Novel Doping of Diamond using C_{60}

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Diamond is a truly remarkable material for several reasons. Apart from its celebrated optical properties that make it suitable for use as a gemstone, diamond's large electronic band gap, exceptionally high thermal conductivity, and high tolerance to radiation - amongst other properties - suggest that it would exhibit outstanding performance in applications such as power diodes, high-frequency field-effect transistors, and particle detectors.

However, the development of such diamond-based electronic devices has been held back by technological problems. One of these is the lack of suitable shallow donors and acceptors for efficient doping of the diamond bulk. The best bulk dopants are boron, with an acceptor level at 0.37 eV, and phosphorus, which has a donor level at 0.6 eV. Although there has been intensive study to try to find shallow donors - and several computational studies have been carried out [1, 2] - up to now there has been little success. Some reports have suggested that sulphur [3] and boron-hydrogen defects [4] would form shallow donors, but these claims have not been substantiated.

It is less well known that diamond also possesses a number of outstanding surface properties. Of particular interest here is the possibility to lower the ionisation potential substantially by bonding the surface atoms to hydrogen. This effect is due to the dipole moment of the heteropolar bond between H and C. In contrast with most other constituents of semiconductor devices such as Si, Ge, Ga, or As, carbon (with a Pauling electronegativity of 2.5) is more electronegative than H (at 2.1), and thus the dipole layer associated with the hydrogen termination of diamond creates a downward potential energy step of ~1.5 eV, lowering the work function for any electron that attempts to escape. This leads to an ionisation potential of around 4 eV, and as a consequence, electron transfer from the valence band to physisorbed adsorbates can be energetically favourable. Figure 1 shows the band structures referenced to the vacuum level for hydrogenated, oxygenated, and OH-terminated (001) surfaces. The negative electron affinity clearly arises from the conduction band states lying above the vacuum level, especially in the hydrogenated case. A transfer of charge accounts for the *p*-type surface conductivity of hydrogenated diamond [5, 6]. Here, it is believed that OH_3^+ electron acceptors, lying within the ubiquitous water layer on the diamond surface, undergo a chemical reduction to molecular hydrogen and water
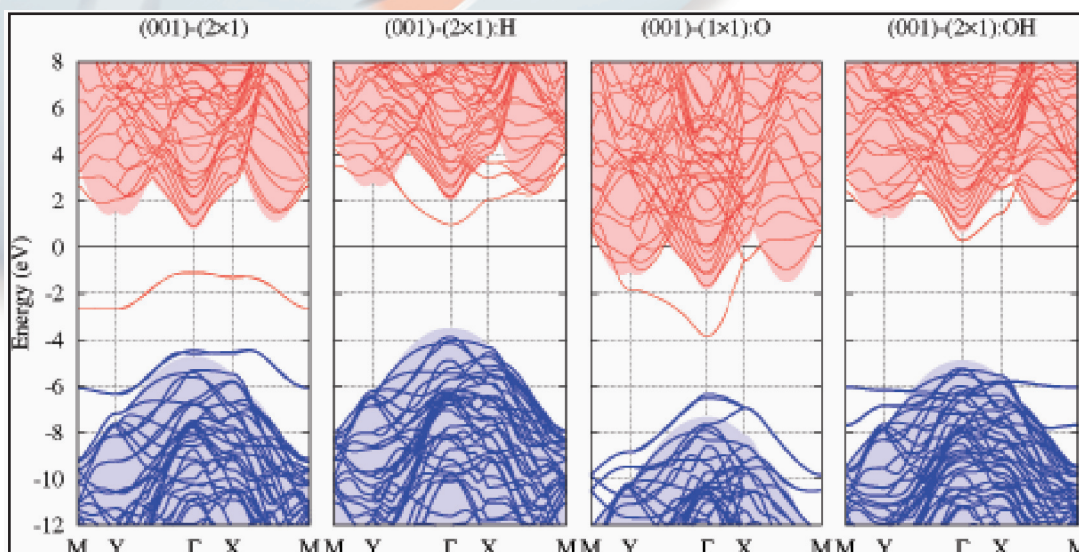

Figure 1: Calculated electronic band structures for the most stable configurations of the different surface terminations considered in these investigations. The zero of the energy scale is the vacuum potential for each system. Occupied and unoccupied levels are shown as thick blue and thin red lines respectively, and are superimposed upon shaded regions that represent the aligned band structure for bulk diamond. Note that the vacuum level lies above the conduction band bottom for all except the oxygenated surface, giving a negative electron affinity. However, this is greatest for the hydrogenated surface.

molecules after electron transfer from diamond. The charge transfer induces an electrostatic potential that confines the holes in a near-surface layer, but leaves them free to move parallel to the surface.

The driving force for the electron transfer between two materials is a low ionisation potential of one material, and a high electron affinity χ of the other. The LUMO level of the aqueous layer on diamond lies below the top of the valence band at the diamond/electrolyte interface and causes charge exchange. The resulting Fermi level lies below the valence band top at the interface and this energy difference determines the density of holes in the diamond.

The complex nature of the atmospheric surface acceptors as part of an electrochemical system of solvated ions brings about a number of obvious disadvantages for electronic applications. The concentration of holes induced is difficult to control and depends sensitively on ambient conditions. Moreover, being physisorbed on the surface, the acceptor layer is of only limited thermal stability and electronic devices based on atmosphere-induced surface conductivity suffer from long-term instabilities. For the production of devices exploiting this effect, a thermally stable, non-volatile, and reproducible surface adsorbate would be preferred. Hence there is significant interest in finding a suitable *solid-state* transfer dopant for diamond. Useful adsorbates would be chemically inert and leave the hydrogenated surface intact. For these reasons alternative adsorbates are highly desirable, and the quest for them can be guided to first order by a value of $\chi \sim 4$ eV.

An initial computational study using the AIMPRO local-density-functional code had predicted a transfer doping of diamond caused by the extraction of electrons from the hydrogenated diamond surfaces by an adsorbed molecule of C_{60} [6]. C_{60} is non-toxic, readily available in bulk quantities, and is unlikely to disrupt the diamond surface. Although its electron affinity is measured as 2.7 eV, our initial calculations found clear evidence for an electron transfer from diamond to C_{60} effected through a strong polarisation of the interface stabilising the charge transfer.

This anticipated experiments carried out in Erlangen that vindicated the theoretical predictions [7].

More recent calculations (see Figure 2) have confirmed the effect. These were carried out in 316-atom cells and the resulting band structure, shown in Figure 3, demonstrates transfer doping between the adsorbate and diamond. These calculations require the largest computers and are at the upper end of useful applications. While most *ab-initio* studies of surfaces are content to study a few adsorbed atoms as in a small molecule, here the adsorbate has 60 atoms!
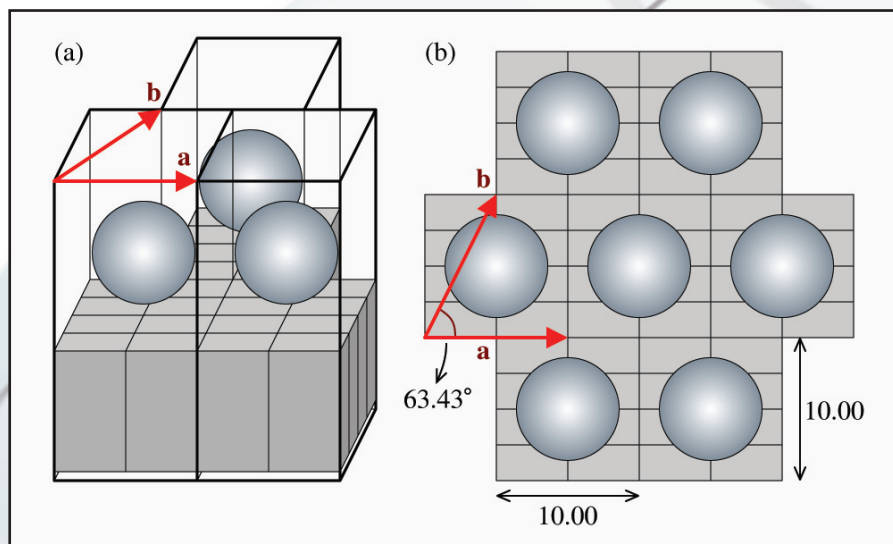
We did not limit ourselves to the study of C_{60}. We then reasoned that $C_{60}F_{36}$ would be a much superior transfer dopant, owing to its larger electron affinity. This has been confirmed with further calculations carried out in a 416-atom cell. Figure 4 demonstrates once again that electron transfer to the molecule will easily occur. These predictions have also been recently verified by the Erlangen group [8]. In summary, *ab-initio* local-density-functional calculations have demonstrated the basis for transfer doping between hydrogenated diamond surfaces and electron-attractive adsorbates. Furthermore, these calculations anticipated experimental results and show the value of computational modelling in addressing complex questions.
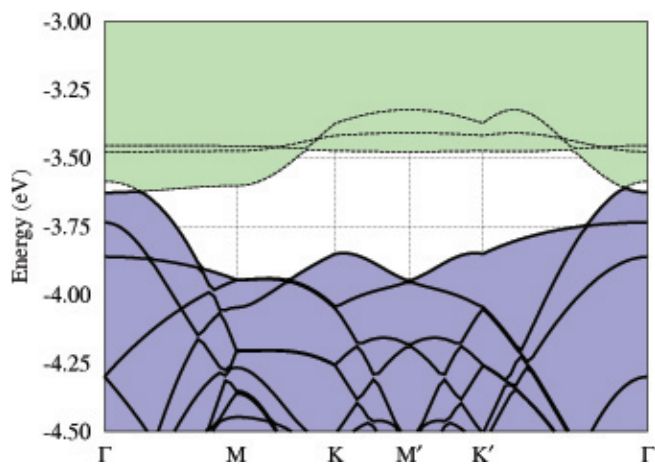

Figure 2: Modelling a monolayer of C_{60} atop the diamond surface. (a) The minimal unit cell for the diamond slab is repeated to form a square 'platform', and a molecule of C_{60} (shown as a large sphere) is placed on the platform. The combined system is repeated via the lattice vectors **a** and **b**, shown as thick arrows. C_{60} is then in a quasi-hexagonal packing, yet the underlying diamond surface tessellates correctly. Dimensions are given in Å. The spacing ~ 10.01 Å between molecules is very close to that found in a (111) plane of solid C_{60}.

Figure 3: Electronic band structure for a C_{60} monolayer adjacent to diamond. The zero of the energy scale is the system vacuum level. Occupied and empty electronic states are shown by thick solid and thin dashed lines respectively. The metallic nature of the system accounts for a transfer doping effect.
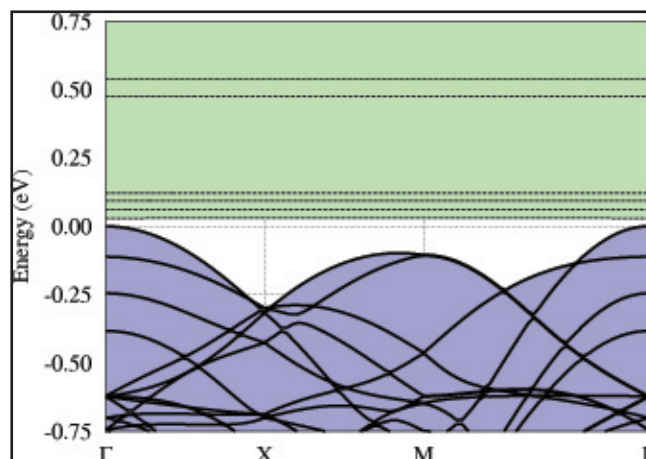

Figure 4: Electronic band structure for $C_{60}F_{36}$ on the diamond surface. The zero of the energy scale has been aligned with the diamond valence band top. Occupied and empty electronic states are shown by thick solid and thin dashed lines respectively. The tiny separation between occupied and empty levels imply transfer doping can occur in this system.

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