum system with a FEI Nova scanning electron microscope using 5 keV incident electrons. The SEE yield ( $\delta$ ) was determined by measuring the sample current, with an applied sample bias of +27 V ( $I^+$ ) and -27 V ( $I^-$ ), and an incident current ( $I$ ) of 82.6 pA, such that  $\delta = (I^- - I^+)/I$ .

### III. RESULTS AND DISCUSSION

A C 1s core level spectrum for the pristine H:C(100) surface is shown in the top trace (labeled I) in Fig. 1. The main contribution to this peak is the C 1s core level associated with the diamond bulk at a BE of 284.3 eV and a small component at a BE shifted by +0.35 eV, with respect to the diamond bulk component, which may be attributed to remaining hydrocarbon. There is no indication of a component on the lower-BE side of the bulk peak, which would be attributed to the free C(100) surface,<sup>14</sup> hence proving the complete

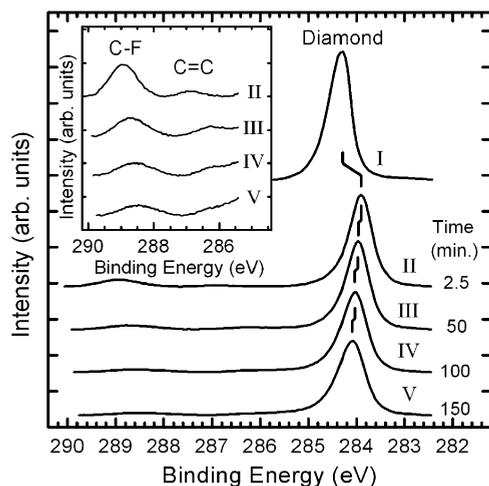


FIG. 1. C 1s core level ( $\hbar\omega = 330$  eV) of the H:C(100) surface before (I) and after adsorption of  $C_{60}F_{48}$  molecules with 0.1 ML coverage as a function of irradiation time (II–V). The inset shows the fluorofullerene peaks with  $\times 5$  magnification.

hydrogenation of the surface. In addition, the H-terminated surface was found to be robust against synchrotron beam irradiation for the exposure times used in this experiment. Figure 1 also shows a series of spectra (II–V) obtained following the deposition of  $C_{60}F_{48}$  with 0.1 ML coverage, illustrating the evolution of the C 1s features related to both the diamond surface and to the fluorofullerenes as a function of irradiation time. The fluorofullerene layer introduces two further C 1s lines positioned to the high-BE side of the diamond peak. These correspond to  $sp^2$ -hybridized carbon of the  $C_{60}$  cage with bonds to three neighboring carbon atoms (labeled C=C) and to  $C_{60}F_{48}$  carbon atoms bonded to fluorine (C-F).<sup>15</sup> They are separated by  $2.07 \pm 0.05$  eV. The  $C_{60}F_{48}$  adlayer induces a shift of  $-0.4$  eV in the position of the diamond peak (spectrum II), which is consistent with recent experiments reported elsewhere and signals an upward band bending due to surface transfer doping.<sup>16</sup> Exposure to synchrotron radiation has two effects on the spectra: a reduction in the shift of the diamond peak and a downward shift in BE of the peaks related to the fluorofullerene, accompanied by a decrease in intensity of the C-F peak and increase in the intensity of the C=C peak. The relative intensity of the two fluorofullerene components is related to the molecular stoichiometry, and the evolution of these peaks with irradiation time indicates that exposure to synchrotron radiation causes the dissociation of F atoms from  $C_{60}F_{48}$  to a form of  $C_{60}$  with a reduced degree of fluorination. The shift of the diamond peak to higher BE corresponds to a reduced band bending. The corresponding reduction in charge transfer could be due either to the reduced fluorination of the surface acceptors,<sup>17</sup> or to an increase in the diamond ionization energy on account of changes in surface termination. Measurements were performed with higher  $C_{60}F_{48}$  coverage to quantify which of these effects is dominant. Figure 2 shows a series of C 1s core level spectra for the same sample with a  $C_{60}F_{48}$  coverage of 1 ML. The

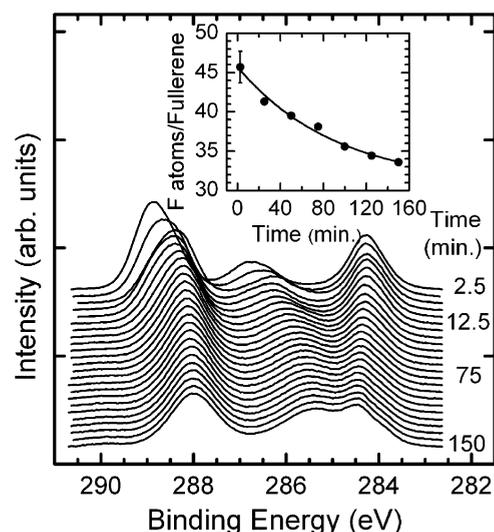


FIG. 2. Evolution of the C 1s core level spectra ( $\hbar\omega = 330$  eV) for a  $C_{60}F_{48}$  adlayer of 1 ML coverage. The inset indicates the variation in stoichiometry of the fluorofullerene with irradiation time. The line in the inset is a fit of the form  $F = F_0 + a \exp[-(t - t_0)/\tau]$ , where  $\tau = 93$  min and  $F_0 = 30.7$ .

peaks related to the fluorofullerenes were fitted and from the relative intensities the average number of fluorine atoms per molecule determined as a function of irradiation time, as shown in the inset, assuming the F atoms were removed isotropically from the  $C_{60}$  cage. For a total exposure time of 150 min the average number of F atoms per  $C_{60}$  molecule decreased from  $46 \pm 2$  to a level of  $34 \pm 2$ . The EA of the fluorofullerenes increases with fluorination, so that molecules with fewer F atoms are less effective as acceptors in the surface transfer doping of H-terminated diamond.<sup>17</sup> However, conductivity measurements performed by Strobel *et al.*,<sup>17</sup> with different fluorofullerene species suggest that an adlayer of  $C_{60}F_{36}$  with 1 ML coverage is sufficient to saturate the hole carrier density induced by transfer doping at a level comparable to that reached by  $C_{60}F_{48}$ ; it is therefore unlikely that the reduction in transferred charge is a direct consequence of the reduction in fluorination of the surface acceptors. We therefore look to the effect of the dissociated F atoms on the underlying surface.

Figure 3 shows a series of PE spectra obtained after annealing the sample to remove the irradiated adlayers. All C 1s components due to the fluorofullerenes initially at 286.96 and 289.03 eV BE are gone. A new C 1s peak, with a BE approximately at +2.3 eV with respect to the diamond bulk, grows in intensity with higher initial  $C_{60}F_{48}$  coverage. The chemical shift of this peak corresponds to the shift of +2.25 eV measured for the C-F bond in the form of a monofluoride on the diamond C(100) surface.<sup>12</sup> The diamond peak increases in BE with higher initial  $C_{60}F_{48}$  coverage, indicating downward band bending induced by the chemisorption of F to the surface, and broadens, presumably because the strong electronegativity of the surface fluorine causes small chemical shifts in the core levels of the near-surface carbon atoms. F 1s PE spectra, shown in the inset to Fig. 3, also indicate the formation of a monofluoride via the formation of a peak at 685.8 eV, in contrast to a peak at higher BE observed prior to annealing which is associated with the F atoms within the fluorofullerene. The structure of the photo-modified surface was investigated by LEED, revealing a  $(2 \times 1)$  pattern as expected for the diamond monofluoride surface. Photodissociated F atoms are likely to abstract H from the surface as hydrogen fluoride, allowing the attachment of chemisorbed F to form a fluorine-terminated diamond surface. The areal density of surface atoms on C(100) is  $1.57 \times 10^{15} \text{ cm}^{-2}$  and the density of molecules in an adlayer of  $C_{60}F_{48}$  with 1 ML coverage is approximately  $8 \times 10^{13} \text{ cm}^{-2}$ . During irradiation of the adlayer for 150 min approximately 14 F atoms are lost per molecule, giving  $1.1 \times 10^{15} \text{ cm}^{-2}$  F atoms for a 1 ML coverage of fluorofullerenes. However, for each F atom bonded to the surface, an extra F atom per site is required to break the C-H bond and form HF. This means that no more than 35% of a monolayer of C-H bonds can be replaced by C-F bonds for each ML of  $C_{60}F_{48}$ , suggesting that at least 3 ML of  $C_{60}F_{48}$  must be irradiated to fully fluorinate the C(100) surface. This has been verified with a second diamond sample, for which a series of  $C_{60}F_{48}$  adlayers each of 1 ML coverage were irradiated. After annealing the sample to remove each irradiated adlayer, C 1s core level spectra were obtained and the intensity of the monofluoride C 1s peak was monitored with respect to the diamond peak. The intensity of the monofluoride C 1s peak was found to become saturated for a total  $C_{60}F_{48}$  coverage of 3 ML.

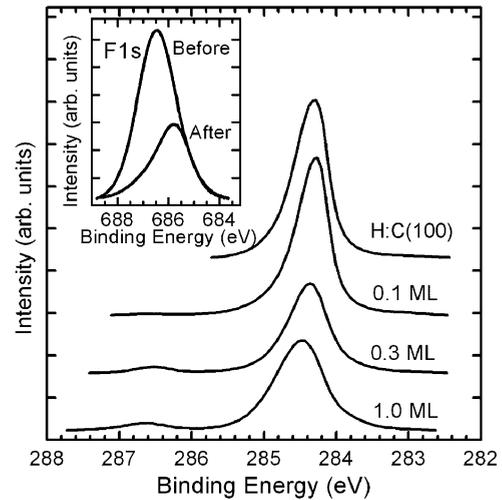


FIG. 3. C 1s spectra ( $\hbar\omega = 330$  eV) obtained after annealing to 550 °C to remove photo-modified fluorofullerene, showing the formation of a C-F feature as a function of coverage. Inset: F 1s core level spectra ( $\hbar\omega = 730$  eV) obtained for a 1 ML adlayer of  $C_{60}F_{48}$  before and after annealing at 550 °C.

F termination will increase the EA of the surface and this will increase the activation energy for surface charge transfer to the fluorofullerene acceptors, resulting in a reduced hole concentration and band bending. The fact that the diamond C 1s peak shifts to higher BE upon beam irradiation suggests that the F termination occurs already in the course of photoinduced dissociation and is not a consequence of a thermally activated process during the subsequent annealing step. A simple test of the change in EA and hence ionization potential through the replacement of C-H bonds by C-F bonds is based upon the SEE yield for the four regions of the sample referred to above. A scanning electron microscope (SEM) image of the photomodified sample is shown in Fig. 4(a). Region  $R_4$ , which was not exposed to the synchrotron beam, had the characteristic high SEE yield (13.5) of the diamond monohydride surface. The SEE yield measurements for regions  $R_1$ ,  $R_2$ , and  $R_3$  are illustrated as a function of the irradiation time in Fig. 4(b). The SEE yield is seen to decrease quickly with exposure to the synchrotron beam, suggesting a significant increase in the EA. The measured SEE yield for region  $R_1$  of close to unity is characteristic for a positive EA. However, prior to SEE measurement the sample was irradiated with an accumulated  $C_{60}F_{48}$  coverage of 1.4 ML, so that less than 50% of the surface would be expected to be fluorinated for region  $R_1$  and the question remains as to whether that coverage is indeed sufficient to achieve a positive EA as indicated by the SEE yield. To determine the fluorine coverage that is needed to drive the EA from negative to positive we have calculated the variation in EA with F and H coverage by extending a simple dipole model by Maier *et al.*<sup>5</sup> to include estimation of the C-F dipole moment. The surface charge transfer is estimated from the difference in electronegativity of F compared to H atoms, and the polarizability is taken to be that of the C-O bond. It is found that only 11% of a monolayer of C-H must be replaced with C-F to achieve a surface with positive EA, which is consistent with the SEE yield result.

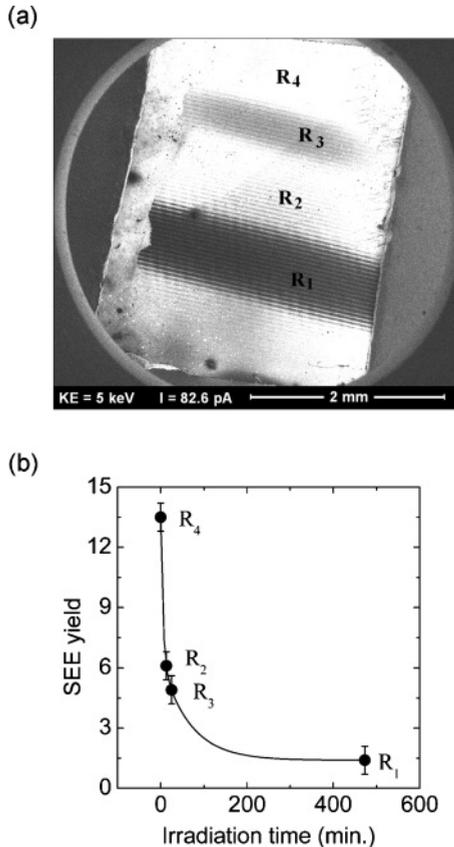


FIG. 4. (a) SEM image of the photomodified sample, illustrating pristine ( $R_1$ ) and irradiated ( $R_2$ ,  $R_3$ , and  $R_4$ ) regions from which SEE yield measurements were obtained. (b) Variation in SEE yield with irradiation time. The line in (b) is a fit of the form  $Y = Y_0 + a \exp[-(t - t_0)/\tau]$ , where  $\tau = 20$  min and  $Y_0 = 1.36$ .

Finally, we make a few remarks about the possible processes that might lead to the dissociation of fluorofullerenes. To this end we have performed damage studies at two photon energies, one (150 eV) below the C  $1s$  threshold and one (330 eV) above, for a  $C_{60}F_{48}$  adlayer of coverage about 0.7 ML on a freshly H-terminated C(100) sample. In both cases the dissociation was monitored from C  $1s$  spectra taken with a photon energy of 330 eV and the average number of fluorine atoms per molecule was determined as before from the relative intensities of the fitted fluorofullerene peaks. The resulting data, illustrated in Fig. 5, show that the same loss of F atoms requires five times the integrated photon flux at a photon energy of 150 eV compared to 330 eV, suggesting that the dissociation rate in the latter case is five times that at 150 eV. In order to put that result into perspective, we have to consider the possible pathways to dissociation of the fluorofullerenes. The first is by direct photoionization and subsequent decay of the ion into fragments. This process has been widely investigated for small molecules. For photoelectron energies well above threshold ( $\sim 45$  eV), photoionization leads with high probability to photofragmentation. The fragmentation yield of  $SF_6$ , for example, was measured to be close to 100% for photon energies of about 22 eV,<sup>18</sup> whereas it amounts to about 40% for  $Cl_2$  at a photon energy of 80 eV.<sup>19</sup> There are no comparable measurements for fluorofullerene available and we can only

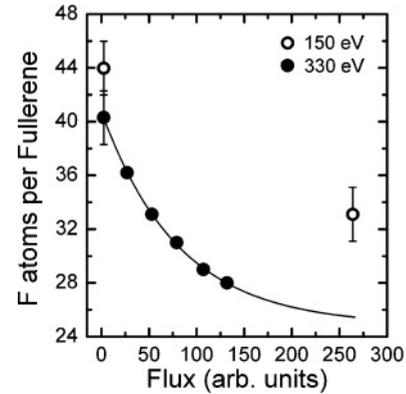


FIG. 5. The variation in stoichiometry of the fluorofullerene, with incident flux at  $\hbar\omega = 150$  eV (open symbols) and  $\hbar\omega = 330$  eV (closed symbols). All data are derived from fits of C  $1s$  core level spectra taken with  $\hbar\omega = 330$  eV. The line is a fit of the form  $F = F_0 + a \exp[-(x - x_0)/\tau_F]$ , where  $\tau_F = 81$  (1/flux) and  $F_0 = 25$ .

proceed by assuming that the fragmentation yield well above the photoionization threshold is high and energy independent. In that case, the fragmentation cross section should scale with the photoionization cross section because 150 and 330 eV are well above the ionization energy of fluorofullerene of 12 eV,<sup>20</sup> and the C  $1s$  ionization threshold at 285 eV, respectively. The relevant photoionisation cross sections for  $C_{60}F_{48}$ , calculated as the sums of atomic cross sections, are  $6.93 \times 10^{-17} \text{ cm}^{-2}$  for 150 eV and  $5.41 \times 10^{-17} \text{ cm}^{-2}$  for 330 eV.<sup>21</sup> Hence, the cross section is higher at photon energies below the C  $1s$  threshold. One would therefore expect a higher fragmentation rate at 150 eV with the current assumptions, which is contrary to the observation of Fig. 5, suggesting that another dissociation mechanism is operative here.

Since the fluorofullerenes are placed on H-terminated diamond, they are subject to an intense flux of low-energy electrons that emanate from the diamond surface with negative EA. The flux has its origin in the photoexcited primary electrons in diamond that after thermalization and multiplication by  $e-h$  excitation reach the surface and escape without barrier into vacuum. They have an energy distribution with a maximum at zero kinetic energy and a tail extending a few eV above. The number of primary electrons is again determined predominantly by the photoionization cross section of diamond. Here the values are  $0.22 \times 10^{-18} \text{ cm}^{-2}$  at 150 eV photon energy and  $0.76 \times 10^{-18} \text{ cm}^{-2}$  at 330 eV, i.e., a factor of approximately three times higher in the latter case. This ratio will not directly translate into an equal ratio for the flux of secondary electrons at the two photon energies because the multiplication factors, equal to the number of secondary electrons produced by each photoexcited electron, arising from the thermalization process are likely to be lower for a photon energy ( $\hbar\omega$ ) of 330 eV than for 150 eV. For  $\hbar\omega = 150$  eV the kinetic energy of the primary electrons is about 130 eV ( $\hbar\omega$  minus the binding energy of the valence band). For  $\hbar\omega = 330$  eV the primary electrons will have an energy of only 45 eV (330–285 eV) since the primary excitation is from the C  $1s$  core level. In addition, core level excitation results in the emission of an Auger electron of kinetic energy 270 eV. Multiplication

takes place by excitation of  $e-h$  pairs across the band gap of 5.5 eV in diamond. Hence, there are more opportunities the higher the primary (or Auger) electron energy is. At the energies discussed, the ratio of multiplication is larger in the case of  $\hbar\omega = 330$  eV by a factor that does not exceed 2 by consideration of the data of Shih *et al.*<sup>22</sup> Therefore, with all the inherent uncertainties in these estimates, taking into account the photoionization cross sections and the multiplication factor yields a secondary-electron flux ratio of about 6 in favor of 330 eV. This is consistent with the higher dissociation rate observed at  $\hbar\omega = 330$  eV.

There are two mechanisms active in freeing F atoms from fluorofullerenes by low-energy electrons. One is by electron-impact-induced ionization of fluorofullerenes with subsequent dissociation. While no data for the dissociation cross sections of fluorofullerenes by electron impact are available, the work of Ward *et al.* on CH<sub>4</sub> suggests that electron impact ionization even at 30 eV leads to dissociation efficiency of near 100%.<sup>23</sup> For the case at hand that would nevertheless require electrons in the high-energy tail of the secondary-electron distribution, where the electron flux is much smaller than for thermal energies. An alternative, second mechanism is the capture of thermal electrons by the fluorofullerene. On account of the high electron affinity of fluorofullerenes of 4.06 eV the capture of thermal electrons by fluorofullerenes is an efficient way to strip F atoms from C<sub>60</sub>F<sub>48</sub>, as was shown by Vasil'ev *et al.*<sup>24</sup>

Let us, finally, comment on the exponential photon flux dependence of the F removal as depicted in Fig. 5. Normally, such an exponential drop would correspond to a situation where F removal requires a certain species, C<sub>60</sub>F<sub>48</sub> in this case, that is depleted in the process, i.e.,  $dn_{C_{60}F_{48}}/dt = -n_{C_{60}F_{48}}R$ ,

where  $R$  is the rate of F removal. This situation holds here with the added complication that similar rate equations probably hold for the subfluorides C<sub>60</sub>F<sub>48-x</sub> as well with not necessarily the same rate constants. Another mechanism might be operative here. As explained above, the removal of F from C<sub>60</sub>F<sub>48</sub> is accompanied by a replacement of C-H by C-F bonds at the diamond surface. This leads to a local loss of negative EA and hence a decrease in secondary-electron yield as demonstrated in Fig. 4(b). As defluorination of C<sub>60</sub>F<sub>48</sub> progresses, the source of electrons for dissociation therefore diminishes. The secondary-electron yield is observed to drop exponentially with irradiation time [Fig. 4(b)] at a rate that is significantly faster than the corresponding rate of C<sub>60</sub>F<sub>48</sub> dissociation (Fig. 2). Therefore, the decrease in SEE yield associated with the loss of negative EA would be expected at least to contribute to the reduction in C<sub>60</sub>F<sub>48</sub> dissociation.

In conclusion, the effect of synchrotron beam damage of C<sub>60</sub>F<sub>48</sub> adlayers on the H-terminated C(100) surface has been examined via PES. Irradiation causes the photodissociation of fluorofullerene and the formation of a F-terminated surface with a (2×1) surface reconstruction. The simplicity of this technique makes it highly applicable to surface patterning for surface electronic and functionalization applications.

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