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2005 J. Phys.: Condens. Matter 17 L21

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LETTER TO THE EDITOR

First-principles study of C_{60} and $C_{60}F_{36}$ as transfer dopants for p-type diamond

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Received 15 November 2004, in final form 3 December 2004

Published 20 December 2004

Online at stacks.iop.org/JPhysCM/17/L21**Abstract**

Ab initio density-functional-theory has been used to investigate transfer doping between C_{60} monolayers and the hydrogenated (100) diamond surface. An electron transfer from diamond to C_{60} is predicted for a C_{60} coverage of around one monolayer, and the possibility of electron transfer is expected to increase for higher coverages, leading to an accumulation of holes at the diamond surface. It has been found that the greater electron affinity of *fluorinated* C_{60} is likely to enhance the effect. Results are reported on the structural and electronic properties of isolated C_{60} and $C_{60}F_{36}$ molecules, solid C_{60} , and a monolayer of each material adjacent to the (100)-(2 × 1):H diamond surface.

(Some figures in this article are in colour only in the electronic version)

Presently, the favoured model explaining the p-type surface conductivity discovered on hydrogenated diamond surfaces [1] is that of *transfer doping* [2–4], in which a constituent of the atmosphere, likely present in an aqueous layer on the diamond surface, extracts electrons from the near-surface region and causes an accumulation of holes. However, 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.

Previous theoretical work based on cluster calculations has predicted the extraction of an electron from a hydrogenated diamond surface by an adsorbed molecule of C_{60} [5], suggesting that, in its solid form, C_{60} could be a suitable transfer dopant. C_{60} is non-toxic, readily available in bulk quantities, and is unlikely to disrupt the diamond surface C–H bonds. This letter describes an in-depth study of C_{60} on diamond using the supercell formalism. Systems of molecular C_{60} , solid C_{60} , and C_{60} adjacent to the (100), 2 × 1-reconstructed, mono-hydrogenated diamond surface have been investigated using *ab initio* density-functional-theory

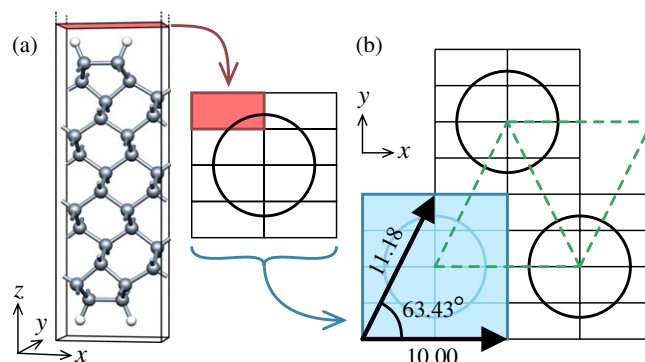


Figure 1. Method used to model a monolayer of C_{60} on the diamond surface. (a) The minimal unit cell for the diamond slab was repeated in x and y to form a square ‘platform’. (b) A molecule of C_{60} (shown as a large circle) was placed on the platform, and the combined system was repeated via the lattice vectors shown as thick black arrows. C_{60} is then quasi-hexagonally packed, yet the underlying diamond surface still tessellates correctly. Dimensions are given in Å. Note that the spacing between molecule centres in a (111) monolayer of solid C_{60} is ~ 10.01 Å.

(DFT) supercell calculations, as implemented in the AIMPRO code [6]. Preliminary results from these calculations have been reported earlier [7].

It is known both theoretically [8, 9] and experimentally [10] that the fluorinated derivatives of C_{60} have increased electron affinities. $C_{60}F_{36}$ is a particularly stable [11] fluorinated fullerene that has been modelled [12], synthesized [13], and studied [14]. It is expected to be more efficient at extracting electrons from diamond than C_{60} , hence it has also been considered in this investigation.

The (100)-(2 × 1):H diamond surface will be referred to in this work as simply the (100) surface. An orthorhombic unit cell (shown in figure 1(a)) was devised, such that when repeated by suitable lattice vectors, slabs composed of 14 monolayer planes of diamond with infinite planar extent were formed, with repeating slabs separated by layers of vacuum 20 Å thick.

Under normal conditions, C_{60} is stable as a face-centred cubic (fcc) packed crystal with a conventional lattice parameter of 14.16–14.17 Å [15, 16], and 14.16 Å has been adopted in these calculations. Isolated C_{60} molecules have been simulated by progressively increasing the lattice parameter of the solid until the total energy converged to within 1×10^{-4} Ha. C_{60} has also been simulated in a slab geometry in order to assess the electron affinity of the solid. A supercell was constructed that repeats to form four of the hexagonally-packed (111) monolayer planes of solid C_{60} , with a vacuum gap of 20 Å separating repeating slabs. For modelling C_{60} on diamond, a monolayer covering the diamond surface was created using the method described in figure 1. This combined C_{60} -and-diamond supercell contains a total of 316 atoms. In addition, the separate C_{60} -monolayer and diamond-substrate components of this system were each modelled in isolation.

Due to the larger size of the fluorinated fullerene molecule, $C_{60}F_{36}$ required a larger diamond platform than that used with C_{60} , hence a 14.14 Å-square area of (100) surface was used as the base. With this increased number of atoms in the supercell, the size of the calculation became prohibitive unless the number of layers in the diamond slab was reduced. Therefore, a slab containing 8 rather than 14 monolayers of diamond was used with $C_{60}F_{36}$, giving a combined system containing a total of 416 atoms.

Carbon and fluorine atoms were treated using HGH pseudopotentials [17], while atoms of hydrogen used the bare Coulomb potential. The basis sets employed consisted of s, p, and d Gaussian orbital functions with four exponents, centred at the atomic sites. Monkhorst–Pack

grids [18] of special k -points were generated to sample the system Brillouin zones. Grid parameters were varied independently for each system until total energies were converged to within 1×10^{-5} Ha. Charge densities were Fourier-transformed using plane waves, and total energies for all systems were likewise converged for a plane-wave energy cut-off of 300 Ha. Atomic relaxations were performed via a conjugate-gradients scheme until the energy change between subsequent iterations of structural optimization became less than 1×10^{-5} Ha.

For systems containing vacuum, the electrostatic potential energy was calculated along straight line paths passing through the material and into vacuum. Each system's value for the vacuum level E_{vac} was therefore determined, so that the electrical levels of different systems could be compared by aligning their respective values of E_{vac} . For the diamond slab, the value of E_{vac} was verified using the results of a plane-averaged potential calculated along a path normal to the planes.

Electron transfer from diamond to a candidate adsorbate can be anticipated if the electron affinity χ of the latter is greater than the diamond ionization potential (IP) I . To first order, these quantities are $-E_{\text{LU}}$ and $-E_{\text{HO}}$ respectively, where E_{LU} and E_{HO} are the energies of the lowest unoccupied (LU) and highest occupied (HO) levels of the separated adsorbate and diamond slab respectively, stated with respect to their vacuum levels. However, in a combined diamond and adsorbate system, these energy levels could be affected by both charge transfer and polarization. To properly treat these effects, a calculation of the levels of the combined system is therefore essential. The character of the resulting HO and LU levels can be found from Mulliken bond population analysis or by inspection of their wavefunctions.

The atomic geometry for the relaxed diamond surface is similar to that found in other theoretical work [19] and seen in experiment [20]. Line and plane-averaged potentials for the slab and for pure bulk diamond compared favourably. In addition, the energy difference between the valence-band top (VBT) and the average potential in the middle of the slab was calculated, and is within 0.02 eV of the same value calculated for bulk diamond. These results suggest that the slab is adequately thick, and that the position of the VBT in the slab is correctly described. The calculated IP for the slab is 3.90 eV, and so a candidate adsorbate material found to have χ around or greater than 3.90 eV could be expected to induce an exothermic electron transfer when combined with this diamond surface.

The calculated energy gap E_{g} for the *isolated* C_{60} molecule is 1.75 eV, which compares well with results from other theoretical work using various methods [9, 21, 22], and indeed very favourably with the experimental value of 1.8 eV [23, 24]. However, the energy levels of C_{60} altered significantly as it went from a molecule to a solid. The results are summarized in table 1. In particular, E_{g} for solid C_{60} is just 61.7% of the value calculated for isolated molecules. This demonstrates that clustering of C_{60} leads to increased values of χ and decreased values of the IP, while the position of the centre of the band gap remains approximately unchanged. Accordingly, higher coverages of C_{60} on diamond should increase the possibility of charge transfer. Nevertheless, χ remained smaller than the IP of diamond, and charge transfer was not anticipated at this stage.

However, considerable shifts were observed in the energy levels of C_{60} and the diamond slab when the combined system was modelled. Relative to their values for separated systems, the C_{60} energy levels have fallen by ~ 0.36 eV while those of the diamond have risen by ~ 0.30 eV. This is sufficient to bring the C_{60} monolayer's LU state 0.04 eV below the VBT of the diamond at the Γ point of the calculation. Therefore, a direct electron transfer is observed (see figure 2). Mulliken and wavefunction analyses performed at Γ confirm that the LU (hole) state is localized primarily in the diamond.

The C_{60} molecule was stable on the diamond surface with its lowermost C atoms separated from the surface H layer by around 1.93 Å. The binding energy E_{b} of C_{60} to the diamond

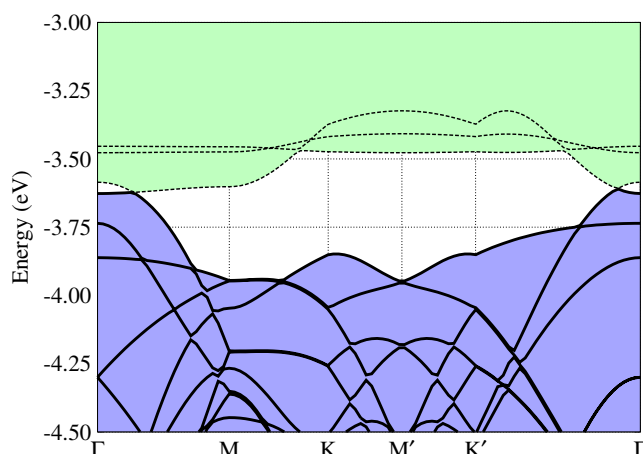


Figure 2. Electronic band structure for a C_{60} monolayer adjacent to diamond. The zero of the energy scale is the system vacuum level. Occupied and empty electronic states are shown by thick solid and thin dashed lines respectively.

Table 1. Summary of calculated values in eV, where χ : electron affinity; I : ionization potential; E_g : minimal energy gap between highest occupied and lowest unoccupied electronic states.

System	χ	I	E_g
C(100)-(2 × 1):H	—	3.90	—
C_{60} (isolated molecule)	3.09	4.84	1.75
C_{60} (monolayer)	3.27	4.63	1.36
C_{60} (four-layer slab)	3.43	4.57	1.15
C_{60} (fcc solid)	—	—	1.08
$C_{60}F_{36}$ (isolated molecule)	4.94	8.60	3.65

surface was determined, firstly from $E_b = [E(C_{60}) + E(\text{Di})] - E(C_{60}\text{-Di})$ (where $E(C_{60})$, $E(\text{Di})$, and $E(C_{60}\text{-Di})$ are the relaxed total energies of the isolated C_{60} monolayer, isolated diamond platform, and combined system respectively), and secondly by steadily increasing the separation of the C_{60} monolayer and the diamond slab and noting the effect on the total energy. Values for E_b found from the two methods are +1.50 and +1.52 eV respectively, indicating that the C_{60} monolayer is bound to the hydrogenated diamond surface by about 1.5 eV per molecule.

For the calculations on $C_{60}F_{36}$, a low-energy structure derived from Hartree-Fock calculations [26] was used. For the isolated $C_{60}F_{36}$ molecule, the calculated energy gap, electron affinity, and IP are 3.65, 4.94, and 8.60 eV respectively. As expected, the electron affinity of the $C_{60}F_{36}$ molecule greatly exceeds that of C_{60} . In the combined $C_{60}F_{36}$ and (8-monolayer) diamond system, the relaxed separation between the diamond surface H atoms and the F atoms on the molecule is 1.76 Å. Electronically, the unoccupied states due to the adsorbate lie above the diamond valence band throughout k -space. The $C_{60}F_{36}$ states do not show any significant dispersion, indicating that there is negligible inter-molecular interaction within the $C_{60}F_{36}$ monolayer, most likely as a consequence of the inability of the molecules to pack together as closely as in C_{60} . However, at the Γ point, the electronic energy gap is a negligible 0.03 eV (see figure 3), hence electron transfer is expected in practice at room temperature, even for very low coverages of $C_{60}F_{36}$. Indeed, the use of $k_B T = 0.01$ eV for the

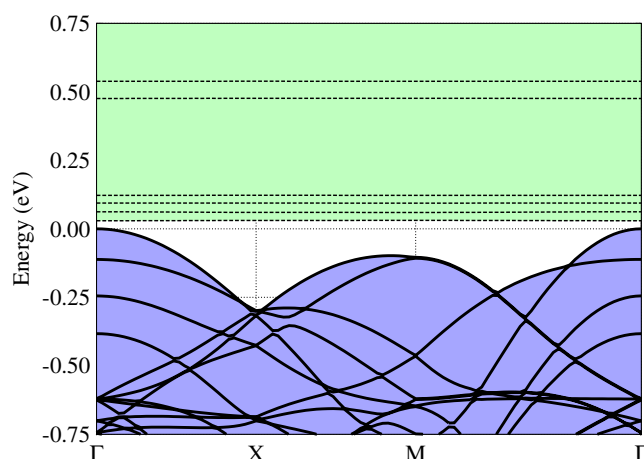


Figure 3. Electronic band structure for $C_{60}F_{36}$ on the diamond surface. The zero of the energy scale has been aligned with the diamond valence band top. Occupied and empty electronic states are shown by thick solid and thin dashed lines respectively.

Fermi filling in this calculation resulted in Γ -point occupancies of 1.62, 0.36, and 0.02 electrons respectively in the diamond VBT and the lowermost two states on the $C_{60}F_{36}$ molecule. This acceptor level 0.03 eV above the VBT represents an improvement in p-type doping of over an order of magnitude when compared against the 0.37 eV acceptor level of substitutional boron defects in the bulk. As was observed in the C_{60} -Di system, the $C_{60}F_{36}$ molecule does not significantly disturb the hydrogenated diamond surface.

In conclusion, *ab initio* density-functional-theory calculations have been performed to determine the structural and electronic properties of: molecular and solid C_{60} , C_{60} adjacent to the (100)-(2 × 1):H diamond surface, molecular $C_{60}F_{36}$, and $C_{60}F_{36}$ adjacent to the same surface. Dispersion of its electronic levels as C_{60} undergoes a molecule-to-solid transition increases the material's electron affinity, and hence its potential for transfer doping. Electron transfer from diamond to a C_{60} adsorbate has been observed for a coverage of one monolayer. However, the underestimation of the energy gap inherent in DFT suggests that the transfer may occur in practice for greater coverages, which would agree well with emergent experimental results [27, 25]. The electron affinity of $C_{60}F_{36}$ is greater than that of C_{60} , and electron transfer is predicted for $C_{60}F_{36}$ on diamond, even for very low coverages.

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