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Tuning the charge carriers in epitaxial graphene on SiC(0001) from electron to hole via molecular doping with C₆₀F₄₈

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We demonstrate that the intrinsic electron doping of monolayer epitaxial graphene on SiC(0001) can be tuned in a controlled fashion to holes via molecular doping with the fluorinated fullerene C₆₀F₄₈. *In situ* angle-resolved photoemission is used to measure an upward shift of (0.6 ± 0.05) eV in the Dirac point from -0.43 eV to $+0.17$ eV relative to the Fermi level. The carrier density is observed to change from $n \sim (1 \times 10^{13} \pm 0.1 \times 10^{13}) \text{ cm}^{-2}$ to $p \sim (2 \times 10^{12} \pm 1 \times 10^{12}) \text{ cm}^{-2}$. We introduce a doping model employing Fermi-Dirac statistics which explicitly takes temperature and the highly correlated nature of molecular orbitals into account. The model describes the observed doping behaviour in our experiment and readily explains why net *p*-type doping was not achieved in a previous study [Coletti *et al.*, Phys. Rev. B **81**, 8 (2010)] which used tetrafluorotetra-cyanoquinodimethane (F4-TCNQ). © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4811248>]

For electronic applications incorporating graphene, epitaxial graphene grown on silicon carbide (SiC) appears to be one of the more promising routes towards high quality wafer size samples.^{1,2} Many of these applications require the ability to control the doping of graphene such that charge carrier regions of electrons (*n*-type) and holes (*p*-type) can be defined within the device. However, since as-grown epitaxial graphene on SiC is intrinsically *n*-type as a result of the graphene/SiC interface properties,^{3,4} creating a *p*-type state requires some means of electron withdrawal from the graphene layer. A layer of hydrogen or fluorine intercalated between graphene and SiC (0001) has been shown to induce a net *p*-type doping^{5,6} as a result of the intrinsic polarization of the hexagonal SiC(0001) substrate.⁷ Nevertheless, the ability to selectively *p*-type dope regions (e.g., via patterning) of epitaxial graphene without significant modification of the graphene/SiC interface is of considerable interest. The use of small inorganic molecular adsorbates such as NO₂, H₂O, and O₂ has been shown to cause *p*-type doping;⁸ however, such species are often either highly reactive or require low temperatures to remain on the surface,⁹ which does not lend itself well for practical devices. Surface transfer doping using strongly electron-accepting and thermally stable organic molecules is a promising route to this end. However, only charge compensation to a state at which the graphene layer becomes neutral has been demonstrated for the molecule tetrafluorotetra-cyanoquinodimethane (F4-TCNQ). This has been independently shown in studies employing angle-resolved photoelectron spectroscopy (ARPES),^{10,11} as well as room temperature transport measurements.¹² Therefore, no true *p*-type doping of graphene grown on SiC using organic molecules has been achieved as yet. Here, we show that an

increasing coverage of the high electron affinity molecule C₆₀F₄₈ on graphene is able to control the carrier concentration and change the sign of the carriers from *n*-type to *p*-type.

In order to monitor the doping process, we use ARPES to measure the Dirac energy relative to the Fermi level, and the size of the Fermi surface to determine the sign and magnitude of the carrier density, as a function of C₆₀F₄₈ coverage on monolayer epitaxial graphene grown on SiC(0001). A model of the charge transfer process is applied which accurately describes the doping process, and which explains why C₆₀F₄₈ is able to create a net *p*-type doping of monolayer graphene (MLG) while F4-TCNQ cannot. The same model is able to predict the doping efficiency of any organic molecule once its electron affinity and areal interface capacitance are known.

Experiments were performed on an epitaxial MLG sample that was prepared via the standard method of thermal decomposition of 6H-SiC in an argon atmosphere developed by Emtsev *et al.*² The thickness of the graphene layer was confirmed to be 1 ML using laboratory based X-ray photoelectron spectroscopy (XPS) immediately after the growth process at the University of Erlangen-Nürnberg. ARPES measurements of the π -band dispersion near E_F and also the Fermi surface were performed using the toroidal angle-resolving endstation at the U125-2/SGM beamline at BESSY II, Berlin, Germany.¹³ The energy distribution curve (EDC) measurements of the π -band were performed along the $\Gamma - K$ surface direction at room temperature, using linearly polarised undulator radiation ($h\nu = 50$ eV) at normal incidence to the sample. The sample was introduced into vacuum and then annealed at 350–400 °C for 3 h to remove hydrocarbon and airborne contamination. With the samples at room temperature, deposition of C₆₀F₄₈ was performed using a commercial effusion cell (MBE Komponenten GmbH) operating at 195 °C. Coverage was increased in increments between

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FIG. 1. (a) ARPES measurements of the π -band around the K point (upper panels), and corresponding Fermi surface images (lower panels), for selected $C_{60}F_{48}$ coverages on MLG on SiC(0001). The inset in the upper left panel indicates the measurement direction in the graphene Brillouin Zone. (b) Sequence of MDCs evaluated at the Fermi energy for all $C_{60}F_{48}$ coverages. The vertical dashed line indicates the position of the K point.

measurements and monitored using a quartz crystal microbalance (QCM), where 1 ML of $C_{60}F_{48}$ represents an areal concentration of 7.8×10^{13} molecules/cm². In order to avoid possible beam damage of the molecules, a different measurement position was used after each deposition.

As has been previously established,^{14,15} the sign and magnitude of the carrier density in graphene can be directly obtained from ARPES measurements of the π -band dispersion, or Dirac cone, in the vicinity of the K point in the Brillouin zone. Figure 1(a) depicts the ARPES results for a subset of the $C_{60}F_{48}$ coverages deposited onto MLG. The upper panel sequence shows the EDC measurements of the Dirac cone, taken along the $\Gamma - K$ surface direction and centred upon the K point (note: binding energies are referenced to the Fermi energy). The lower panel sequence in Figure 1(a) shows the corresponding Fermi surface contours measured at the same coverages. Within all of the images, a vertical dashed line representing the position of the K point has been drawn as a guide to the eye. To highlight the changes in the π -band at the Fermi level, Figure 1(b) displays a series of momentum distribution curves (MDCs) taken at the Fermi energy from the complete set of π -band measurements. We note that within the ARPES data, we only see one branch of the Dirac cone along $\Gamma - K$ due to the interplay between p -polarised radiation and the pseudo-spin properties of the two sublattices in graphene for this particular measurement geometry.^{16–19} This manifests itself in each MDC as a single peak at E_F , rather than two symmetrically disposed about K, and the relative position of the peak with respect to the K point yields the carrier polarity. Figure 1 clearly shows the transition from an n -type to p -type doped graphene layer. As the coverage is increased the Dirac cone shifts upward, with E_D coinciding with the Fermi energy at approximately 0.15 ML $C_{60}F_{48}$, and

then lying above it for higher coverages. This behaviour is mirrored quite clearly in the MDC sequence: The single peak at E_F is initially located at $k_x > 0$ (n -type doping) before moving towards and then crossing the K point to $k_x < 0$ (p -type doping) as the coverage is increased. The Fermi surface results also agree with the trends seen in the π -band. The initial “horseshoe” shaped contour of pure MLG shrinks to a minimum waist at 0.15 ML before enlarging and inverting its position with respect to the K point.

Although the spectral function of graphene near E_F is not strictly linear,¹⁴ it is usual to approximate the band-structure by a linear function, which directly yields the quantities of interest, namely the Dirac energy and the carrier concentration. First, the value of the fit at $k_x = 0$ gives the Dirac energy E_D relative to the Fermi level, $(E_D - E_F)$. Second, the intercept of the linear fit with the Fermi level yields a value of k_F , which represents the extent of the K-centred Fermi surface pocket along $\Gamma - K$. The charge carrier density (either electron or hole) is then calculated in a straightforward way using $n(p) = (k_F)^2/\pi$, assuming a circular Fermi surface of radius k_F .

Figure 2 summarises the experimentally determined charge density and $E_D - E_F$ values for all $C_{60}F_{48}$ coverages (red circles) along with the well-known relationship for graphene’s linear dispersion near E_F (blue line).^{20–22} The fact that the experimental data closely follow the relationship between the Dirac energy and the carrier concentration for ideal monolayer graphene demonstrates that the integrity of the electronic structure is maintained even in the presence of a substantial coverage of $C_{60}F_{48}$. Indeed, the average Fermi velocity over all coverages (as determined from the slope of the experimental bands near E_F) was $\hbar v_F = 7.3 \pm 0.3$ eV·Å, which is consistent with values in the literature.^{14,22}

FIG. 2. Experimentally determined values of the carrier density plotted against the measured Dirac energy for the complete set of $C_{60}F_{48}$ coverages (red circles). The dashed line represents charge neutrality. The well-known relationship between carrier density and Dirac energy for graphene is also plotted for comparison (blue line).

Beginning with the pristine MLG surface, the Dirac energy is found to be located at (-0.43 ± 0.05) eV below the Fermi level, accompanied by an electron density of $(1.1 \times 10^{13} \pm 0.1 \times 10^{13})$ cm^{-2} which is in good agreement with previous studies.^{2,14,15} Subsequent deposition of $C_{60}F_{48}$ results in an immediate upward shift of E_D , with E_D reaching the Fermi energy after only 0.15 ML (1.17×10^{13} molecules/ cm^2) of $C_{60}F_{48}$, which corresponds to charge neutrality of the graphene layer. For coverages of 0.2 ML (1.56×10^{13} molecules/ cm^2) and greater, E_D moves above E_F and thus the graphene layer becomes p -type doped. A total shift of (0.60 ± 0.05) eV from the clean MLG surface is finally measured for 0.80 ML (6.24×10^{13} molecules/ cm^2) of $C_{60}F_{48}$. Here the Dirac energy is $(+0.17 \pm 0.05)$ eV above the Fermi level, with a measured hole density of $(2.0 \times 10^{12} \pm 1 \times 10^{12})$ cm^{-2} . It should be pointed out that although not shown here, the changes in E_D with respect to E_F are in excellent agreement with the measured concomitant shifts of the bottom of the π -band at Γ , confirming a rigid shift of the bandstructure with respect to E_F . The uncertainty in the carrier density of $1 \times 10^{12} \text{ cm}^{-2}$ was calculated from the error in k_F obtained from a 0.95 confidence level interval in the linear fitting procedure, as was the error in the Dirac energy (± 0.05 eV).

Given that fluorine has been shown to intercalate the buffer layer on SiC, resulting in a free standing p -type doped graphene layer,⁶ it is natural to ask whether the p -type doping observed here is the result of F intercalation where the fluorine stems from disintegrated $C_{60}F_{48}$. Recent work has investigated the thermal decomposition of $C_{60}F_{48}$ on a SiC substrate containing separate regions of monolayer graphene and just the carbon “buffer layer.” It was shown that fluorine intercalation only occurred on the buffer layer regions, with the monolayer graphene unaffected by the decomposition of the $C_{60}F_{48}$.²³ As we are dealing here with a uniform MLG sample, and no heating of the substrate was performed after $C_{60}F_{48}$ deposition, we are convinced that the p -type doping observed in this study is a result of surface charge transfer

between the graphene and the molecular overlayer, and not due to a modification of the graphene/SiC interface. This view is strengthened by a quantitative description of the doping process which we turn to now.

It is important to understand the mechanism for charge transfer, in particular why $C_{60}F_{48}$ is able to induce p -type doping in comparison to other molecules such as F4-TCNQ which can only obtain charge neutrality in the underlying graphene. It has been shown that the charge transfer process from a substrate to a molecular overlayer is governed by Fermi-Dirac statistics applied to the molecular level into which the electron is transferred to.^{24–26} This is the lowest unoccupied molecular orbital (LUMO) of $C_{60}F_{48}$. With all energies referred to the vacuum level, the LUMO energy corresponds to the electron affinity of neutral $C_{60}F_{48}$ in contact with the graphene, $\chi_{C_{60}F_{48}}$. The doping efficiency η (i.e., the probability that an electron is transferred) can be expressed in its full form as

$$\eta = \frac{N_A^-}{N_A + N_A^-} = \frac{1}{\frac{1}{g} \exp[(\Delta_0 + \Delta\Phi + (E_D - E_F))/k_B T] + 1}. \quad (1)$$

Here N_A and N_A^- are the neutral and ionised areal density of $C_{60}F_{48}$ molecules, respectively, with the sum representing the total concentration of molecules. N_A^- is equal to the change in charge density in the graphene layer, since only one electron is transferred per $C_{60}F_{48}$ molecule on account of strong intermolecular Coulomb interaction yielding a positive effective correlation energy. The degeneracy factor of the $C_{60}F_{48}$ LUMO is $g=6$,²⁵ and Δ_0 is the initial activation energy before charge transfer has taken place. Δ_0 can be expressed as $\Delta_0 = \phi_{MLG} - (E_D - E_F) - \chi_{C_{60}F_{48}}$. The work function of our clean epitaxial graphene was measured to be $\phi_{MLG} = 4.34$ eV,²⁷ the initial Dirac point relative to the Fermi level as mentioned above is $E_D - E_F = -0.43$ eV, and the electron affinity of neutral $C_{60}F_{48}$ sitting on the surface is $\chi_{C_{60}F_{48}} = 5.27$ eV,²⁶ giving $\Delta_0 = -0.50$ eV. Note that the value for the electron affinity is higher than the gas phase value for $C_{60}F_{48}$ (4.0 eV) (Ref. 28) due to extra-molecular screening from the substrate, causing a shift of the LUMO state away from the vacuum level. $\Delta\Phi$ represents the interface dipole potential due to the charge transfer. In the case of transfer doping of diamond with $C_{60}F_{48}$ it has been shown that $\Delta\Phi$ is well represented by a simple capacitor model such that $\Delta\Phi = eQ/C_{\square}$, where e is the elemental charge, Q is the areal charge density and $C_{\square} = 3.25 \times 10^{13}$ $\text{eV}^{-1} \text{ cm}^{-1}$ is the areal capacitance of the charge-free region between the oppositely charged layers in diamond and $C_{60}F_{48}$.^{24,29} The thickness of the charge-free region in the $C_{60}F_{48}$ /diamond system in that study was found to be ~ 0.5 nm. In the present case, assuming a simple model of $C_{60}F_{48}$ molecules (diameter 1 nm) in direct contact with the graphene, surface charge transfer to the centre of the fullerene cage would result in the same charge-free distance in the surface-perpendicular direction. The average lateral spacing of the molecules should be similar both on graphene and on diamond. There is no covalent bonding to either substrate, instead only the electrostatic interaction between the identically (single electron) charged molecules in both systems and the underlying 2D hole layer. Therefore, it is not unreasonable to

assume that the $C_{60}F_{48}$ /graphene interface would have a similar areal capacitance to the $C_{60}F_{48}$ /diamond interface.

The previous work on molecular doping of graphene using F4-TCNQ by Coletti *et al.* also measured the shift in the Dirac energy and the change in charge density using ARPES. In addition, measurements of the change in work function using low energy cut-off spectroscopy were also employed to determine the interface dipole generated by the charge transfer as a function of F4-TCNQ coverage. From their work, considering the changes in interface dipole potential and charge density they report, we are able to estimate an areal capacitance for the F4-TCNQ/graphene system of $C_{\square} \sim 2.0 \times 10^{13} \text{ eV}^{-1} \text{ cm}^{-2}$, which is lower than our aforementioned value for the $C_{60}F_{48}$ /graphene system. This places us in a position to compare quantitatively the doping efficiency of both the $C_{60}F_{48}$ /graphene and the F4-TCNQ/graphene interfaces. In Fig. 3, we plot the doping efficiency calculated using (1) as a function of $E_D - E_F$ for $C_{60}F_{48}$ in this study ($T = 295 \text{ K}$, red line). The doping efficiency for F4-TCNQ ($T = 80 \text{ K}$, black dashed line) is calculated using $C_{\square}$ from Coletti *et al.* along with an electron affinity for F4-TCNQ of 5.24 eV , giving an initial activation energy of -0.47 eV .¹⁰ The red squares on the graph represent the doping efficiencies for each $C_{60}F_{48}$ deposition used in this study. The coverage values are calculated using (1) and agree within a factor of two with the nominal QCM values.

Both systems display a doping efficiency of 1 when the Dirac energy is well below the Fermi level. As more and more charge is transferred (molecular coverage increases), the Dirac energy approaches the Fermi level and it is at this point where the two systems behave differently; for $C_{60}F_{48}$ there is still a doping efficiency of 1 whereas for F4-TCNQ at $T = 80 \text{ K}$, the probability of electron transfer drops rapidly towards zero. As we reach the charge neutrality point and start to p -type dope the system, the probability for further charge transfer using F4-TCNQ at $T = 80 \text{ K}$ is zero, which is why Coletti *et al.* found it impossible to net p -type dope

FIG. 3. Doping efficiency of MLG as a function of the Dirac energy for $C_{60}F_{48}$ at $T = 295 \text{ K}$ (red solid line), F4-TCNQ from Coletti *et al.* at $T = 80 \text{ K}$ (black dashed line), and F4-TCNQ at $T = 295 \text{ K}$ for comparison (blue dashed-dotted line). The red squares represent the doping efficiency calculated at each stage of $C_{60}F_{48}$ deposition; the resultant molecular coverages of $C_{60}F_{48}$ as determined from the doping model are indicated.

graphene with F4-TCNQ in their study. The $C_{60}F_{48}$ on the other hand continues to draw electrons from the graphene sheet with a doping efficiency of unity (i.e., every $C_{60}F_{48}$ molecule accepts an electron) until the Dirac energy is around 0.05 eV above the Fermi level where the doping becomes less efficient and at around $\sim 0.17 \text{ eV}$ the probability of electron transfer drops to zero because the interface dipole potential has pushed the LUMO well above the Fermi energy and charge transfer ceases. One might postulate that the difference in temperature between the two studies accounts for the difference in doping efficiency. To demonstrate that this is not the case, a theoretical doping efficiency curve of F4-TCNQ deposited at room temperature is shown in Fig. 3 (blue line). It is clear that the probability of charge transfer when E_D is above E_F is still zero. Therefore according to our model it is not possible to induce overall p -type doping using F4-TCNQ on MLG even at room temperature.

With temperature now ruled out as a contributing factor to the difference in doping behaviour, it remains to state that the two main reasons which allow $C_{60}F_{48}$ to achieve a net p -type doping whilst F4-TCNQ only reaches charge neutrality are (1) the larger areal capacitance of the $C_{60}F_{48}$ /graphene interface, which allows a greater amount of transferred charge for a given change in interface dipole potential and (2) the slightly higher electron affinity of $C_{60}F_{48}$ which lowers the initial activation energy. Importantly, not only is it clear that this quantitative model is quite accurate in predicting the observed doping behaviour of F4-TCNQ and $C_{60}F_{48}$ deposited onto epitaxial graphene, it should be equally applicable to other tailored electron affinity organic molecules, representing a powerful framework within which doping behaviour can be predicted. Our successful description of the doping process differs significantly from that given previously in terms of independent particle band structure calculations^{30,31} in that it takes the highly correlated nature of molecular orbitals and the temperature dependence of doping efficiency properly into account.

In summary, we have shown that $C_{60}F_{48}$ on account of its high electron affinity is an effective surface acceptor for graphene. At a coverage of approximately 0.8 ML , it turns the original n -type monolayer graphene on SiC into p -type with a hole density of $2 \times 10^{12} \text{ cm}^{-2}$. A standard model of surface transfer doping has been used to explain why this molecule is able to achieve p -type doping compared to another candidate molecule, F4-TCNQ. These results show promise for the creation of p -type and n -type patterned regions on graphene, provided the molecules can be positioned sufficiently accurately. Also, our model provides a roadmap for the proper choice of molecules suitable for transfer doping of graphene.

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