JOURNAL OF
Materials
CHEMISTRY

Fluorination of polycrystalline diamond films and powders. An investigation using FTIR spectroscopy, SEM, energy-filtered TEM, XPS and fluorine-18 radiotracer methods†

Christopher P. Kealey,[a] Thomas M. Klapötke,[b] David W. McComb,*[a] Max I. Robertson[c] and John M. Winfield*[a]

[a]*Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ.*
E-mail: J.Winfield@chem.gla.ac.uk; Tel: 0141-330-5134; Fax: 0141-330-4888
[b]*Department of Chemistry, Ludwig-Maximilians University of Munich, D-81377 Munich, Germany*
[c]*Logitech Ltd., Erskine Ferry Rd., Old Kilpatrick, Glasgow, UK G60 5EU*

Received 21st August 2000, Accepted 14th December 2000
First published as an Advance Article on the web 5th February 2001

Polycrystalline diamond films and diamond powders, treated with elementary fluorine, chlorine trifluoride or anhydrous hydrogen fluoride under various conditions, have been examined using spectroscopic and microscopy techniques. Formation of C–F bonds occurs when F_2 or ClF_3 are used, the surface groups present being tentatively identified from XPS and FTIR measurements. Surprisingly, the interaction between HF and diamond is substantial and its extent has been quantified using fluorine-18 labelling. Hydrogen fluoride deposited on diamond is labile with respect to exchange with $H^{18}F$ and undergoes slow hydrolysis on exposure to moist air. This treatment, therefore, results in an unusual hydrophilic surface. In contrast, there is no observable [^{18}F] exchange between F-terminated diamond and HF.

Introduction

Following the classic studies of the fluorination of graphite made by N. Watanabe and his school,[2] fluorination of carbon elementary forms, including carbon black,[3] pitch,[4] carbon fibres,[5] diamond,[6] fullerenes,[7] and carbon nanotubes[8] has been extensively studied. Desirable properties of a fluorinated diamond surface from the standpoint of potential applications include its hydrophobic nature[6a,h] and its thermal and chemical stability in a corrosive environment.[6a] From investigations of single crystal diamond (100)[9] and (111) surfaces[10] using X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED), it has been concluded that fluorination of the surface is limited kinetically and that formation of a C–F surface monolayer is incomplete. There is no evidence for the sub-surface penetration of F atoms, which would be required to form the simplest etch product, difluorocarbene, CF_2.

Rather different results have been reported from the fluorination of diamond powders.[6d,e,11] Reactions between hydrogen- or oxygen-terminated diamond surfaces and F_2 or CF_4 plasma have been studied under various conditions. Analysis of the fluorine-treated surface was performed using diffuse reflectance Fourier transform IR spectroscopy (DRIFTS) and mass spectrometry to identify thermal desorption products. In the reaction of hydrogen-terminated diamond surfaces with F_2, complete replacement of hydrogen for fluorine was observed at a reaction temperature of 263 K. As the reaction temperature was gradually increased up to 773 K, at least three new vibrational spectroscopic bands were identified and assigned to CF, CF_2 and CF_3 functionalities. Further evidence to support the formation of highly fluorinated species was obtained by monitoring the sample weight as a function of reaction temperature. Weights were found to increase as the reaction temperature was increased, and, at 773 K, corresponded to a coverage of two or three fluorine atoms per carbon. Thermal desorption analysis above 873 K indicated desorption of HF and CF_3. Oxygen-terminated diamond powder was fluorinated less easily, presumably due to the greater carbon–oxygen bond strength. Although fluorination could be accomplished, traces of surface oxygen were still observed even after reaction at 773 K.

The work described here was undertaken to determine whether elementary difluorine or strongly oxidizing binary fluorides such as chlorine trifluoride could be used to etch polycrystalline diamond films, grown by chemical vapour deposition. These are used often as heat sinks in device manufacture. We have investigated the nature of the fluorinated surfaces so produced and find that they resemble the surfaces that result from fluorination of diamond powders. The lability of the surface fluorine has been investigated using the short-lived radioisotope fluorine-18 [$t_{1/2}=110$ min, $\beta^+(\gamma)$ emitter]. As expected, fluorinated diamond is inert to [^{18}F] exchange with $H^{18}F$ but, unexpectedly, there is a detectable interaction between HF and hydrogen- or oxygen-terminated diamond surfaces.

Experimental

Samples and reagents

All diamond samples were obtained from Logitech Ltd. Powders were available in a range of particle sizes but most work was performed with 1 μm material. Polycrystalline film samples (1 cm^3, grown by CVD) were unsupported. All samples were hydrogenated before use under flow conditions in a Monel tube reactor, the conditions being H_2 (99.9%), flow rate 30 $cm^3\ min^{-1}$ at 1173 K for 1 h. Oxygen-terminated samples were prepared by subsequent flow of O_2/Ar (20 : 80), flow rate 30 $cm^3\ min^{-1}$ at 673 K for 1 h. In all cases samples were allowed to cool to ambient temperature under gas flow

---

†For a preliminary account of this work see ref. 1.

DOI: 10.1039/b006800o

and were transferred to a glove box ($H_2O \leqslant 5$ ppm) in the sealed reactor.

Elementary fluorine (MG Gas Products), chlorine trifluoride (Fluorochem Ltd.) and anhydrous hydrogen fluoride (Air Products) were handled in Monel metal vacuum lines equipped with Monel vessels and Bourdon gauges (Heise, Budenberg or Air Products) for pressure measurements (± 1 Torr). Trace HF in F_2 and ClF_3 was removed by multiple exposures of aliquots to activated NaF *in vacuo*, its removal being monitored by IR spectroscopy.

Fluorination of diamond surfaces

A diamond sample (typically 1 cm^2 film or 1 g powder), previously hydrogenated or hydrogenated then oxygenated as described above, was loaded in the glove box into a Monel pressure vessel or tube reactor, in both cases equipped with Monel valves (Whitey). Following transfer to the Monel line and evacuation, the appropriate gas, F_2, ClF_3 or anhydrous HF, was admitted to give *ca.* 760 Torr and the mixture allowed to react at ambient temperature or at specific temperatures in the range 523–673 K for 24 h. The material volatile at room temperature after reaction was examined by FTIR spectroscopy using a Monel cell equipped with AgCl windows. Fluorinated samples were transferred to the glove box for subsequent examination.

[^{18}F] Measurements

Fluorine-18 was prepared at the John Mallard Scottish PET Centre, Aberdeen, by the nuclear reaction, ^{20}Ne (d,α) ^{18}F, and transported to Glasgow as an effectively 'no carrier added' aqueous fluoride anion solution (*ca.* 50 MBq). This material, diluted to 2–3 cm^3, was added to 40% aqueous HF (4 cm^3) and mixed with aqueous CsOH (Aldrich, 3 g in 10 cm^3 H_2O). The mixture was heated to dryness and the $Cs^{18}F$ obtained (*ca.* 3 g) was allowed to react with anhydrous HF (20 mmol) at 523 K for 45–60 min in a Monel metal bomb *in vacuo*. The specific count rate of each batch so prepared was determined by condensing an aliquot of $H^{18}F$ (usually 1.0 mmol) on to freshly dried CsF, contained in an FEP counting tube, equipped with a Monel stop-cock (Whitey), which fitted snugly into a NaI/Tl well scintillation counter equipped with a scalar ratemeter. The identity of [^{18}F] was confirmed by determination of its characteristic β^+ annihilation γ-ray spectrum. Counts were determined over a period of 1–2 h to ensure that reaction to give $CsHF_2$ was complete. Typical specific count rates were in the range 500–1000 count s^{-1} $mmol^{-1}$ to ensure that radiochemical errors were $<1\%$.

Pre-treated diamond powder (1 µm, 1.0 g) was loaded into a Monel pressure vessel in the glove box, transferred to the Monel line and $H^{18}F$ (3.5 mmol) added by vacuum distillation. Reaction was allowed to occur at ambient temperature or 573 K for 45 min; the components were separated and the diamond sample transferred to a FEP tube and counted for an appropriate time, normally 100 s, to accumulate 10^4 counts. Finally the sample was reweighed. In some experiments diamond samples, contained in FEP counting tubes equipped with Monel valves, were allowed to react with $H^{18}F$, then without exposure to air were treated with aliquots of non-active HF in order to determine the extent of exchange. In these experiments, the specific count rate of $H^{18}F$ was determined after exposure, and in some experiments the diamond samples were also counted. In all cases the usual corrections for background and [^{18}F] decay were applied.

Physical examination of diamond samples

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were collected using a Nicolet Magna 550 spectrometer with an MCT detector. Spectra were accumulated from 60 scans in the region 4000–400 cm^{-1}. B.E.T. areas of powder samples (0.1 g) were determined by N_2 adsorption using a Micromeritics Gemini 1275 instrument, samples being predried under N_2 flow at 383 K for 24 h. Barrett, Joyner and Halenda (BJH)[12] areas and pore volumes were also determined. Scanning electron microscopy (SEM) was used to examine surface morphology, before and after F_2 treatment. Samples were coated with gold and mounted on an Al stub using conductive carbon tape before examination in a Philips 515 SEM fitted with an energy-dispersive X-ray (EDX) spectrometer (Oxford Instruments). Energy-filtered transmission electron microscopy (EFTEM) was used to map sp^2- and sp^3-dominated regions in two diamond film samples, as-grown and after ClF_3 treatment at 623 K for 24 h. The samples were thinned to <0.1 µm by back ion-milling using a precision ion polishing system (PIPS). Images were collected using a field emission gun TEM (Philips CM20) equipped with a Gatan imaging filter. The microscope was operated at an accelerating voltage of 200 kV using a 100 µm condenser aperture and an energy slit width (ΔE) of 5 eV. The EFTEM maps were obtained using the standard three-window method[13] with the pre-edge windows centred at 250 and 270 eV and the post-edge windows at 284 and 303 eV for the sp^2 and sp^3 maps, respectively. Images were acquired from regions where the edge of grains, as well as grain boundaries within the film, were observed.

X-Ray photoelectron spectroscopy (XPS) was performed on two diamond film samples which had been fluorinated (F_2) for 24 h at ambient temperature or 523 K in a PTFE boat to minimise contamination with NiF_2. A hydrogenated film was used as a reference sample. Spectra were obtained on a UHV SEM system (VG HB100) equipped with an XPS facility using a Mg Kα X-ray source. Specimens were flash-coated with gold to prevent specimen charging and the Au $4f_{7/2}$ (83.8 eV) and $4f_{5/2}$ (87.5 eV) excitations were used for energy calibration. The raw data obtained were fitted (Origin, Microcal Software) to multiple Voigt functions, in accordance with other XPS studies of fluorinated carbon materials.[2c,3c,5b,14]

Results

IR spectroscopic studies

Exposure of hydrogen-terminated polycrystalline powders or films to elementary fluorine or chlorine trifluoride vapours at ambient temperature resulted in the formation of hydrogen fluoride as the only identified volatile product (Table 1). At 673 K, mixtures of fluorocarbons, identified by comparison of well resolved bands in the FTIR spectra with those of model compounds,[15–17] were also formed and, in the case of ClF_3, hydrogen chloride was a product. The facile replacement of surface hydrogen by fluorine has been noted previously.[6d,e,11]

Table 1 Volatile compounds identified after reactions between diamond and F_2 or ClF_3

Conditions[a]	Compounds identified[b]
Diamond powder + F_2 Ambient temperature	HF
Diamond powder + F_2 673 K	HF, CF_4, C_2F_6, CHF_3 (?)
Diamond film + F_2 Ambient temperature	HF
Diamond film + F_2 673 K	HF, CF_4, C_nF_{2n+2} ($n = 2$–5), C_2F_4 (?)
Diamond powder + ClF_3 Ambient temperature	HF
Diamond powder + ClF_3 673 K	HF, HCl, CF_4, C_2F_6, $C_2Cl_{6-n}F_n$ (?)

[a] Samples were hydrogenated prior to reaction. [b] By FTIR; spectra compared with those of known compounds.

Table 2 Surface areas, pore characteristics and DRIFTS of pre-treated diamond powders

Pre-treatment	BET area/m^2 g^{-1}	BJH area/m^2 g^{-1}	Desorption volume[a]/cm^3 g^{-1}	Ave. pore diameter[b]/nm	ν_{max}/cm^{-1}	Band assignment
Hydrogenated	13.0[c]	6.4[c]	0.025[c]	15.6[c]	2937	ν(CH)
					2860	ν(CH)
					2837	ν(CH)
Oxygenated	14.3[c]	[d]	[d]	[d]	3453	ν(OH)
					1774	ν(CO)
					1645	δ(OH)
					1128	ν(CO)
Fluorinated	10.2[c]	12.8[c]	0.065[c]	20.2[c]	1358	ν(CF)
					1260	ν(CF)
					1090	ν(CF)

[a]Cumulative desorption volume of pores between 1.7 and 300 nm diameter. [b]BJH desorption average pore diameter. [c]Relative error < 5%. [d]Not determined.

Repeated exposures of H-terminated diamond powder to F_2 or ClF_3 at 673 K led to marked decreases in IR bands attributable to C_nF_{2n+2} compounds and no volatile products were detected after the third exposure. This was consistent with passivation of the powder surface by prolonged fluorination.

Surface areas and diffuse reflectance IR Fourier transform spectra (DRIFTS) of fluorinated, hydrogenated and oxygenated diamond powders are compared in Table 2. Fluorination had little effect on BET areas. Pore volume distributions obtained from BJH analyses[12] probably reflected the effect of inter-particle voids and the data were more consistent with irregular surfaces than with porous materials. There appeared to be a greater degree of irregularity in the fluorinated diamond surface (Table 2) which was not inconsistent with the evidence for etching of H-terminated diamond obtained from the FTIR spectra after reaction (Table 1). DRIFTS indicated that replacement of C–H by C–F at the surface was extensive after F_2 treatment at 673 K. Treatment of H-terminated diamond with dioxygen at 673 K also resulted in the apparent removal of C–H groups (Table 2).

Microscopy – SEM and EFTEM

Although fluorination of H-terminated films and powders led to the formation of small quantities of fluorocarbons, examination of the materials by scanning electron microscopy (SEM) before and after F_2 treatment indicated that no gross changes in surface morphology had occurred. SEM images acquired from three film samples, which had been hydrogenated at 1173 K or hydrogenated and then fluorinated with F_2 at room temperature or 673 K, are shown in Fig. 1. All samples were from the same parent film sample, so that any significant change in surface morphology as a result of reaction would be easily detectable. The polycrystalline nature of the diamond film is shown in Fig. 1(a); crystallites are orientated in various directions, which is presumably a result of random nucleation in the CVD growth process. Examination at higher magnification, Fig. 1(b), suggested that the surface could be described as a combination of {100}, {110} and {111} planes. There was no observable change in the gross surface morphology of the diamond film as a result of room temperature F_2 treatment; the crystallites were still faceted with defined crystal planes evident, Fig. 1(c). Nor was any change in surface morphology evident after F_2 treatment at 673 K, since the rough jagged surface was maintained and facets were clearly observed, Fig. 1(d). Despite the fact that the FTIR spectroscopic study showed that fluorocarbon etch products were formed following reaction at 673 K, there was no evidence in the SEM images for pitting or rounding of peaks as would be expected from an extensive etching reaction. In contrast, the reaction of polycrystalline diamond film with molecular oxygen at 723 K results in a severely pitted surface and the formation of the etch products CO and CO_2.[18]

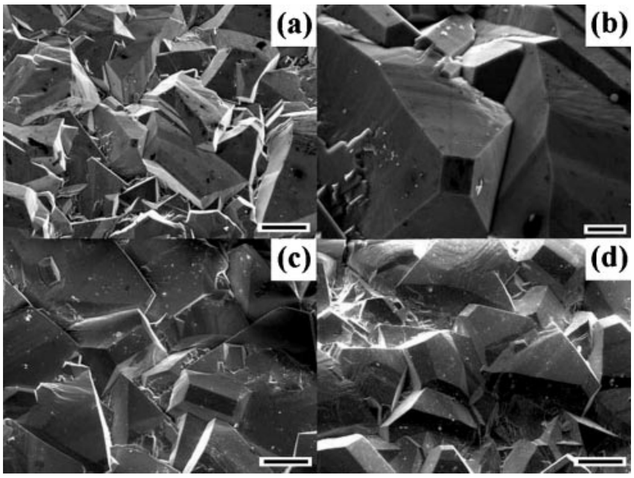

Fig. 1 SEM images showing the morphology of polycrystalline diamond films: (a) hydrogenated (scale bar = 50 µm), (b) hydrogenated, at higher magnification (scale bar = 10 µm), (c) after treatment with F_2 at ambient temperature (scale bar = 50 µm), (d) after treatment with F_2 at 673 K (scale bar = 50 µm).

Although the morphology of the diamond surface following fluorine treatment was apparently unchanged, the SEM investigations provided some evidence for a change in the chemical nature of the surface. After treatment the samples appeared to be susceptible to electron beam damage. It appeared that a surface layer could be modified or removed by increasing the electron dose in small regions. The identity of this surface layer could not be determined; however, it was possible that the electron beam was responsible for the removal of fluorine atoms and/or fluorocarbon species.

SEM examination of diamond powder samples, which were taken from a single batch and given identical treatments to the films, yielded similar results to those described above. The images revealed the presence of non-spherical particles that showed evidence of facets, although the facets were less well defined than on the film samples. The morphology of the powder was essentially the same before and after the fluorination treatments. Hence the SEM results indicate that, in all cases examined, an extensive etching reaction involving F_2 did not occur.

On occasion, debris was observed on the fluorinated film surfaces and was shown by EDX analysis to contain Ni and F. This observation suggested that NiF_2 had been formed by fluorination of the Ni sample boat. Using a PTFE sample boat and coating the inner surface of the reactor with a PTFE spray eliminated this problem.

The energy-filtered transmission electron microscopy (EFTEM) investigations provided more detailed information relating to the effects of fluorination of a polycrystalline diamond film. EFTEM is based on electron energy-loss spectroscopy (EELS), a technique for analysing inelastic interactions between the fast imaging electrons in the TEM

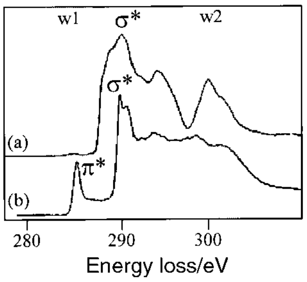

Fig. 2 Electron energy-loss spectra of (a) diamond and (b) graphite. A peak due to the 1s→σ* transition (*ca.* 290 eV) is present in both spectra. The presence of sp^2 hybridised carbon atoms in graphite results in the creation of an antibonding π* energy level, and hence an extra peak due to the 1s→π* transition (286 eV) is observed in the spectrum of graphite. The energy windows, w1 and w2, correspond to those used to form maps of the sp^2 and sp^3 bonding, respectively.

and the specimen. The fast electron can lose energy by exciting electrons from occupied to unoccupied energy levels in the specimen. The quantity of energy lost is element-specific. In this work the excitation of interest is associated with transitions from the carbon 1s core level to the symmetry-allowed p-like conduction band states and is described as a carbon K-edge. Since the distribution of unoccupied energy levels, *i.e.* the density of states (DOS), is sensitive to the local bonding environment of the excited atom, the shape of the carbon K-edge provides information on the local chemistry. To illustrate this effect, the carbon K-edges of diamond and graphite are displayed in Fig. 2. Both spectra exhibit a strong peak centred at about 290 eV due to the 1s→σ* excitation. However, in the graphite spectrum an additional peak, absent in that of diamond, due to the 1s→π* excitation is observed at about 286 eV. In addition to analysing the details of the energy-loss spectra, with appropriate electron optics it is possible to select the electrons that have lost energy within a certain energy window and to form a map showing the spatial variation of the energy-loss signal in the sample region of interest. Thus, a map formed with a narrow energy window ($\Delta E = 5$ eV) centred on the 1s→π* transition will effectively show the relative distribution of sp^2 bonding, shown as w1 in Fig. 2. While the obvious approach to imaging the distribution of sp3 bonding is to centre a window at 290 eV (1s→σ*), this is potentially misleading as it is possible that the tail of the 1s→π* peak might contribute some intensity in this window. To avoid this effect, a window centred at 303 eV, w2 in Fig. 2, was selected as this corresponds to a strong feature in the diamond energy-loss spectrum.

The results obtained from polycrystalline diamond films before and after treatment with ClF_3 at 623 K are shown in Fig. 3. The images of the untreated sample showed the presence of three grain boundaries. In the centre of the grains the bonding is largely sp^3 in nature, as expected in a diamond sample, Fig. 3(a). However, it is clear that there is a significant contribution from sp^2 hybridised carbon in the region of the grain boundaries, Fig. 3(b), evidenced by the bright contrast in the sp^2 map. In the sp^3 map of the ClF_3-treated sample, Fig. 3(c), grain boundaries were again observed. However, in contrast to the untreated sample, the sp^2 map of this region, Fig. 3(d), showed no evidence of any bright contrast at the grain boundaries indicating that sp^2 hybridised carbon was absent. The lack of sp^2 carbon on the ClF_3-treated sample can be explained as a result of reaction to produce C–F bonds. It can also be concluded that graphitisation did not occur during the fluorination reaction and that the surface was most likely to be terminated by fluorine.

The EFTEM study provided new information on the nature of fluorination reactions between diamond surfaces and highly aggressive reagents like F_2 and ClF_3. The involvement of sp^2 hybridised carbon, present at defects or cracks, cannot be ignored. Hydrogenation would be expected to remove most, if not all, graphitic carbon. However, if hydrogenation were incomplete or graphite formation occurred post-hydrogenation as a result of the clipping of dangling bonds, then the fluorination of sp^2 hybridised carbon could have occurred. This carbon is likely to react preferentially to give F-terminated, sp^3 hybridised carbon in the early stages of reaction. Grain boundaries or edges are high-energy sites where initial reaction is favoured. An etching reaction to produce fluorocarbons is possible and if unlimited, a large pit would be formed. The SEM study showed that gross pitting did not occur, supporting the FTIR evidence for a self-limiting reaction. However, EFTEM showed that surface defects such as cracks were present and pore volume analysis of fluorinated diamond powders was consistent with an irregular surface.

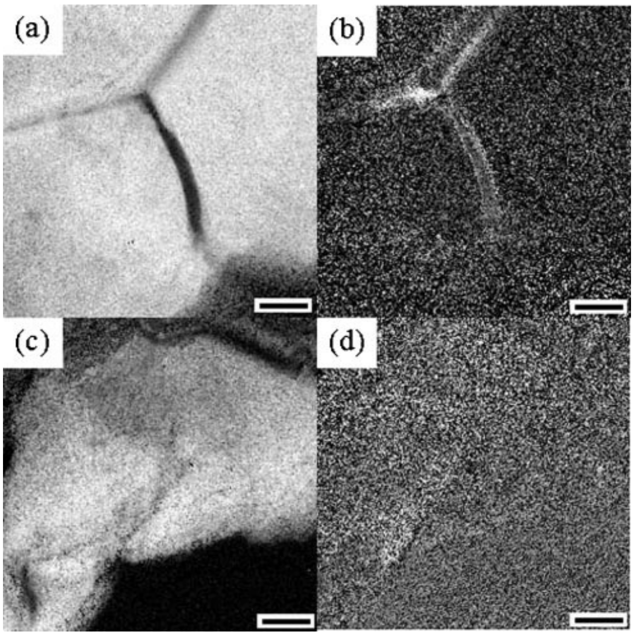

Fig. 3 Energy-filtered transmission electron micrographs of diamond films before and after treatment with ClF_3 at 673 K. Images (a) and (b) show the sp^3 and sp^2 maps, respectively, of the untreated film showing the presence of sp^2 at the grain boundaries. Images (c) and (d) show the sp^3 and sp^2 maps, respectively, of the fluorinated film showing that sp^2 bonding is absent at the boundaries. Scale bar = 20 nm.

X-Ray photoelectron spectroscopy (XPS)

XPS has been applied widely to the study of carbon–fluorine materials such as fluoropolymers, graphite fluorides, fluorinated carbon black, pitch and carbon fibre.[2c,3c,5b] Owing to the influence of the ligand electronegativity on the screening of the nuclear charge, fluorination of carbon results in a shift of the C(1s) binding energy to higher values, the size of the shift depending principally upon the number of fluorine atoms bound to the carbon atom. The degree of fluorination is often a result of the conditions employed. For example, higher C(1s) binding energies were observed from fluorinated carbon fibre when more vigorous conditions were employed.[5b] The surrounding environment of the carbon atom in question is important. It is clear from previous studies that secondary effects, *e.g.* substitution on neighbouring atoms, can shift further the binding energy.[2c,3c,5b] The F(1s) binding energy also increases with increased fluorination but the effect is much less marked compared with C(1s). In practice, differentiating among CF, CF_2 and CF_3 groups using F(1s) data is difficult; therefore, assignments are usually made on the basis of the C(1s) data. Nevertheless, F(1s) binding energy data can be useful since they provide information about the bonding

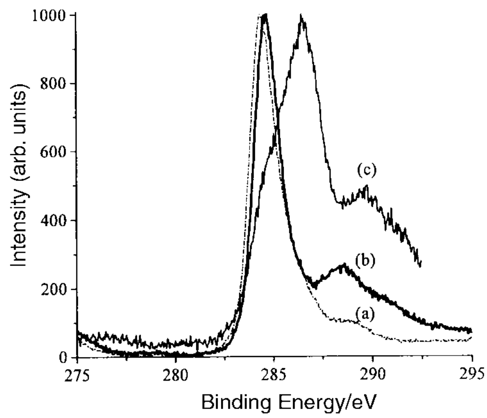

Fig. 4 Carbon (1s) binding energy envelopes in the XPS of (a) unfluorinated diamond film, (b) fluorinated (F_2) at 298 K and (c) fluorinated (F_2) at 523 K.

present. A value of *ca.* 684.5 eV is diagnostic for ionic species (*e.g.* LiF) whilst a higher value (*ca.* 689.6 eV) suggests covalent bonding, for example in $(CF)_n$.[2c,19]

In previous XPS studies involving diamond, the chemisorption of hydrogen, oxygen and halogen atoms on well defined single crystal surfaces has been investigated.[9,10] Fluorine chemisorption at ambient temperature was characterised by the appearance of a shoulder on the high energy side of the bulk carbon peak in the C(1s) spectrum. This feature, occurring at 286.8 eV (1.8 eV higher than the bulk signal), has been attributed to a carbon monofluoride (CF) species which forms an adlayer with a coverage of about three-quarters of a monolayer. There was no evidence for more highly fluorinated species like CF_2 or CF_3 and the shift in binding energy observed was smaller than expected for the formation of a covalent C–F bond. This was rationalised as a consequence of the less than monolayer coverage.[9,10]

Inspection of the raw spectra obtained in the present work revealed that the C(1s) binding energy envelopes consisted of more than one peak. (Fig. 4) As described in the Experimental section, an iterative fitting procedure was used to identify the components that make up the individual spectra. Binding energies obtained from this fitting routine are presented in Table 3. Tentative assignments of the peaks have been made in accordance with previous measurements, although some are ambiguous as indicated in Table 3. Consistent with earlier literature reports, it was observed that fluorine treatment resulted in the formation of peaks in the C(1s) binding energy envelope which were shifted to higher energy. Fluorine was present on the surface as evidenced by strong peaks in the F(1s) region.

In the hydrogenated film, the spectrum was dominated by the bulk carbon signal at 284.4 eV. The shoulder observed at higher binding energy, Fig. 4, could be decomposed into two contributions with maxima at 286.3 and 288.7 eV which can be attributed to oxygenated species (Table 3). The presence of oxygen was confirmed in a survey spectrum, which contained a peak at 533 eV. Assignments of C(1s) features were made in accordance with literature values for C–O bonding.[20] Following fluorination at room temperature, a similar situation was observed and the parent peak was fitted to three maxima, at 284.7, 288.2 and 291.2 eV. The first feature was assigned to the bulk carbon signal while the other two were assigned tentatively to both oxygenated and fluorinated species, Table 3. The survey spectrum revealed the presence of surface oxygen (534 eV) and two F(1s) peaks at 680.0, a very weak feature, and 689.7 eV. The latter can be assigned to covalently bound fluorine. The former peak was probably due to contamination by trace NiF_2. The C(1s) binding energy envelope following fluorination at 523 K was significantly different from the reference and the sample treated with F_2 at room temperature. The relative intensity of the peak at *ca.* 284 eV due to bulk carbon was significantly reduced, suggesting that a sub-surface fluorination reaction had occurred. In addition to the bulk carbon, the raw spectrum could be fitted to three maxima. The peaks at 289.4 and 291.6 eV were assigned primarily to CF, CF_2 and, possibly, to CF_3 species (Table 3). The peak at 286.6 eV could be due to COH or COC species; the absence of such a feature in the spectrum of the sample treated with F_2 at room temperature suggested that this could be a misleading assignment. Therefore, this feature was tentatively assigned to secondary (or β) effects. Overall, the observation of these three features is indicative of a highly fluorinated surface exhibiting secondary effects due to the presence of other C–F groupings in the local environment. Here also, the survey spectrum revealed the presence of oxygen, although the intensity of the oxygen peak was reduced compared with the sample treated with F_2 at room temperature. A very strong fluorine peak was observed at 690.2 eV, confirming the presence of surface fluorine. The other F(1s) peak, *ca.* 680 eV, was very weak. Since a sub-surface reaction could have occurred only with the removal of surface carbon atoms, these observations and the tentative assignments made are consistent with the FTIR results described above.

Fluorine-18 radiotracer experiments

Surface CF, CF_2 and CF_3 groups that are present in well-fluorinated materials should result in a hydrophobic surface in which fluorine is kinetically inert to substitution. This was shown to be correct from fluorine-18 exchange experiments involving $H^{18}F$; however, the interaction between $H^{18}F$ and H- or O-terminated diamond powders was unexpectedly large and, for this reason, was studied in some detail. The results (Table 4) are expressed in terms of uptake of $H^{18}F$ as determined from the solids after exposure. They were calculated from the $[^{18}F]$ count rate of the solid and the specific $[^{18}F]$ count rate of the $H^{18}F$ used [expressed in count min^{-1} (mg atom $F)^{-1}$]. The latter was determined for each sample of $H^{18}F$ used during the course of each experiment. Uptakes of fluorine by H-terminated samples were in the range 0.58–0.90 and 0.36–0.58 (mg atom F) g^{-1} respectively following reaction at room temperature and 573 K. There was some data scatter, which is common in this type of study. Taking this into account, fluorine uptakes were greater following reactions at room temperature. The behaviour of O-terminated samples was similar, with comparable or slightly greater fluorine uptake values, Table 4, indicating that a significant reaction had occurred on the O-terminated surface. The fluorine uptakes were consistently greater following reactions with $H^{18}F$ at room temperature.

Table 3 Fluorine (1s) and carbon (1s) binding energy data determined from fits to XPS data of diamond films. Errors are estimated as $< \pm 0.2$ eV

Sample	F(1s) binding energy/eV	C(1s) binding energy/eV	C(1s) assignments
Hydrogenated	—	284.4	Bulk C
		286.3	COH or COC
		288.7	CO
Fluorinated (F_2)	680.0	284.7	Bulk C
at ambient temperature	689.7	288.2	CO and CF
		291.2	CF_2
Fluorinated (F_2) at 523 K	680.0	284.7	Bulk C
	690.2	286.6	CF[a] β-effects[b]
		289.4	CO and CF β-effects[b]
		291.6	CF_2 and CF_3

[a] CF adjacent to non-fluorinated C. [b] C adjacent to fluorinated C.

Table 4 Uptake of $H^{18}F$ by hydrogen- or oxygen-terminated diamond powders[a]

Sample	Temp./K	No. of expts.	Uptake range[b]/ (mg atom F) g^{-1}	Mean uptake/ (mg atom F) g^{-1}
H-terminated	Ambient	5	0.58–0.90	0.73
H-terminated	573	5	0.36–0.58	0.48
O-terminated	Ambient	3	0.84–1.12	0.96
O-terminated	573	3	0.44–0.65	0.53

[a] Exposure time = 0.75 h. [b] Relative errors in the four series of experiments were, respectively, ⩽1.4, 0.8, 0.5 and 0.5%.

The results of $H^{18}F$ uptake experiments on fluorinated diamond powder samples that had been pre-treated under a variety of conditions are contained in Table 5. The most obvious feature of these results, compared with those obtained for hydrogen- or oxygen-terminated surfaces, was the marked reduction in fluorine uptake. An approximate ten-fold decrease from many samples was observed as a consequence of surface fluorination. Under comparable conditions, the behaviour of samples fluorinated using ClF_3 was generally similar to those fluorinated with F_2. Both reagents were expected to lead to extensive formation of C–F bonds and very small uptakes were expected. The results obtained from samples that were originally H-terminated (Table 5) indicate that this was the case.

The data in Table 5 demonstrate indirectly the effect that O-termination of diamond has in the subsequent fluorination process. Carbon–oxygen surface groups are more resistant to fluorination than C–H and are likely to survive a subsequent fluorination process, at least when it is performed at room temperature.[21] Reactions between $H^{18}F$ and O-terminated diamond that had been fluorinated at room temperature, resulted in greater [^{18}F] uptakes than those observed from O-terminated diamond that had then been fluorinated at 623 K (Table 5). The fluorine uptakes that resulted from exposure of F-terminated samples to $H^{18}F$ at ambient temperature were always greater than those that resulted from 523 K, although the differences were smaller than those found using H- or O-terminated samples. It was concluded, therefore, that the reactions were similar in all cases but that [^{18}F] fluorine uptakes on highly fluorinated surfaces that were derived from O-terminated samples were the result, at least in part, of reaction between $H^{18}F$ and surface oxygen, which had not been removed completely by F_2.

The behaviour of anhydrous HF vapour towards H- or O-terminated diamond was not typical of a fluorination reaction, since uptake of [^{18}F] at 523 K was less than at ambient temperature (Table 4). In order to explain this feature and to elucidate the nature of the HF reaction with H-, O- or F-terminated surfaces, [^{18}F] exchange experiments were carried out. The results of exposure of H- or O-terminated diamond powders, previously labelled with [^{18}F] by room temperature treatment with $H^{18}F$, to aliquots of unlabelled HF, also at room temperature, are given in Table 6. Room temperature fluorine exchange or $H^{19}F$/$H^{18}F$ displacement occurred between an [^{18}F]-labelled diamond surface and unlabelled HF vapour. In every case, less than 20% of the original [^{18}F] activity remained on the diamond surface following successive exposures to three aliquots of unlabelled HF, indicating that a pool of labile fluorine was present on the diamond surface. In three out of the four samples examined, the greatest relative effect occurred following treatment with the second aliquot of HF, suggesting that the extent of the interaction may have been determined other than by purely statistical factors, for example by the sample geometry. [^{18}F] Exchange in the reverse direction was investigated by determining the dilution in the [^{18}F] activity of $H^{18}F$ after its exposure to H- or O-terminated diamond powder samples that had been pre-treated with unlabelled HF (Table 7). In all cases the fraction of [^{18}F] activity exchanged, f, determined from $H^{18}F$ specific count rate measurements before and after exposure, was ⩾85%. Values of f determined using [^{18}F] count rates from vapour and solid after exposure were in good agreement with those determined purely from vapour phase measurements (Table 7). This indicated that the process involved [^{18}F] exchange and/or $H^{18}F/H^{19}F$ displacement at the surface and that additional uptakes of $H^{18}F$ during an exchange reaction were very small.

Table 6 Room temperature reactions between HF and [^{18}F]-labelled H- or O-terminated diamond powders[a]

Sample	HF aliquot no.	Uptake of [^{18}F] (mg atom F) g^{-1}	Fraction of original uptake remaining(%)
H-terminated		0.600 ± 0.003	
	1	0.265 ± 0.001	44.1
	2	0.147 ± 0.001	24.6
	3	0.115 ± 0.001	19.2
H-terminated		0.739 ± 0.001	
	1	0.505 ± 0.002	68.3
	2	0.152 ± 0.001	20.7
	3	0.104 ± 0.001	14.1
O-terminated		1.116 ± 0.003	
	1	0.814 ± 0.002	72.9
	2	0.317 ± 0.001	28.4
	3	0.169 ± 0.001	15.2
O-terminated		0.939 ± 0.002	
	1	0.635 ± 0.001	67.7
	2	0.214 ± 0.001	22.8
	3	0.126 ± 0.001	13.5

[a] Diamond powders (1.0 g) labelled by treatment with $H^{18}F$ (1.0 mmol) at ambient temperature. HF added in three (1.0 mmol) aliquots. Exposure time 0.5 h in each case.

Table 5 Uptake of $H^{18}F$ by fluorine-terminated diamond powders

Pre-treatment	Fluorination conditions	Temperature of $H^{18}F$ treatment/K	Uptake of [^{18}F]/(mg atom F) g^{-1}
H_2 flow	F_2 at ambient temperature	Ambient	0.118 ± 0.001
H_2 flow	F_2 at 673 K	Ambient	0.090 ± 0.001
H_2 flow	ClF_3 at ambient temperature	Ambient	0.068 ± 0.001
H_2 flow	ClF_3 at 673 K	Ambient	0.038 ± 0.001
H_2 flow	F_2 at ambient temperature	523	0.091 ± 0.001
H_2 flow	F_2 at 673 K	523	0.082 ± 0.001
H_2 flow	ClF_3 at ambient temperature	523	0.052 ± 0.001
H_2 flow	ClF_3 at 673 K	523	0.021 ± 0.001
H_2 then O_2 flow	F_2 at ambient temperature	Ambient	0.361 ± 0.001
H_2 then O_2 flow	F_2 at ambient temperature	Ambient	0.531 ± 0.001
H_2 then O_2 flow	F_2 at 623 K	Ambient	0.139 ± 0.001
H_2 then O_2 flow	F_2 at 623 K	Ambient	0.183 ± 0.001
H_2 then O_2 flow	F_2 at ambient temperature	523	0.259 ± 0.001
H_2 then O_2 flow	F_2 at ambient temperature	523	0.408 ± 0.002
H_2 then O_2 flow	F_2 at 623 K	523	0.107 ± 0.005
H_2 then O_2 flow	F_2 at 623 K	523	0.086 ± 0.001

Table 7 [^{18}F] Exchange between HF-pre-treated, H- or O-terminated diamond powders and H^{18}F[a]

Sample[b]	Temperature/K	Fraction of [^{18}F] exchanged, *f* Determined from H^{18}F counts before and after exchange	Fraction of [^{18}F] exchanged, *f* Determined from H^{18}F and solid counts after exchange[c]
H-terminated	Ambient temperature	0.94	
H-terminated	Ambient temperature	0.85	0.89
H-terminated	573	1.03	
H-terminated	573	0.90	1.08
O-terminated	Ambient temperature	0.88	0.92
O-terminated	Ambient temperature	0.96	
O-terminated	573	0.93	1.04
O-terminated	573	1.08	

[a]Exchange time 1 h; *ca.* 3.5 mmol. H^{18}F used in each case. [b]Samples (1.0 g) pre-treated with HF; uptakes of HF were determined from control experiments using H^{18}F under identical conditions. [c]Radiochemical balance = 100% in all cases.

In contrast there was no observable exchange between H^{18}F and F-terminated diamond under comparable conditions (Table 8). The count rates of H^{18}F before and after reaction were identical within experimental error.

To summarise, the interaction between anhydrous HF and hydrogenated or oxygenated diamond powder was more extensive at ambient temperature than at 523 K. It resulted in a surface where essentially all adsorbed fluorine was labile with respect to further interaction with HF. Both observations were inconsistent with the formation of C–F bonds. The reaction of diamond powder with F_2 or ClF_3 resulted in surface fluorine that was not exchangeable with HF, consistent with C–F bond formation.

DRIFTS of HF-treated diamond

DRIFTS of H-terminated diamond powder, following treatment with HF at room temperature, were performed immediately, several days and several weeks after the treatment. The sample remained exposed to moist air during this period. Prior to HF exposure, the spectrum contained three bands, ν_{max} 2937, 2860 and 2837 cm^{-1}, attributable to CH_2 and CH_3 groups, Table 2. Immediately following the reaction with HF, the C–H bands were absent but there was no evidence for C–F bond formation. Except for a weak band in the O–H stretching region, ν_{max} at 3547 cm^{-1}, the spectrum was featureless. A spectrum recorded several days after the reaction between hydrogen-terminated diamond and HF contained a strong band at 3843 cm^{-1} and a weaker band at 1656 cm^{-1}. These were assigned to the stretching and bending modes respectively of water. Weak bands at 2937 and 2837 cm^{-1} were assigned to CH stretching vibrations. The other spectral features were bands at 1897 cm^{-1}, due possibly to a C=O stretch, and at 1016 cm^{-1}.

Discussion

The results described above enable the behaviour of F_2 and ClF_3 towards polycrystalline diamond films and powders to be rationalised. The existence of faces, edges and boundaries between crystallites results in a range of different sites at which chemical attack can occur. For steric reasons and in order to minimise electronic repulsion, edges and boundaries are sites at which the formation of CF_2, and possibly CF_3, surface groups is most likely, with formation of surface CF being restricted to faces. Removal of difluorocarbene, CF_2, from the surface and the subsequent formation of gaseous perfluorocarbons is certainly possible at 673 K, the fluorination temperature being used to observe the formation of fluorocarbon products. The XPS data obtained from a film that had been fluorinated at 523 K are consistent with similar behaviour occurring at this temperature also. It appears likely that etching occurs only at the more reactive edge and boundary sites and this enables F_2 to react with the sub-surface. The fluorinated layer so formed is apparently greater than a monolayer.

Formation of this layer is possible only if transport of F_2 or F into the lattice is permitted or if a thin layer of amorphous carbon, similar to that formed in the uncontrolled fluorination of graphite,[2c] is formed in the early stages of the high temperature fluorination. However, the EFTEM from a fluorinated film provided no evidence for the presence of sp^2 C, which would have been expected were amorphous carbon present. In previous studies of the surface fluorination of single crystal diamond,[9,10] the possibility of transport of F into the lattice has been discounted because of the energetically unfavourable lattice distortion that would be required. More forcing conditions were employed in the present work, however, and these, with the very imperfect nature of the diamond used, lead us to suggest that reaction with the sub-surface is a possibility.

Irrespective of the precise nature of the process, it is clear that the reaction with F_2 is limited kinetically. Fluorocarbons were not detected when previously fluorinated diamond was exposed to F_2 at 673 K and SEM examination indicated that massive etching did not occur. The observed behaviour is similar to that found for graphite fluoride, which does not react further with F_2 at 873 K,[2a] and to fluorinated silicon, in which the surface fluorinated layer inhibits further attack at Si.[22]

The interactions between HF and H-, O- and F-terminated diamond powders, demonstrated by the [^{18}F] measurements, are unexpected. The retention of significant quantities of H^{18}F when material volatile at room temperature is removed, suggests that it is not simply physically adsorbed. Uptake of H^{18}F by H- and O-terminated samples, Table 4, is greater than that by F-terminated samples, although the latter (Table 5) are readily detected. In all cases, the extent of the interaction is less after exposure to H^{18}F at high temperature. Fluorination of an O-terminated surface with F_2 at room temperature has been shown by DRIFTS to produce a surface which contains more oxygen than fluorine.[6d,e,11] The reverse is the case after fluorination at 673 K, although the O (1s) XPS results obtained here indicate that surface oxygen is still present. The greater

Table 8 [^{18}F] Specific count rates of H^{18}F before and after exposure to fluorinated diamond powders at ambient temperature[a]

Sample[b]	[^{18}F] Specific count rate/count s^{-1} mmol^{-1} Before exposure	[^{18}F] Specific count rate/count s^{-1} mmol^{-1} After exposure
F_2 fluorination at ambient temperature	642	636
F_2 fluorination at ambient temperature	1025	1009
F_2 fluorination at 673 K	642	640
F_2 fluorination at 673 K	1025	1015

[a]Exposure time 1 h. [b]H-terminated.

uptake of [^{18}F] observed at ambient temperature suggests strongly that a specific interaction between HF and C–O surface atoms is present. By analogy, a specific interaction between HF and C–H surface atoms is suggested. Hydrogen fluoride bound to an H-terminated surface is labile with respect to [^{18}F] exchange with HF and it reacts with water on exposure to moist air. This is a rare example of a 'hydrophilic' diamond surface at variance with the normal expectation of a fluorinated surface. In contrast, but as expected, there is no [^{18}F] exchange observable between H^{18}F and F-terminated diamond.

Hydrogen bonding between HF and functionalities such as C=O, COC and COH groups, all of which are known to be present on the surface of O-terminated diamond,[21] is well documented[23] and could account for the observations made. The increased uptakes of HF that result from room temperature interaction are accounted for by the increased clustering of HF molecules to form oligomeric species, which is a characteristic of the vapour phase of HF.[24] Hydrogen bonding interactions between HF and H-terminated diamond are more problematic, although evidence for weak interactions of the type XHHR, where X is a very electronegative element and R is an electropositive element or moiety, is beginning to emerge.[25] Such weak hydrogen bonds have been shown to be feasible, for example when $X = F$ and $R = Li$[26] and when $X = F$ and RH is a d-block hydride.[26,27]

Although there are recent examples of compounds that exhibit relatively short CFHY ($Y = O$, N or C) contacts in the solid state,[28] the current view is that a C–F group is unlikely to function as an H-bond acceptor.[29] The extent of H^{18}F interaction follows the order O-terminated $\geqslant$ H-terminated $\gg$ F-terminated diamond and it is considered that this can be accounted for by hydrogen bond interactions that involve O- or H-terminated surfaces and HF. The small uptakes observed by F-terminated surfaces may be the result of unfluorinated C–O and, possibly, C–H sites.

Acknowledgements

We thank EPSRC and Logitech Limited for financial support and staff at the John Mallard PET Centre (Aberdeen), the University of Dundee and the Materials Technology Laboratory (NRCan, Ottawa) for assistance with [^{18}F], XPS and EFTEM measurements respectively. D. W. M. thanks the RSC for the provision of a J. W. T. Jones Travelling Fellowship.

References

1 For a preliminary account of this work see: J. M. Winfield, C. P. Kealey, T. M. Klapötke, D. W. McComb and M. I. Robertson, *Fluorine in Coatings III*, International Centre for Coatings Technology, Orlando, FL, Jan. 1999, Paper 26.

2 For example: (*a*) N. Watanabe, A. Izumi and T. Nakajima, *J. Fluorine Chem.*, 1981, **18**, 475; (*b*) N. Watanabe, *J. Fluorine Chem.*, 1986, **33**, 335; (*c*) N. Watanabe, T. Nakajima and H. Touhara, *Graphite Fluorides*, Elsevier, Amsterdam, 1998.

3 (*a*) N. Watanabe, Y. Kita and O. Mochizuki, *Carbon*, 1979, **17**, 359; (*b*) N. Watanabe and K. Ueno, *Bull, Chem. Soc. Jpn.*, 1981, **54**, 127; (*c*) G. Nanse, E. Papirer, P. Fioux, F. Moguet and A. Tressaud, *Carbon*, 1997, **35**, 175; G. Nanse, E. Papirer, P. Fioux, F. Moguet and A. Tressaud, *Carbon*, 1997, **35**, 371; G. Nanse, E. Papirer, P. Fioux, F. Moguet and A. Tressaud, *Carbon*, 1997, **35**, 515.

4 H. Fujimoto, T. Maeda, M. Yoshikawa and N. Watanabe, *J. Fluorine Chem.*, 1993, **60**, 69.

5 (*a*) Y.-b. Chong and H. Ohara, *J. Fluorine Chem.*, 1992, **57**, 169; (*b*) A. Bismarck, R. Tahhan, J. Springer, A. Schulz, T. M. Klapötke, H. Zell and W. Michaeli, *J. Fluorine Chem.*, 1997, **84**, 127.

6 (*a*) P. A. Molian, B. Janvrin and A. M. Molian, *Wear*, 1993, **165**, 133; (*b*) S. Miyake, *Appl. Phys. Lett.*, 1994, **65**, 1109; (*c*) C. Vinensang, G. Turban, E. Anger and G. Giiquel, *Diamond Relat. Mater.*, 1994, **3**, 645; (*d*) T. Ando, K. Yamamoto, M. Kamo, Y. Sato, Y. Takamatsu, S. Kawasaki, F. Okino and H. Touhara, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3209; (*e*) F. Okino, M. Matsuzawa, S. Kawasaki, H. Touhara, T. Ando, T. Aizawa and Y. Sato, *Abs., 21st Fluorine Conf. Jpn.*, 1997, O-07; (*f*) T. I. Hukka, T. A. Pakkanen and M. P. D'Evelyn, *J. Phys. Chem.*, 1995, **99**, 4710; (*g*) V. S. Smentkowski and J. T. Yates Jr., *Science*, 1996, **271**, 193; (*h*) R. S. Butter, D. R. Waterman, A. H. Lettington, R. T. Ramos and E. J. Fordham, *Thin Solid Films*, 1997, **311**, 106.

7 H. Selig, C. Lifshitz, T. Peres, J. E. Fischer, A. R. McGhie, W. J. Romanow, J. P. McCauley Jr. and A. B. Smith III, *J. Am. Chem. Soc.*, 1991, **113**, 5475; J. H. Holloway, E. G. Hope, R. Taylor, G. J. Langley, A. G. Avent, T. J. Dennis, J. P. Hare, H. W. Kroto and D. M. R. Walton, *J. Chem. Soc., Chem. Commun.*, 1991, 966; A. A. Tuinman, A. A. Gakh, J. L. Adcock and R. N. Compton, *J. Am. Chem. Soc.*, 1993, **115**, 5885; Y. Matsuo, T. Nakajima and S. Kasamatsu, *J. Fluorine Chem.*, 1996, **78**, 7.

8 T. Nakajima, S. Kasamatsu and Y. Matsuo, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 831; A. Hamwi, H. Alvergnat, S. Bonnamy and F. Beguin, *Carbon*, 1997, **35**, 723.

9 A. Freedman and C. D. Stinespring, *Appl. Phys. Lett.*, 1990, **57**, 1194.

10 T. Yamada, T. J. Chuang, H. Seki and Y. Mitsuda, *Mol. Phys.*, 1991, **76**, 887; A. Freedman, *J. Appl. Phys.*, 1994, **75**, 3112; J. F. Morar, F. J. Himpsel, G. Hollinger, J. L. Jordan, G. Hughes and F. R. McFeely, *Phys. Rev. B*, 1986, **33**, 1340.

11 T. Ando, J. Tanaka, M. Ishii, M. Kamo, Y. Sato, N. Ohashi and S. Shimosaki, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3105.

12 E. P. Barrett, L. S. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373.

13 R. F. Egerton, *Electron Energy-loss Spectroscopy in the Electron Microscope*, Plenum, New York, 2nd edn., 1996.

14 D. Briggs and M. P. Seah, *Practical Surface Analysis*, Wiley, London, 1994.

15 C. J. Pouchert, *The Aldrich Library of FTIR Spectra – Vapour Phase*, Aldrich Chemical Co. Inc., Milwaukee, USA, 1st edn., 1989, vol. 3.

16 *Catalogue of Infrared Spectral Data, 2nd edn.*, American Petroleum Institute Research Project, Texas A and M University, College Station, TX, USA, 1974, vol. 44.

17 D. G. Weiblen, in *Fluorine Chemistry*, ed. J. H. Simons, Academic Press, New York, 1954, vol. 2, p. 449.

18 Q. Sun and M. Alam, *J. Mater. Sci.*, 1992, **27**, 5857.

19 P. Swift, D. Shuttleworth and M. P. Seah, in *Handbook of X-Ray and Ultraviolet Spectroscopy*, ed. D. Briggs, Heyden, London, 1978; T. Nakajima and N. Watanabe, *Graphite Fluorides and Carbon–Fluorine Compounds*, CRC Press, Boca Raton, FL, 1991.

20 J. C. Vickerman, *Surface Analysis – The Principal Techniques*, John Wiley and Sons, Chichester, 1997.

21 T. Ando, K. Yamamoto, M. Ishii, M. Kamo and Y. Sato, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3635.

22 F. R. McFeely, J. F. Morar, N. D. Shinn, G. Landgren and F. J. Himpsel, *Phys. Rev. B*, 1984, **30**, 764; F. R. McFeely, J. F. Morar and F. J. Himpsel, *Surf. Sci.*, 1986, **165**, 277; B. Roop, S. Joyce, J. C. Schultz and J. I. Steinfeld, *Surf. Sci.*, 1986, **173**, 455.

23 A. C. Legon and D. J. Millen, *Chem. Rev.*, 1986, **86**, 635; A. C. Legon and D. J. Millen, *Can. J. Chem.*, 1989, **67**, 1683.

24 R. L. Redington, *J. Phys. Chem.*, 1982, **86**, 552; R. L. Redington, *J. Phys. Chem.*, 1982, **86**, 561; J. M. Beckerdite, D. R. Powell and E. T. Adams Jr., *J. Chem. Eng. Data*, 1983, **28**, 287.

25 M. J. Calhorda, *Chem. Commun.*, 2000, 801.

26 Q. Liu and R. Hoffmann, *J. Am. Chem. Soc.*, 1995, **117**, 10108.

27 G. Orlova and S. Scheiner, *J. Phys. Chem, A*, 1998, **102**, 260.

28 J. H. Golden, P. F. Mutolo, E. B. Lobkovsky and F. J. DiSalvo, *Inorg. Chem.*, 1994, **33**, 5374; D. J. Telf, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1997, **36**, 4372; M. Pham, M. Gdaniec and T. Połoński, *J. Org. Chem.*, 1998, **63**, 3731.

29 J. D. Dunitz and R. Taylor, *Chem. Eur. J.*, 1997, **3**, 89.