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p-type doping of graphene with F4-TCNQ

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Online at stacks.iop.org/JPhysCM/21/402001**Abstract**

We use local density function theory to study the electronic properties of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) deposited on a graphene surface. We show that charge transfer of 0.3 holes/molecule between graphene and F4-TCNQ occurs, which makes graphene p-type doped. These results are in agreement with experimental findings on F4-TCNQ.

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

1. Introduction

Graphene, a single atomic layer of carbon atoms that can be considered as a zero-gap semiconductor, is being intensively studied due to its unique properties such as high carrier mobility and extreme sensitivity to molecular adsorbates [1]. The type and the concentration of carriers in graphene, electron or holes, can be controlled by the introduction of metals or molecules on the graphene surface, thus making graphene of importance for electrical and optical applications. Both n-type and p-type doping have been successfully demonstrated: titanium and potassium [2] atoms and NH₃ [3] molecules as n-type dopants and NO₂ [4] and possibly tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) [5] effect p-type doping. F4-TCNQ (C₁₂N₄F₄) is an organic molecule that has a strong electron affinity and can be deposited easily for the fabrication of electronic devices. Along with C₆₀ and fluorinated C₆₀ [6, 7], it has been shown to be effective in p-doping diamond [8] as well as nanotubes [9].

In recent work [5], synchrotron-based high resolution photoemission spectroscopy (PES) has been used to study the effect of F4-TCNQ on the work function of epitaxial graphene (EG). The authors interpret their measurements as showing that the hole concentration on EG can be controlled by the deposition of F4-TCNQ. After 0.1 nm F4-TCNQ deposition the work function increased from 4.0 eV (pristine graphene) to 4.7 eV. After the deposition of 0.2 nm F4-TCNQ the work function increased to 5.3 eV. For greater thicknesses of F4-TCNQ the work function remained almost constant and this

was interpreted as indicating that the transfer of charge occurs at the F4-TCNQ/EG interface and becomes saturated with bulk depositions. The increase of the work function due to the F4-TCNQ deposition is a direct evidence of the charge transfer from the EG to the F4-TCNQ molecules. F4-TCNQ is also known to dope p-type carbon nanotube field-effect transistors where both the channel resistance and contact resistance were reduced by layer deposition of F4-TCNQ molecules.

In this paper we present the results of density functional theory calculations of the effect of F4-TCNQ upon the electronic properties of graphene. The results support the p-type doping of graphene by F4-TCNQ.

2. Method

All the calculations were performed using the AIMPRO density functional code [10]. The local density approximation (LDA) was used to represent the exchange correlation potential. It should be remarked that GGA calculations tend to give much lower binding energies and in many cases the fragments are not bound. This is the consequence of the neglect of van der Waals binding. In the present application, charge transfer is found which should lead to a greater binding energy.

The core electron of the atoms were treated using the Hartwigsen Goedecker Hutter (HGH) pseudopotentials [11]. The orbitals of the valence electrons consist of independent s-, p-, d-like Gaussian functions centred on atoms. The electronic levels were filled using Fermi–Dirac statistics with $k_B T = 0.01$ eV and metallic filling. The system was modelled using

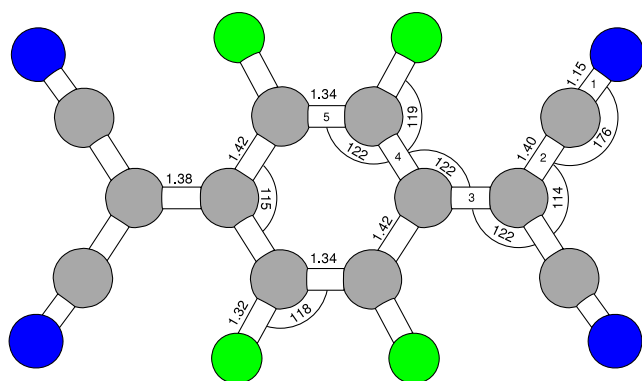


Figure 1. Molecular structure of F4-TCNQ. Bond lengths are in Å and angles in degrees.

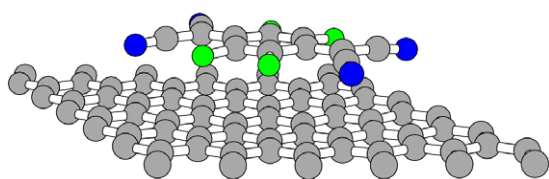


Figure 2. Molecule of F4-TCNQ on top of graphene.

Table 1. Comparison between present calculations of bond lengths in F4-TCNQ (Å), with previous GGA calculations. For comparison purposes, the last column shows the experimental bond lengths of TCNQ.

Bond	Present calculations	Previous calculations [14]	TCNQ [15]
1 (N–C)	1.15	1.19	1.14
2 (C–C)	1.40	1.43	1.44
3 (C–C)	1.38	1.40	1.37
4 (C–C)	1.42	1.44	1.44
5 (C–C)	1.34	1.37	1.34

periodic boundary conditions, as in the supercell method. The Brillouin zone was sampled with a grid of $8 \times 8 \times 1$ k -points within the Monkhorst–Pack scheme [12]. Charge densities were Fourier-transformed using plane waves with an energy cut-off of 5442.2 eV (200 ha). To study the charge transfer, one molecule of F4-TCNQ was placed onto a graphene $6 \times 6 \times 1$ supercell containing 72 carbon atoms. This lead to a separation of atoms belonging to two molecules in adjacent unit cells of at least 5.19 Å. The inter-layer separation of molecules in different cells was 14 Å of vacuum. During the relaxation all the atoms were allowed to move to their equilibrium positions. A final calculation was carried out with a larger $8 \times 8 \times 1$ supercell where the separation of molecules in different cells was at least 10.0 Å. The band structure obtained and the consequent charge transfer were very similar although the Dirac point is now at K.

3. Results

Figure 1 shows the structure and the calculated geometric bond lengths for the isolated F4-TCNQ molecule. In table 1

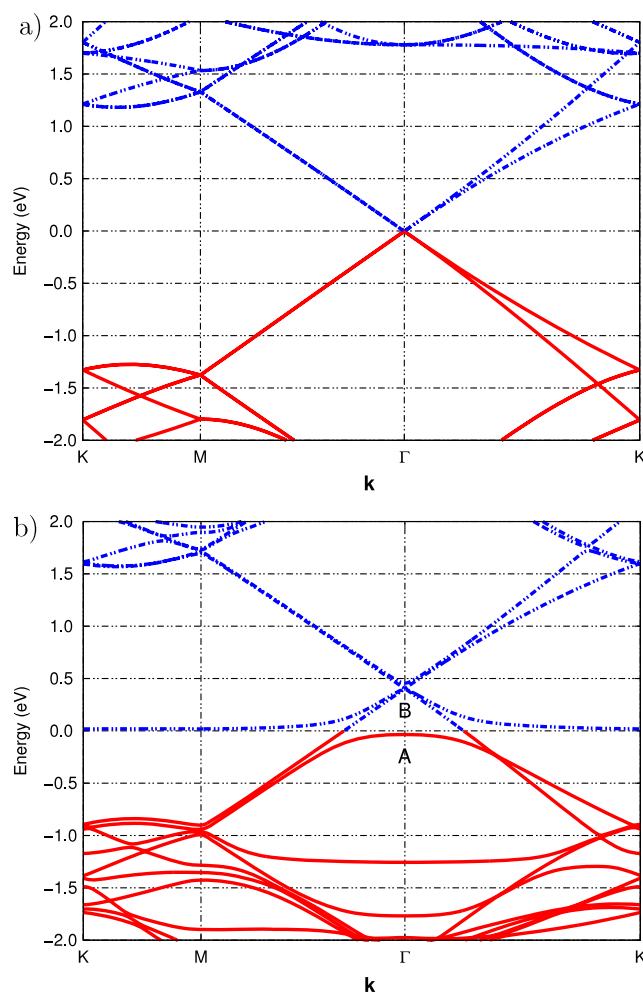


Figure 3. Band structure (eV) of (a) pristine graphene and (b) F4-TCNQ on top of graphene plotted in the vicinity of the Fermi energy along the high symmetry branches of the graphene Brillouin zone. The Fermi level is set to zero. Full lines denote occupied states while dashed lines show empty levels. The Fermi level is placed at zero. The curves show the unoccupied F4-TCNQ levels around 0 eV become occupied near the Dirac point indicating charge transfer.

we compare our calculations with previous calculations [14] and with experimental measurements of the precursor TCNQ molecule [15]. The calculated bond lengths are slightly smaller than the previous calculations which is due to the fact we used LDA for the exchange correlation potential in contrast with the generalized gradient approximation (GGA). Nevertheless, both sets of results are close to experimental bond lengths of TCNQ.

The electron affinity of a molecule is given approximately by the energy difference between the lowest unoccupied molecular level (LUMO) and the vacuum level, which is the value of the electrostatic potential at a great distance from the material.

The electron affinity can be approximately estimated to be 5.25 eV from the position of the LUMO level and the electrostatic potential at infinity distance from the molecule. The calculated electron affinity of F4-TCNQ molecule is in good agreement with experimental measurement [13] of 5.2 eV. This is much greater than the work function of graphene

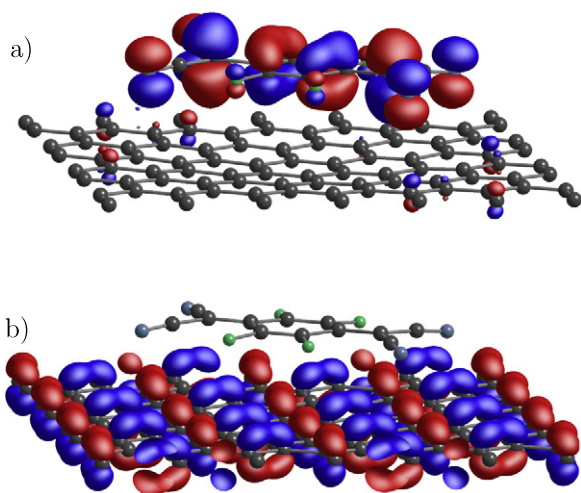


Figure 4. Plot of the wavefunction of the (a) HOMO level at Γ marked A in figure 3(b) shows strong localization on F4-TCNQ and (b) LUMO level at Γ marked B in figure 3(b) shows strong delocalization of a pi-bonding orbital over graphene but avoids F4-TCNQ. Red and blue lobes are of equal amplitude and opposite sign.

~ 4.5 eV [16] and indicates that F4-TCNQ is potentially a strong electron acceptor.

Figure 2 shows the relaxed structure of the molecule on graphene. The molecule adopts an approximately planar geometry 3.1 Å above the graphene sheet. The calculated binding energy of the molecule to graphene is 1.26 eV, we estimate the effect of the basis set superposition error (BSSE) to be approximately 0.2 eV. The large value found here shows that forces in addition to van der Waals are operating and probably arise from a charge transfer. The electronic band structure of pristine graphene and graphene together with the molecule is shown in figures 3(a) and (b), respectively. The Fermi level of each is set to zero. Because of the band folding, the Dirac point, where the π and π^* bonding and anti-bonding levels of the graphene substrate meet, occurs at Γ instead of the K point in the $6 \times 6 \times 1$ graphene supercell used here.

The electronic band structure calculated for the F4-TCNQ adsorbed on graphene is shown in figure 3(b). We note now the appearance of a flat band at E_F , related to F4-TCNQ, crossing the graphene π band below the Dirac point. This results in charge transfer from the π bonding levels of graphene near the Dirac point to the LUMO level of F4-TCNQ. Knowing that the integrated density of states within an energy E of the Dirac point may be approximated by $0.026E^2/C$ atom within a few tenths of an eV [17], we estimate a transfer of 0.3 electrons from graphene to a molecule of F4-TCNQ.

Figures 4(a) and (b) show the wavefunctions of the HOMO level marked A and LUMO level marked B. The localization of the wavefunctions confirms that the HOMO level in figure 3(b) is now localized on F4-TCNQ whereas the LUMO level is a pi-bonding state which is delocalized over graphene and has little overlap with F4-TCNQ. This supports further the conclusion that there is a transfer of electrons from the top of the graphene π state into the LUMO state of the F4-TCNQ molecule.

4. Conclusions

In conclusion, we have shown that the F4-TCNQ molecule is a p-type dopant for graphene. The electronic band structure of F4-TCNQ on graphene combined with the plots of the wavefunctions near to the Fermi level suggests the electron transfer of $0.3e$ /molecule from the highest occupied electronic state on graphene to the lowest unoccupied electronic state of the F4-TCNQ molecule. These results are in agreement with synchrotron-based high resolution photoemission spectroscopy measurements which show an increase of the work function with the increase of the thickness of F4-TCNQ on top of graphene [5]. The calculated binding energy of 1.26 eV indicates that the system is thermally stable at room temperature. One issue which has not been considered is the effect of the molecule on the carrier mobility of graphene. We are inclined to the view that the additional Coulomb scattering from the charged molecules will reduce the mobility like that of metallic clusters [2] and unlike that of NH_3 or NO_2 . Possible reasons for this will be discussed in another paper.

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