Identification of Functional Groups on the Surface of a Fluorinated Diamond Crystal by Photoelectron Spectroscopy

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Summary CF_3, CF_2, and CF surface groups formed when diamond is exposed to microwave-discharged SF_6 may be characterized and quantitatively estimated by *X*-ray photoelectron spectroscopy.

We report the first unambiguous identification of functional groups, formed by the chemisorption of heteroatoms, on a single-crystal elemental carbon surface. Previous attempts[1-3] to characterize, by i.r. spectroscopy, vacuum thermogravimetry, electrochemical and classical, wet-chemical methods, the nature of various adsorbed species on a wide range of carbons have been inconclusive. Moreover, where such techniques have achieved qualified success (as *e.g.*, in the i.r. reflectance spectroscopic study of carbon–oxygen surface complexes) it has been necessary to use solids possessing very large areas (typically 1200 m^2 g^{-1} for a polyvinylidene chloride carbon[3] and 20—200 m^2 g^{-1} for diamond powder[2]). Because of its sensitivity, *X*-ray photoelectron spectroscopy (XPS) is capable of readily detecting submonolayer amounts of heteroatoms on very low area (*ca* 0·5 cm^2) solid surfaces. We have demonstrated elsewhere[4,5] the merit of this technique for the elucidation of differences in adsorbability between the prismatic and basal faces of graphite.

The diamond single crystal, with (111) surface predominant, was 'saturated' with chemisorbed fluorine by exposing it to fluorine atoms[6] generated in a quartz vessel by microwave-discharged (2450 MHz) SF_6 vapour at a pressure of 10^{-3} Torr for times ranging from a few minutes to several hours. A monolayer† of covalent fluoride formed (see below) in a few minutes, and it is probable that there is a good deal of concomitant gasification (just as with excited oxygen,[5,7] also at room temperature, there is simultaneous

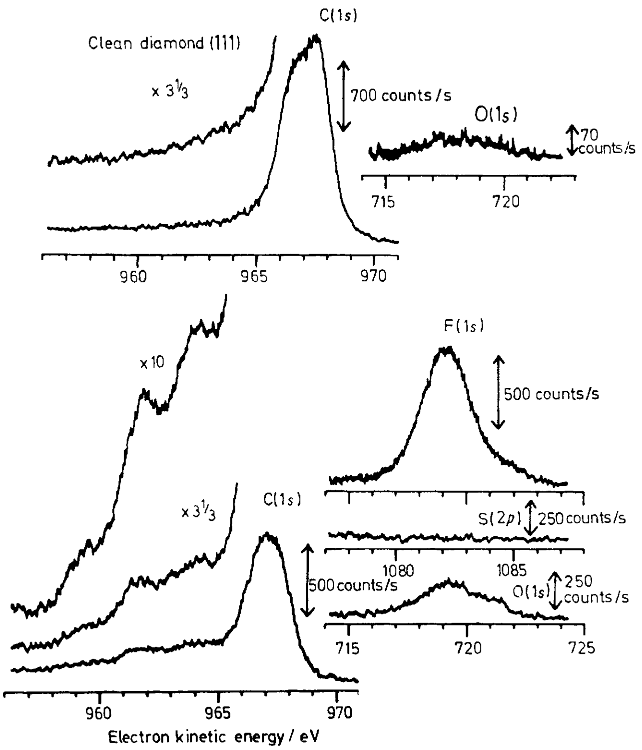

Figure 1. Typical XPS spectra [C(1*s*) region] of a diamond (111) face before and after exposure to fluorine atoms. Note production of high-B.E. satellites at *ca.* 3·1, 5·3, and 7·8 eV from main C(1*s*) (diamond) peak.

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† A monolayer of the (111) face refers to half a single puckered-hexagon plane.

formation of stable surface oxide and gasification yielding volatile CO and CO_2).

The C(1*s*) region of the XP spectrum‡ contains three satellites (Figure 1) at higher binding energy (B.E.) from the main C(1*s*) diamond peak: these occur at *ca* 3·1, 5·3, and 7·8 eV, values which are close to the expected shifts for CF, CF_2, and CF_3 groups on the basis of previous data[8] for the C(1*s*) peaks in progressing along the series CH_4, CFH_3, CF_2H_2, and CF_3H (see Figure 2). Since the photoelectric cross-sections of F(1*s*) and C(1*s*) for Mg-K_α (the *X*-ray radiation used here) are known,[9,10] we may independently estimate, from the total observed C(1*s*) satellite peak intensity, the F(1*s*) intensity arising from the three fluorocarbon peaks. The computed figure tallies within 5% with the observed F(1*s*) peak intensity, thus confirming our assignments. Since the escape depth of diamond is also known[11] to be 2·4 ± 0·4 nm, we may compute that, after 20 min exposure to excited SF_6, an average thickness of some two monolayers of diamond is converted into fluorocarbon, 1·3 layers being composed of $\geqslant CF$ groups, 0·6 of $>CF_2$, and 0·2 of $-CF_3$. (No sulphur, *i.e.* less than 0·03 monolayers, is chemisorbed). As gasification proceeds the total average thickness of surface fluoride increases only gradually, but the proportion of CF_2 continues to rise, a fact which is indicative of enhanced surface roughening since $-CF_2$ groups occur at ledge sites on (111) faces. The proportion of CF_3 groups, which would be favoured at kink sites, diminishes somewhat as reaction proceeds, but all such ratios are doubtless temperature and pressure sensitive. Fuller details of XPS studies of fluorinated diamond and graphite crystals, involving a variety of fluorinating agents, will be described elsewhere.

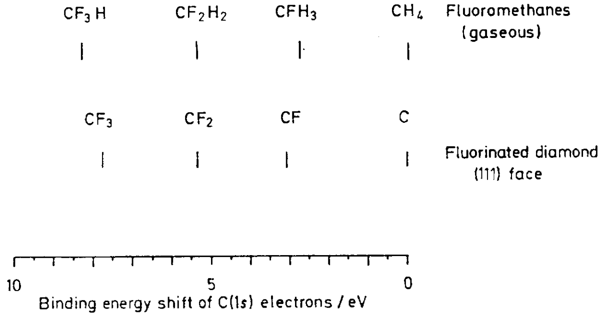

FIGURE 2. Comparison of C(1*s*) B.E. shifts observed in the series CH_4, CH_3F, CH_2F_2, and CHF_3 (for isolated gas molecules)[8] and the shifts measured here for fluorinated diamond.

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‡ Discharged SF_6 is too corrosive to be used *in situ* in the spectrometer chamber. Traces of oxygen are picked up by the diamond upon transfer to the spectrometer, but the presence of the oxygen (shown in the spectra) does not invalidate our conclusions.

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