Origin of carbon 1s binding energy variance in diamond.

Michael Walter,¹,²,³, Filippo Mangolini,⁴ J. Brandon McClimon,⁵ Robert W. Carpick,⁶ and Michael Moseler¹,⁷,³

¹Fraunhofer IWM, MikroTribologie Centrum μTC, Wöhlerstrasse 11, D-79108 Freiburg, Germany
²FIT Freiburg Centre for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany
³Institute of Physics, University of Freiburg, Herrmann-Herder-Straße 3, D-79104 Freiburg, Germany
⁴Materials Science and Engineering Program and Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA
⁵Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia 19104, USA
⁶Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA
⁷Freiburger Materialforschungszentrum, Universität Freiburg, Stefan-Meier-Straße 21, D-79104 Freiburg, Germany

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The quantitative evaluation of the carbon hybridization state by X-ray photoelectron spectroscopy (XPS) has been a surface-analysis problem for the last three decades due to the challenges associated with the unambiguous identification of the characteristic binding energy values for sp² and sp³-bonded carbon. While the sp³ binding energy is well established, there is disagreement for the sp³ value in the literature. Here, we compute the binding energy values for model structures of pure and doped-diamond using density functional theory. The simulation results indicate that the large band-gap of diamond allows defects to pin the Fermi level, which results in large variations of the C(1s) core electron energies for sp³-bonded carbon, in agreement with the broad range of experimental C(1s) binding energy values for sp³ carbon reported in the literature. Fermi level pinning by boron is demonstrated by experimental C(1s) binding energies of highly B-doped ultrananocrystalline diamond that are in good agreement to simulations.

X-ray photoelectron spectroscopy is one of the most powerful tools for the characterization of carbon-based materials. The analysis of the bonding configuration of carbon is normally carried out by XPS through the acquisition of carbon 1s (C(1s)) spectra. The spectra are often fitted with two distinct features, one assigned to threefold-coordinated (sp²) carbon and one assigned to fourfold-coordinated (sp³) carbon. In spite of the wide use of this analytical procedure for the quantitative evaluation of the carbon hybridization state on the basis of C(1s) XPS signals, the validity of this methodology has recently been questioned²⁷ and still remains a matter of discussion in the literature.

We have recently shown that absolute XPS peak positions can be predicted by facile spin-paired DFT calculations within the frozen core approximation⁷. In this approach, an empirical shift appears that can be obtained from experimental gas-phase XPS data. The main difficulty in assigning core hole energies in general, and C(1s) energies in particular, is the unambiguous definition of the reference energy. This is not the case for gas-phase investigations, where the energy of an electron in vacuum far away from the mother ion can be used as a well-defined reference for the core electron binding energy $E_B$.

For solid samples the Fermi energy is usually used as the reference energy level but this energy can only be defined correctly for systems without a band gap, i.e., metals or semi-metallic systems like graphite. Accordingly, the experimental variation in C(1s) energies of semi-metal graphite is moderate and found to range from 284.28 eV to 284.63 eV²¹. Diamond, in contrast, has a very large band gap (its experimental value is 5.5 eV²²), which hinders the consistent definition of an energy reference. Additional difficulties arise from the presence of defects, impurities, and dopants in diamond (such as nitrogen or boron²³,²⁴), which may pin the Fermi energy. These factors, together with effects of surface charging when acquiring XPS spectra on diamond, have resulted in the publication of a wide range of binding energy values for the C(1s) signal of sp³-bonded carbon. Despite the difficulties in unambiguously assigning a characteristic binding energy value to sp³-bonded carbon, the quantitative evaluation of the carbon hybridization state on the basis of C(1s) XPS signals is still widely performed on the basis of fitting the C(1s) XPS spectra with two synthetic peaks, one assigned to sp²-hybridized carbon and one to sp³-hybridized carbon. Here, we use DFT calculations to compute the characteristic C(1s) binding energy values for sp³-bonded carbon in diamond and sp²-bonded carbon in graphite.

Our spin-unpolarized DFT calculations were carried out with the GPAW²⁹ package, an implementation of the projector augmented wave (PAW) method. The PAW method splits the Kohn-Sham wave functions into a smooth part, representable on configuration or momentum space grids, and corrections that are local near to the atoms. We use the configuration space grid implementation, and apply a grid spacing of 0.2 Å for representing the smooth part of the Kohn-Sham wavefunctions, unless noted otherwise. The exchange correlation energy was approximated by the generalized gradient correction.

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as proposed by Perdew, Burke and Ernzerhof (PBE)\cite{Perdew1996}. The structures were relaxed until all forces on the atoms dropped below 0.05 eV Å\(^{-1}\).

Lower energy atomic states can be conveniently held fixed in their atomic form within the frozen core approximation, where we include the 1s electrons for C and the diamond dopant atoms B, N, and the 1s, 2s, 2p electrons for the diamond dopant atom P in our calculations. A similar approach is adopted to describe the core hole by lowering the occupation of the relevant state in the atomic calculation by one. The resulting Kohn-Sham orbitals are then used to construct the frozen core.

XPS energies of molecules or clusters in the gas phase are well defined by the many body ground state energy \(E_0\) and the core hole excited energy \(E_{ch}^{+}\). The latter can be approximated as the ground state of the system with a core hole in the frozen core, where the self-consistent calculation of the valence orbitals in the field of the core hole automatically takes into account relaxation effects. The photoelectrons’ binding energy is then:

\[
E_B = E_{ch}^{+} - E_0 .
\]

(1)

XPS energies for periodic systems as modeled here have to be treated in a mixed many-body and single-particle picture. Experimentally, the core level energy is measured relative to the single particle Fermi level \(\varepsilon_F\) that is aligned to the Fermi level of the detector by holding them at a common ground:

\[
E_F^B = E_{ch}^{+} - E_0 + \varepsilon_F .
\]

(2)

The computational difficulty of charged super-cells\cite{Jackson1985} for the description of the core ionized final state can be overcome by neutralizing the super-cell by an extra electron. This electron will locate itself in the lowest unoccupied “molecular” orbital (LUMO). Neglecting all other contributions due to the change in the electron density, this approach adds the energy \(\varepsilon_L\) to \(E_{ch}^{+}\). We obtain a binding energy in the neutralized system of the form:

\[
E_B^0 = (E_{ch}^{+} + \varepsilon_L) - E_0 = E_F^B + \varepsilon_L - \varepsilon_F .
\]

(3)

For a system without a band gap, \(\varepsilon_F = \varepsilon_L\) and hence conveniently \(E_F^B = E_B^0\). Systems with a band gap pose several problems, however. The position of the Fermi level \(\varepsilon_F\) is not defined in these systems which prohibits a defined value for \(E_F^B\).

In the first step, we consider the case of bulk diamond, which is the most problematic system due to its large band-gap. We model diamond by unit cells containing 64 atoms in tetrahedral configurations with the experimental lattice constant of 3.5669 Å\cite{InternationalTables} resulting in a CC bond-length of 1.55 Å. We are particularly interested in the effect of defects and impurities on the expected C(1s) value.

One of the most common impurities in natural diamond gemstones is nitrogen\cite{Rimmer1994} which can be present in amounts of up to 0.5 at. %\cite{Korolev1995}. Different possibilities for the presence of nitrogen are considered in the literature, where the replacement of a C atom with a N atom with or without a neighboring vacancy are believed to be the most common configurations\cite{Korolev1995}. In the former case, the P1 center\cite{Pickard1988} is modeled as the replacement of a single C atom by N (C\(_{60}\)N). The nitrogen vacancy (NV) center\cite{Pickard1997} is modeled by the replacement of a single C atom by N and a neighboring vacancy (C\(_{60}\)N). The A center\cite{Korolev1995} is two neighboring N atoms (C\(_{62}\)N\(_2\)), and the N3 center\cite{Korolev1995} consists of three nitrogen atoms near to a vacancy (C\(_{60}\)N\(_3\)). The B center\cite{Korolev1995} is four N surrounding a vacancy (C\(_{59}\)N\(_4\)).

Other common impurities are boron or phosphorus\cite{Korolev1994}. These elements are either present in natural diamonds (type Ib in the case of boron\cite{Pickard1995} or introduced artificially\cite{Pickard1988}. Boron- or phosphorus-doped structures are modeled by replacing a single C atom by B (C\(_{60}\)B) or P (C\(_{60}\)P), respectively. All model structures were relaxed to their next local minimum while the unit cell was kept fixed.

Fig. 1 shows the effect of defects on the diamond band structure. While the overall band-structure is rather similar in all cases, the defects or dopants introduce states at different positions within the diamond band gap. The gap is found to be 4.42 eV wide according to PBE\cite{Perdew1996}. Boron- or phosphorus-doped structures are modeled by replacing a single C atom by B (C\(_{60}\)B) or P (C\(_{60}\)P), respectively. All model structures were relaxed to their next local minimum while the unit cell was kept fixed.

The two N in C\(_{60}\)N\(_2\) slightly disturb a high lying unoccupied (acceptor) levels near to the conduction band edge \(\varepsilon_c\) and introduce a rather high occupied (donor) level above the valence band edge \(\varepsilon_v\) thus reducing the band gap. These levels show some variation with the wave vector in our calculation indicating interaction between periodic images. A similar effect is observed in C\(_{59}\)N\(_3\), where mainly states slightly above \(\varepsilon_v\) are introduced. Similar to pure diamond, the Fermi level \(\varepsilon_F\) is located in the middle between the maximum of the highest occupied and the minimum of the lowest unoccupied band. An infinitesimal charge could move the Fermi energy towards the valence or the conduction band depending on its sign.

The freedom of moving the Fermi level by slight charging is not the case anymore for the other models presented in Fig. 1 as these contain an unpaired electron. There, \(\varepsilon_F\) is pinned by this half-filled state and is therefore well defined. The exact positions of the Fermi level relative to the band structure of diamond varies largely depending on the nature of the defect, however. While the half filled state is close to the conduction band in C\(_{63}\)N, it is found in the middle of the band gap for C\(_{59}\)N and C\(_{60}\)N\(_3\). The most extreme positions are found in C\(_{63}\)B where the partially filled states (degenerate at the Γ-point) are near to \(\varepsilon_v\)\cite{Korolev1995} and for C\(_{60}\)P where partially filled states are found near to \(\varepsilon_c\).
Figure 1. Band structure of diamond, pure and with defects. Fully occupied bands are colored in green, partly occupied bands in red and empty bands in blue. The broken line shows the Fermi level $\varepsilon_F$.

Assuming that the C(1s) core level energy relative to the vacuum level $E_B$ is mainly constant for carbon atoms far from any defect, the variation in $\varepsilon_F$ will be reflected in a variation in $E_B^0$ [c.f. eq. (2)], which is indeed the case as will be shown now.

The C(1s) XPS spectra corresponding to the defects are compared to pure diamond in Fig. 2. The unshifted spectra (broken lines, corresponding to $E_B^0$ in eq. (2)) of the C$_{64}$, C$_{62}$N$_2$ and C$_{59}$N$_4$ models are very similar in their main peak as they share the same lowest unoccupied level (c.f. Fig. 1). The spectra are different when they are corrected to $\varepsilon_F$ located at the center of the gap due to the different band gap values. Unshifted $E_B^0$ and shifted $E_B^F$ coincide for the cases involving an unpaired electron as $\varepsilon_F = \varepsilon_F$ in these cases. The largest core level energy is found for C$_{63}$N and the lowest energy for C$_{63}$B as expected from the positions of the unpaired levels in Fig. 1. The main C(1s) energy in C$_{63}$B of 284.27 eV is in good agreement to the value of 284.4 eV measured for artificially boron-doped ultranano-crystalline diamond (UNCD) found at 284.09$\pm$0.05 eV discussed in detail below.

Table I. Pure and defected diamond model structures, their PBE band gaps, the position of their main C(1s) peak and the resulting shift relative to graphite C(1s) (see also Fig. 2).

| Structure     | Model gap [eV] | C(1s) [eV] | Shift [eV] |
|---------------|----------------|------------|------------|
| pure          | C$_{64}$       | 4.42       | 286.36     | 1.85       |
| P1 center     | C$_{63}$N      | 0          | 288.41     | 3.43       |
| NV center     | C$_{62}$N      | 0          | 286.15     | 1.68       |
| A center      | C$_{62}$N$_2$  | 2.64       | 287.17     | 2.65       |
| N3 center     | C$_{60}$N$_3$  | 0          | 286.70     | 2.18       |
| B center      | C$_{60}$N$_4$  | 3.65       | 286.74     | 2.22       |
| B             | C$_{61}$B      | 0          | 284.27     | -0.25      |
| P             | C$_{61}$P      | 0          | 288.41     | 3.89       |
| graphite      | C$_{72}$       | 0          | 284.52     |            |

Figure 2. Absolute XPS spectra for the models derived from the C$_{64}$ models without and with defects and impurities. The broken line is without the correction to $\varepsilon_F$ (i.e., $E_B^F$) and the solid line includes this shift (i.e., $E_B^F$). The spectra are obtained by convoluting with Gaussians of 0.24 eV full width at half maximum (FWHM). The broken vertical line indicates graphite C(1s) energy.
four carbon atoms surrounding N is found in C\textsubscript{63}N. Here, the N has to share the bonds with four C due to symmetry. The NC bond-length is thus much longer (1.60 Å) exceeding the diamond CC bond.

For the N impurity with a neighboring vacancy (C\textsubscript{62}N), the lower energy peak (283.2 eV) is from the three carbons surrounding the cavity and the higher energy peak (287 eV) from the three carbons connected to nitrogen. The NC bond-length of 1.48 Å is quite similar to N(CH\textsubscript{3})\textsubscript{3} again.

The four carbon atoms surrounding the P atom symmetrically with a bond length of 1.70 Å in C\textsubscript{63}P produce the lower energy shoulder in the corresponding C(1s) spectrum. Similarly, the lower energy peak around 283 eV in C\textsubscript{63}B is from the four carbon atoms surrounding B. Structurally, the B impurity atom shares four equal bonds with large CB bond length of 1.59 Å as compared to 1.55 in CC.

Besides these side peaks the main effect is the strong variation of the C(1s) peak with defect type. A defect in diamond dictates the C(1s) position of E\textsubscript{F} even for carbon atoms far apart due to its influence on the Fermi level. Therefore we can conclude that diamond is a problematic system to define the sp\textsuperscript{3} C(1s) energy as the C(1s) energy depends on the nature of defects that are omnipresent in real diamonds. This finding can contribute explaining the broad range of C(1s) values for diamond reported in the literature.

We finally seek for an experimental validation of the computational analysis presented so far. Experimental XPS data were acquired on hydrogen-terminated ultrananocrystalline diamond (UNCD Aqua 25, Advanced Diamond Technologies, Romeoville, IL, USA), boron-doped ultrananocrystalline diamond (UNCD Aqua 25, Advanced Diamond Technologies, Romeoville, IL, USA),\textsuperscript{23} and freshly cleaved highly ordered pyrolytic graphite (HOPG, grade 2, SPI Supplies, West Chester, PA, USA). Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements indicated that the fraction of sp\textsuperscript{3}-bonded carbon in undoped and boron-doped UNCD was 94±/−3% and 96±/−3%, respectively.\textsuperscript{24,25} In the present work, the X-ray source was run at 30 mA and 12 kV, whereas the analyzer was operated in constant-analyzer-energy (CAE) mode. Survey spectra were acquired with the pass energy and step size equal to 200 eV and 1 eV, respectively. For the high-resolution (HR) spectra, the pass energy and step size were, respectively, 100 and 0.05 eV (full width at half maximum (FWHM) of the peak height for the Ag 3d\textsubscript{5/2} equal to 0.57 eV). The curved slit at the entrance of the hemispherical analyzer has a width of 0.8 mm. The residual pressure in the analysis chamber was always below 10\textsuperscript{−6} Pa. The spectrometer was calibrated according to ISO 15472:2001 with an accuracy better than ±0.05 eV. All the XPS results reported here are mean values calculated from at least three independent measurements, with the corresponding standard deviation reported.

The DFT calculations are in good agreement with experimental XPS data acquired on undoped and B-doped UNCD shown in Fig. 3. First, the binding energy of the characteristic C(1s) peak for B-doped UNCD is lower than the binding energy of the C(1s) signal of undoped UNCD (284.09±0.05 eV vs. 284.47±0.05 eV, respectively in experiments) and agrees well with the 284.27 eV from DFT. Second, as in the simulation, there is a clear shoulder on the lower binding energy side in the experiment. Note that the shoulder on the high binding energy side of the experimental spectrum (286-287 eV) is caused by C-O bonds in the near-surface region.

In conclusion, we have shown that the sp\textsuperscript{3} C(1s) binding energies determined from diamond are highly affected by the presence and nature of defects. This strong dependence of the binding energy of the characteristic C(1s) peak for sp\textsuperscript{3} carbon on the type and number density of defects in diamond samples makes the use of diamond as reference material for XPS analysis potentially misleading. This is a consequence of the large gap, i.e. the insulating nature\textsuperscript{26} of undoped carbon and the resulting absence of a defined reference energy within the system.

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