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Work function and electron affinity of the fluorine-terminated (100) diamond surface

K. J. Rietwyk,¹ S. L. Wong,^{2,3} L. Cao,⁴ K. M. O'Donnell,⁵ L. Ley,^{1,6} A. T. S. Wee,³ and C. I. Pakes^{1,a)}

¹Department of Physics, La Trobe University, Victoria 3086, Australia

²NUS Graduate School of Integrative Sciences and Engineering, National University of Singapore, 28 Medical Drive S117456, Singapore

³Department of Physics, National University of Singapore, Singapore 117542, Singapore

⁴Department of Chemistry, National University of Singapore, 3 Science Drive, Singapore 117543, Singapore

⁵Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3168, Australia

⁶Institut für Technische Physik, Universität Erlangen, Erwin-Rommel-Str. 1, 91058 Erlangen, Germany

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The work function and electron affinity of fluorine-terminated (100) diamond surfaces prepared by exposure to dissociated XeF₂ have been determined using synchrotron-based photoemission. After vacuum annealing to 350 °C a clean, monofluoride terminated C(100):F surface was obtained for which an electron affinity of 2.56 eV was measured. This is the highest electron affinity reported for any diamond surface termination so far, and it exceeds the value predicted by recent density functional theory calculations by 0.43 eV. The work function of 7.24 eV measured for the same surface places the Fermi energy of 0.79 eV above the valence band maximum. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4793999>]

There is growing interest in the use of fluorine-terminated diamond in a number of contemporary applications. This super-hydrophobic surface termination¹ has recently been employed as an alternative to oxygen and hydrogen termination to functionalise nanodiamonds to improve the tribological and luminescence properties for biomedical imaging, drug delivery applications, and other biomedical applications.^{2–5} Furthermore, as an electrode material with the widest potential range in aqueous solution,^{6–8} F-terminated diamond is utilised in the development of biological and chemical sensors. In the area of quantum information, F-terminated (111) diamond is proposed as a platform for a solid-state quantum simulator operating at room temperature.⁹

A variety of techniques have been reported for the preparation of F-terminated diamond surfaces with varying degrees of success. These have been based on the exposure of surfaces to fluorine-containing gases (atomic F,^{10–12} F₂,^{2,13} HF,¹³ and XeF₂^{14–16}), molecules (fluorocarbons¹⁷ and fluorofullerenes¹⁸), and plasmas (CF,^{6,19} CHF₃,^{5,20} and C₄F₈^{1,20}). However, many of these techniques are known to damage or etch the surface and provide unsaturated disordered surfaces with an adsorbed fluorocarbon layer.^{5,6,10–12,18,19} The complications with the surface preparation have a much lower impact on the less ordered nano- and polycrystalline diamond substrates but have greatly impeded the study of functionalised single-crystal surfaces. On (100) diamond, surface fluorination with a coverage of up to about 0.75 monolayer (ML) has been achieved via exposure to atomic F,¹⁰ the surface forming a 2 × 1 reconstruction.^{17,18} *Ab initio* calculations state that the 1.0 ML coverage of F is very stable in the 2 × 1 reconstruction with a C–C bond length of 1.61 Å for neighbouring atoms in the dimer and a fluorine atom bonded

to each of these carbons with a C–C–F bond angle of 109.6°.²¹

The large difference in electronegativity between fluorine and carbon, 3.98 and 2.55, respectively, on the Pauling scale, means the C–F bond is highly polar and will give rise to a very high electron affinity even compared to that of O-terminated diamond on account of the potential step associated with the C^{δ+} – F^{δ–} dipole layer at the surface. However, despite its potential application to a number of fields, the electronic properties of the F-terminated diamond surface remarkably are not known. This paper reports the work function, electron affinity, and band bending of the F:C(100) surface prepared via the thermal-induced dissociation of XeF₂, which has become the technique of choice for functionalising other carbon surfaces such as graphene.²² Measurements were performed using core-level and valence band photoelectron spectroscopy (PES) employing synchrotron radiation. The thermal stability of the surface termination was explored by annealing experiments up to 700 °C.

A CVD, boron-doped and (100)-oriented diamond single crystal, was used for this study. Prior to fluorination the sample was boiled in an acid mixture of H₂SO₄/HClO₄/HNO₃ (1:1:1) for 20 min to remove metal and non-diamond contamination and subsequently hydrogen-passivated in a microwave hydrogen plasma. F-termination was carried out in a small stainless steel vacuum chamber, situated within an argon glove box. With the chamber open, the H-terminated sample was first heated to 150 °C in order to remove an adsorbed water layer. About 100 mg XeF₂ was subsequently loaded into the chamber which was then sealed and heated to 240 °C for 3 h to perform the fluorination. After cooling to room temperature, the sample was removed, mounted onto a molybdenum holder using tantalum foil, and transferred into ultra-high vacuum (UHV) at the surface, interface, and nanostructure science (SINS) beamline of the Singapore

^{a)} Author to whom correspondence should be addressed. Electronic mail: c.pakes@latrobe.edu.au.

Synchrotron Light Source where all subsequent processing and photoemission measurements were carried out. During the transfer to UHV the sample was exposed to air for no more than 30 min. LEED measurements performed on an identically prepared F:C(100) sample confirmed a 2×1 surface reconstruction.

Photoemission experiments were conducted at a base pressure of 10^{-10} mbar at normal electron emission. The F1s and C1s core-level spectra were measured with photon energies, $\hbar\omega$, equal to 730 and 330 eV, respectively, chosen in each case to give a photoelectron kinetic energy of about 45 eV, providing a high surface sensitivity and equal transmission function. The binding energy (BE) of all spectra was calibrated using the Au4f_{7/2} core level at a BE of 84.0 eV measured for a gold sample in electrical contact with the diamond. After a Shirley background subtraction, all core-level spectra were fitted using Voigt functions with a fixed Lorentzian width of 0.15 eV. In addition, core-level survey spectra (not shown) were obtained over a large range in BE with $\hbar\omega = 900$ eV to verify that there were no contaminant species other than F present on the surface. Furthermore, the relative intensities of the C1s spectra obtained with photon energies of 330 eV and 730 eV were utilised to assign bulk and surface contributions to the core level spectra obtained.

The work function, ϕ , was derived from the measured position of the low energy cut-off of the secondary electron distribution, E_{co} , measured at a photon energy of 60 eV and with the sample biased at -7.0 V to overcome the spectrometer work function, $\phi_{spec} = 4.35$ eV; the sample bias was confirmed by measuring the corresponding shift of the C1s core-level peaks. The spectrometer work function was accurately determined by measuring the Fermi edge of a freshly sputter gold sample with the first, $\hbar\omega_I$, and second, $\hbar\omega_{II}$, harmonics from the monochromator using $\phi_{spec} = \hbar\omega_I - \hbar\omega_{II} - KE_F$, where KE_F is the kinetic energy of electrons at the Fermi edge measured with $\hbar\omega_I$. The spatially averaged, absolute work function was calculated according to $\phi = E_{co} + eV_{sample} + \phi_{spec}$.

Photoemission measurements were performed on the as-prepared sample and subsequent to annealing in UHV at temperatures in the range of 50–700 °C. For each annealing step the sample temperature was maintained for 30 min and subsequently cooled to below 35 °C prior to commencing photoemission measurements. Survey scans obtained prior to and following annealing revealed no significant surface contamination. A very small O1s peak was present on the as-prepared surface but was no longer detected after annealing to 120 °C; the oxygen signal was therefore ascribed to adsorbed water molecules and need not concern us further.

Figure 1 illustrates the C1s and F1s core-level spectra of the as-prepared surface and its evolution as a function of annealing temperature. In the C1s spectrum for the as-prepared surface four core lines can be identified. A large peak at a BE of 284.6 eV is ascribed to the contribution of carbon atoms in the diamond bulk. A smaller peak with a BE of 286.2 eV that persists even after annealing to 700 °C is ascribed to C atoms bonded to one F because the chemical shift of this line with respect to the diamond bulk peak (+1.6 eV) is similar to that reported for fluorine-terminated (100) and (111) diamond surfaces.^{10,11,14,17} Two further peaks are identified at higher binding energies: a strong peak

FIG. 1. Core-level photoelectron spectra obtained for the as-prepared and annealed surface. (a) C1s spectra obtained with $\hbar\omega = 330$ eV. (b) F1s spectra obtained with $\hbar\omega = 730$ eV. In both cases the spectra are normalised to the photon flux.

at 289.0 eV (labelled CF_I) and one of lower intensity at 291.1 eV (CF_{II}). These lines resemble features reported by Smentkowski *et al.*¹⁶ for C₄F₉I adsorbed on the (100) diamond surface and are hence attributed to CF₂ and CF₃ species, respectively. The core lines CF_I and CF_{II} are similar in BE to those reported by Smentkowski *et al.* and are no longer present after annealing above 350 °C; therefore, they most likely originate from fluorocarbon species which are adsorbed onto the surface during preparation of the sample. We note that after annealing to 350 °C, the diamond bulk peak and C-F peaks increase in intensity, consistent with the removal of adsorbed surface molecules. As we noted above the diamond C-F line remains when annealing to 700 °C. From the literature,¹⁷ it is known that a higher temperature (about 1400 K) is required to fully desorb the surface fluorine. In the present experiment, however, annealing to temperatures exceeding 550 °C causes a small degree of fluorine desorption indicated both by a reduction in the intensity of the diamond C-F line and the development of a shoulder positioned at a BE of about -1 eV with respect to the diamond bulk peak, which is attributed to π -bonded surface carbon atoms.^{23,24}

Figure 1(b) shows the corresponding F1s spectra. The F1s spectra have been fitted with two components which, for

the as-prepared sample, have binding energies of 685.10 eV and 686.15 eV. It is evident that annealing causes the component at higher BE to drop in intensity until it vanishes above 350 °C while the low BE F1s component remains. This behaviour is consistent with the observations made for the C1s data. The F1s line presents after annealing above 350 °C has a BE equal to that reported by Freedman *et al.*^{10,11} for the (100) and (111) surfaces and similar to the 685.8 eV reported by Smentkowski *et al.*¹⁷ and by us for the fluorinated diamond (100) surface;¹⁸ hence, it is due to fluorine bonded to the diamond surface. The higher-BE component, which is removed by annealing, is then assigned to F atoms in the absorbed fluorocarbon species, corresponding to the intense CF₁ component in the C1s spectrum.

Having identified the observed core level features we now consider the electronic properties of the monofluoride diamond surface. The evolution with annealing temperature of the low kinetic energy electron cut off is illustrated in Figure 2. An onset energy of 10.05 eV defined as the edge linearly extrapolated to the base line is measured for the as-prepared surface. This corresponds to a work function of 7.40 ± 0.05 eV. Annealing to 700 °C gives rise to a downward shift of the cut off and corresponding lowering of the work function by 0.62 eV. The electron affinity is given by $\chi = \phi + (E_F - E_{VBM}) - E_{gap}$ and requires, in addition, the position of the Fermi energy, E_F , relative to the valence band maximum E_{VBM} . The value of $(E_F - E_{VBM})$ was determined from the BE of the bulk diamond C1s component and using the known fixed energy separation between the valence band maximum (VBM) and the C1s line of 283.9 ± 0.1 eV as reported by Maier *et al.*²⁵ The band gap of diamond, E_{gap} , is 5.47 eV. The variations of the work function, electron affinity, and $(E_F - E_{VBM})$ with annealing temperature are plotted in Figure 3. The statistical error of the electron affinity is ± 0.1 eV with a systematic uncertainty of ± 0.1 from the determination of $(E_F - E_{VBM})$.

The variation with the temperature of the work function and electron affinity follows two distinct regimes. Starting with a value of 7.40 eV, the work function decreases only a little for annealing temperatures up to 350 °C. Above 350 °C,

FIG. 2. Secondary electron distribution ($\hbar\omega = 60$ eV) for the as-prepared surface and after annealing to the temperatures shown. The solid lines illustrate how the low-energy electron cut-off was determined from the intersection of the baseline with the leading edge of the low energy peak.

FIG. 3. The evolution of the work function (solid squares), electron affinity (open circles), and band bending (inset) for the F:C(100) surface with annealing temperature.

a steeper descent takes the work function to a level of 6.78 eV after the 700 °C anneal. Because the band bending ($E_F - E_{VBM}$) increases almost linearly by a modest 0.2 eV over the whole temperature range (inset of Fig. 3), the electron affinity shows a trend similar to that of the work function, dropping from an initial 2.64 eV to the final 2.20 eV. We assume that the initial changes in ϕ , χ , and band bending are brought about by the thermally induced desorption of physisorbed fluorocarbons while above 350 °C surface-bonded fluorine starts to desorb, albeit at a much smaller rate. The removal of adsorbed fluorocarbon contamination does not make a significant contribution to the dipole potential while even small changes in the concentration of the highly polar surface C–F bonds reduces the dipole density and with it the dipole potential responsible for the F-induced increase in χ and hence ϕ .

Annealing the sample to 350 °C is sufficient to drive the desorption of the majority ($\sim 90\%$) of the adsorbed fluorocarbon, observed as a reduction in the F1s CF₁ peak, but not that of fluorine bonded to the diamond surface atoms since there is no evidence of carbon dimer formation at this temperature in the C1s. In contrast, previous reports showed a distinct π -bonded carbon C1s line for samples that were considered to be fluorine-saturated.^{10,11,14} We therefore consider the surface after annealing at 350 °C to be close to the ideal case, with very little fluorocarbon contamination but an otherwise fully fluorinated (100) diamond surface with one F atom bonded to each surface C atom. For the surface in this state, the work function, electron affinity, and $(E_F - E_{VBM})$ were found to be 7.24 eV, 2.56 eV, and 0.79 eV, respectively. The value of $(E_F - E_{VBM})$ in the bulk is taken to be 0.3 ± 0.1 eV,²⁶ which implies an upward band bending of 0.5 eV at the surface. Figure 4 gives an energy level diagram for this surface. The work function and electron affinity presented here are the highest reported for any diamond surface termination. To put this in context, the corresponding values for the oxygen-terminated (100) surface are 6.4 and 1.7 eV, respectively.²⁵ Furthermore, the experimentally determined electron affinity for F:C(100) is considerably higher than the value of 2.13 eV recently predicted by density functional theory calculations.²¹

FIG. 4. Schematic energy level diagram of the F:C(100)-(2 × 1) surface based upon parameters measured after annealing the sample to 350 °C.

The presence of adsorbed fluorocarbon has been reported for some F-terminated diamond samples,^{19,20} but not for others,^{1,10,11,14} and seems to be a peculiarity of the fluorination technique employed here. The deposition of fluorocarbon adlayers from fluorocarbon plasmas has also been described briefly by Schwartzman *et al.*²⁰ For the case at hand, it is plausible that hydrocarbon molecules in the preparation vacuum chamber are fluorinated along with the sample and adsorb onto its surface as the sample cools. Let us finally remark about the role the fluorocarbon layer plays in governing the properties of the underlying F:C(100) surface. The fluorocarbon adlayer has been suggested to act as a protective layer that prevents oxidation and reduction of the surface.^{19,20} While the presence of an adsorbed fluorocarbon has only a small effect of the work function and electron affinity of the surface, as a hydrophobic layer it may play an important role in protecting the underlying fluorine-terminated diamond surface, yet it can be removed by moderate annealing *in-vacuo* as we have demonstrated.

In summary, synchrotron-based photoelectron spectroscopy has been employed to characterise the fluorine-terminated C(100) diamond surface prepared via the dissociation of XeF₂. After the removal of a fluorocarbon layer via sample annealing at 350 °C, the work function and electron affinity of the surface were measured to be 7.24 eV and 2.56 eV, respectively. The surface has been found to be stable up to at least 350 °C, which is high enough to remove

most of the adsorbed fluorocarbon present after some fluorination procedures.

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