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Doping of graphene: Density functional calculations of charge transfer between GaAs and carbon nanostructures

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Density functional theory is used to show that charge transfer occurs between chemical dopants in GaAs and adsorbates composed of C_{60} or graphene lying on the (110) surface of GaAs. In the case of C_{60}, charge transfer only occurs for *n*-type GaAs, in agreement with previous experimental results. However, the calculations show that transfer between graphene and both *n*- and *p*-type GaAs can occur, which offers a simple way of doping graphene.

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I. INTRODUCTION

Charge transfer between two separate systems, one molecular and the other semiconducting, is of interest as it enables surface conductivity to arise in the semiconductor. The best studied case seems to be aqueous layers on diamond which lead to hole transport in diamond.[1] However the origin of the molecular species, acting as an acceptor, is unknown. In contrast, following predictions by previous theoretical calculations,[2,3] transfer doping between diamonds and C_{60} and fluorinated C_{60} have been observed[4] with the transfer effect due to fluorinated C_{60} being substantially greater than that for C_{60} alone. Predictions of charge transfer between diamond and other molecules[5] have been extended to other semiconducting or semimetallic systems as nanotubes[6] and graphene.[7] For nanotubes there are experimental reports of transfer doping with organic molecules.[8–10]

In addition, there has been reports that C_{60} can effect transfer doping in III–V semiconductors such as GaAs.[11] For these photoemission experiments, C_{60} was deposited on (110) GaAs at 550 °C. The C 1*s* spectra showed an adsorbate induced 0.3 eV upward band bending at the GaAs/C_{60} interface in *n*-GaAs and its absence in *p*-GaAs. The band bending results from an electron transfer from GaAs to C_{60}, showing that empty levels of C_{60} lie in the GaAs band gap. The absence of a charge transfer effect in *p*-GaAs shows that the occupied levels of C_{60} lie below the valence band top. In the case of *n*-GaAs, the band bending implies an electron transfer of $0.02e$ to each fullerene. C_{60} is bonded only weakly to GaAs and there were no changes to the surface reconstruction. The depletion width is estimated to be about 150 μm.

There is currently great interest in the electronic properties of graphene and in wet conditions, charge transfer leading to hole doping of carbon nanotubes and graphene has been reported[12] and is similar to diamond. This suggests that other adsorbates might effect charge transfer and in some cases, the other way, namely, electron transfer into GaAs. The role played by different substrates for graphene is not understood. Epi-graphene prepared by heat treatments of SiC interacts strongly with the substrate, as there are reports that a band gap of ≤ 0.26 eV is opened in the graphene.[13] Scanning tunneling microscopy of graphene produced by intercalation of Ru suggest a buckled graphene layer.[14] Previous density functional calculations of graphene on nickel show hybridization between the Ni *d* bands and the π orbitals of graphene, implying a strong interaction between graphene and Ni.[15] It is desirable to deposit the graphene layer on an inert material, resulting in a band structure in the graphene that is close to the freestanding layer, yet there is sufficient charge transfer that the interface is thermally stable. This may be the case for graphene produced by mechanical exfoliation of graphite deposited on SiO_2, although the substrate is disordered. We show here that as the (110) surface of GaAs is inert, it causes only a minimum distortion of the graphene bands in the neighborhood of the Fermi energy. We also find charge transfer with the sign of the charge that is transferred dependent on the type of GaAs: *n*-GaAs effects an electron transfer to graphene as indeed found for C_{60} on GaAs, but *p*-GaAs can affect the transfer in the opposite direction in contrast to C_{60}. This offers a simple way of doping graphene.

II. METHOD

We investigate the problem of C_{60} and graphene on the (110) surface of GaAs using density functional theory and the AIMPRO code.[16] This is a local density functional code using a basis of Gaussian orbitals with the pseudopotentials of Hartwigsen *et al.*[17] In the calculations described here the basis consisted of *s*- and *p*-Gaussian functions centered on atomic sites with four optimized exponents together with *d*-polarization functions. All structures were modeled using periodic boundary conditions (i.e., the supercell method), and Monkhorst–Pack grids[18] of special *k* points were used to sample the resulting Brillouin zone of each system. Charge densities were Fourier transformed in reciprocal space using plane waves with an energy cutoff of 300 hartree. For representative atomic structures, the density of the *k*-point sampling grid was varied until the total energy converged to within at least 10^{-4} hartree. For each structure, full atomic relaxations were performed (i.e., no atoms were artificially

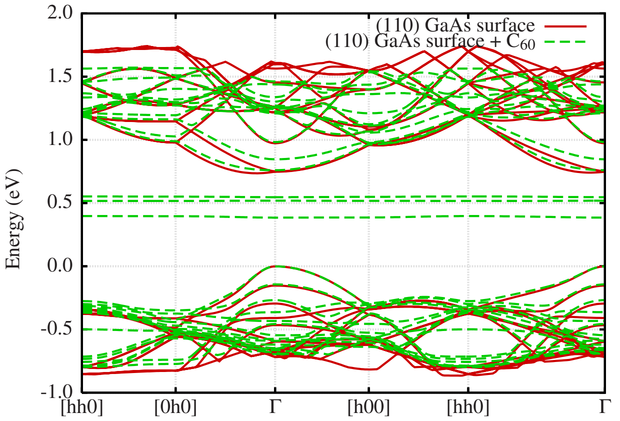

FIG. 1. (Color online) Band structure (eV) of (110) surface of GaAs (red/gray, full line) and that of C_{60} on (110) GaAs (green/light gray, dashed line). Note the 0.77 eV gap of the bare surface is close to the bulk gap obtained using density functional theory. The dashed green/light gray (dashed) lines shows the band structure for the molecule on top of GaAs and the dispersionless empty midgap levels are localized on C_{60}. These bands can be occupied in *n*-GaAs and are responsible for the charge transfer.

constrained) using a conjugate-gradient scheme that proceeded until the change in total energy between subsequent iterations of structural optimization fell to less than 10^{-5} hartree. This criterion resulted in the maximum force acting on any atom in the final iteration of structural optimization being typically less than about 10^{-3} hartree/a.u.

The lattice parameter of GaAs is found to be 5.60 Å, within about 1% of the experimental value of 5.65 Å. The bond length in graphene is 1.41 Å again close to the experimental value for graphite of 1.42 Å. Previous investigations using this method for a variety of structures reproduced structural results obtained by other investigators.[3,7,19]

We choose a unit cell constructed from bulk GaAs and containing a (110) GaAs surface. The cell has a depth of eight atomic layers, which are separated from adjacent slabs by a vacuum layer. The depth of the vacuum layer corresponds to 8 atomic layers for graphene and 12 for C_{60}. In the case of the relaxed free GaAs surface without adsorbates, the surface Ga-As dimer is found to make an angle of 30° with [110], which is in agreement with previous calculations and experimental values of $27°-31°$.[20] Figure 1 shows the band structure of the slab. The band gap of the slab, 0.77 eV, is slightly greater than found for bulk GaAs at 0.56 eV but well below the experimental GaAs gap of 1.52 eV. The underestimate is well known to arise in local density functional theory. The implication is that the surface does not introduce any states into the bulk band gap, in agreement with previous calculations and experiment.[21–23]

III. RESULTS

A. C_{60} on GaAs

The C_{60} molecule was placed on top of the GaAs in an orthorhombic cell with lattice vectors $\mathbf{a}_1 = n(001)a$ and $\mathbf{a}_2 = m(1\bar{1}0)a/2$ with $n=3$ and $m=4$ and one molecule in each cell. Here, a is the calculated lattice parameter of GaAs equal to 5.60 Å. The minimum separation between the centers of C_{60} in different unit cells is 15.8 Å, compared to the diameter of C_{60}, which is 7.0 Å. The ball was first placed above the trench on the surface but on relaxation moved to one side as shown in Fig. 2, which shows the final structure. There is very little distortion to the ball or surface, indicating the absence of any strong chemical bonding between C_{60} and GaAs. This is consistent with the photoemission results.[11] The distance between the nearest carbon and a surface As and Ga atom are 3.08 and 2.91 Å. These separations are much longer than bulk GaAs bonds of 2.43 Å, showing that the ball is weakly bonded to the surface. The binding energy of the fullerene to the surface is 0.85 eV.

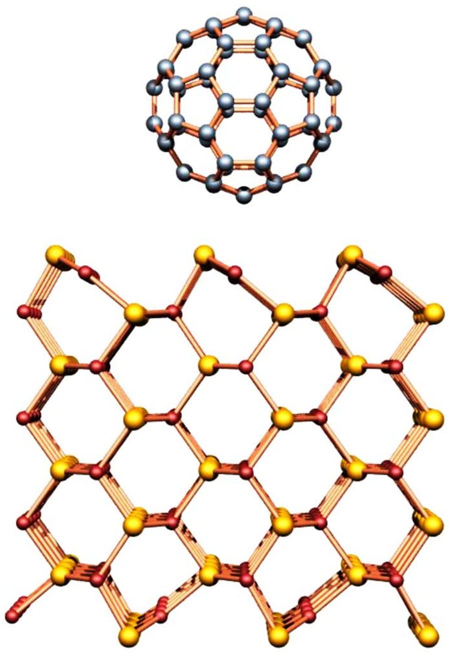

FIG. 2. (Color online) Relaxed structure of C_{60} on top of (110) GaAs. The yellow/light gray (largest) and red/dark gray (smallest) spheres denote As and Ga atoms, respectively. The dark blue/gray (intermediate sized) spheres are carbon.

The band structure for the combined system of C_{60} on top of the surface (Fig. 1) shows that only flat deep *empty* bands localized on C_{60} inhabit the band gap of GaAs. Their position suggests that in *n*-GaAs, electron transfer from chemical donors, with donor levels close to E_c, to C_{60} will occur while charge transfer cannot occur in *p*-GaAs. This is in agreement with the experimental results. The amount of transfer depends on the density of donors in the GaAs. Experimentally a charge transfer of about $0.02e$ was found for each C_{60}, which corresponds to a depletion layer width of about 150 μm. This wide depletion layer prevents a full density functional calculation being carried out for doped GaAs.

B. Graphene on GaAs

We now study the effect of graphene on top of the (110) surface of GaAs. To model this requires a choice of unit cell where the strain introduced by graphene is minimal. We

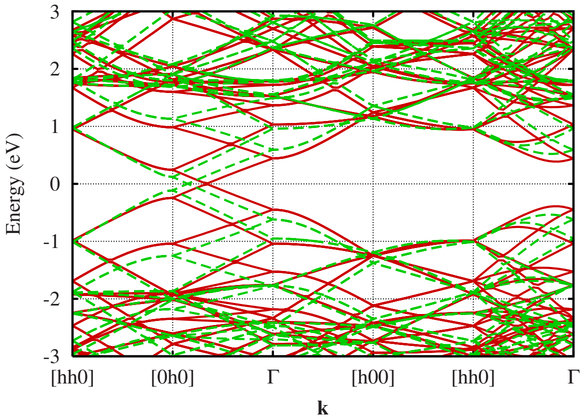

FIG. 3. (Color online) Band structures of graphene in orthorhombic cell with n_g and m_g equal to 4 and 10. The red/gray (full line) curves show the case where there is no strain in the graphene layer, while the green/light gray (dashed) curves are for the case where there is a 2.7% compressive strain along $[1\bar{1}0]$ and 0.7% along [001]. The Fermi level lies at 0, where the bands cross sharply.

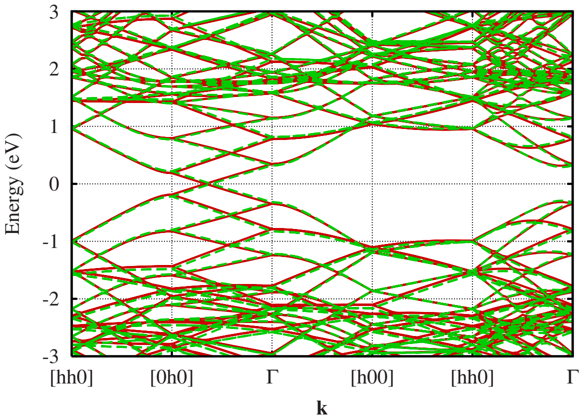

FIG. 4. (Color online) Band structure of graphene in orthorhombic cell where n_g and m_g are equal to 4 and 13. The red/dark gray (full line) curves show the case where there is no strain in the graphene layer, while the green/light gray (dashed) curves show the layer lattice matched to GaAs where there is 0.2% compressive strain along $[1\bar{1}0]$ and 0.7% along [001]. The Fermi level lies at 0, where the bands cross sharply.

again choose an orthorhombic unit cell with lattice vectors $\mathbf{a}_1 = n(001)a$ and $\mathbf{a}_2 = m(1\bar{1}0)a/2$ with a equal to the calculated value for GaAs of 5.60 Å. An orthorhombic cell can also be used for an isolated graphene layer but has lattice vectors $n_g a_g[001]$ and $m_g a_g[1\bar{1}0]/\sqrt{6}$, where a_g is three times the C-C bond length r_b. The calculated value for r_b is 1.41 Å, comparable with the experimental value of 1.42 Å. n_g and m_g are integers controlling the size of the unit cell.

The graphene layer was next placed on top of the GaAs surface with the [001] and $[1\bar{1}0]$ directions parallel to the $[10\bar{1}0]$ and $[1\bar{2}10]$ directions in graphite. The values of n, m, n_g, and m_g are chosen to minimize the strain in the graphene overlayer.

Consider first the strain along the [001] direction. We choose $n=3$, corresponding to a repeat distance along [001] of $3a$ or 16.80 Å. If we choose $n_g=4$, then the unstrained graphene lattice vector along [001] is 16.92 Å and the difference from 16.80 Å represents a compressive strain of only −0.7% in the graphene. It is remarkable and fortunate that the two materials are as closely lattice matched in this direction.

Next we consider the strain in the graphene layer along the $[1\bar{1}0]$ direction. If we choose $m=6$, then the periodic spacing along this direction in GaAs is 23.97 Å. Choosing $m_g=10$ results in a lattice parameter of 24.59 Å or a compressive strain of 2.7%. The band structure of the pure graphene cell with these values of n_g and m_g for both strained and unstrained lattice parameters a_g are shown in Fig. 3. It is readily seen that the Fermi energy lies where the bands cross in a way characteristic of graphene. However, the point of intersection is very different for the unstrained and strained cases being displaced from the correct value of 67% of the distance from G to the zone boundary to about 86% of this distance. Clearly, the strain is too large in this unit cell.

If on the other hand, we choose $m=8$, then the periodic spacing along this direction in GaAs is 31.678 Å. Letting $m_g=13$ gives a repeat distance of 31.748 Å in graphene, which corresponds with a compressive strain of only −0.2% when graphene is placed on top of the GaAs cell. The band structure of the pure graphene layer for both unstrained and strained by −0.2% is shown in Fig. 4. The difference in band structure between the two cases is minimal and the K point lies 2/3 of the distance to the zone boundary. These values of n, m, n_g, and m_g then yield acceptably low values of strain in the graphene but require a unit cell of about 500 atoms.

The graphene was placed about 3 Å away from the GaAs surface and all atoms were allowed to relax. During relaxation the graphene sheet moved away from the surface so that the nearest distance between a carbon atom and a surface As atom is 3.15 Å, while Ga was farther away at a distance of 3.85 Å. These values are somewhat greater than found for C_{60}, but they clearly show that only weak bonds are formed between the graphene and GaAs. The relaxed structure of graphene on top of GaAs is shown in Fig. 5. There is no evidence of bucking of the graphene layer and this might be expected from the weak bonding found here. The angle between the surface Ga-As dimer has increased by 0.6°. This change would alter the work function of GaAs.

Figure 6 shows the band structure of graphene on top of GaAs. It is noticed that the graphene introduces both deep *occupied* and *empty* levels into the band gap. However, the band structure of graphene has not been seriously affected by the presence of GaAs and the Fermi level still lies at the cross in the band structure about 0.1 eV above the top of the surface valence band of GaAs.

The empty levels on the graphene lying in the band gap would promote electron transfer from chemical donors in n-GaAs, just as in the case of C_{60}. However in addition, and unlike C_{60}, we can also expect electron transfer from graphene to chemical acceptors in p-GaAs.

IV. DISCUSSION

We have examined the electronic properties of C_{60} and graphene on top of the (110) surface of GaAs. We have

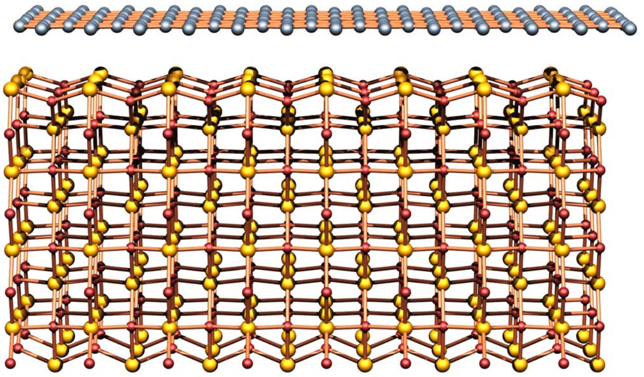

FIG. 5. (Color online) Relaxed cell of graphene on top of (110) surface of GaAs. The horizontal axis is along $[1\bar{1}0]$ and the vertical axis is along [110]. The Ga and As atoms at the extreme right-hand side of the figure are bonded to neighbors in adjacent cells. The strain in the graphene overlayer is −0.2% along $[1\bar{1}0]$ and −0.7% along [001] (out of the plane of the paper). The yellow/light gray (largest), red/dark gray (smallest), and blue/gray (intermediate sized) spheres denote As, Ga, and C atoms, respectively.

shown that, in agreement with previous calculations[20,21] and experiment,[22,23] this surface is inert. Investigations of the bonding and electronic levels of graphene and C_{60} show that they are not seriously affected by the GaAs substrate and hybridization of the π orbitals on carbon with GaAs does not occur. We have found that C_{60} is stable and bound to the surface with an energy of 0.85 eV. The empty electronic levels of adsorbed C_{60} are located in the band gap of GaAs, while the highest occupied level lie in the valence bands of the semiconductor. This accounts for the experimental observation that C_{60} can be doped by *n*-GaAs but not by *p*-GaAs.

The theory also shows that the strain introduced in a monolayer of graphene on top of GaAs is less than 1% for super cells of size of about 20–30 Å and that the band structure of graphene is unaffected by the GaAs surface. For larger strains found in smaller cells, however, there is a large shift of the *K* point. There is no evidence for the size of systems investigated (about 20–30 Å) for rippling of the layer, as found on more reactive metal surfaces. However, the presence of surface terraces on GaAs, with possible Ga or As dangling bonds, might be expected to lead to some rippling. We find that the sharp crossing of the occupied and unoccupied bands that occurs at the *K* point in graphene lies in the lower band gap of GaAs. There was no evidence for the opening of any gap. This suggests that graphene can be electron doped with *n*-GaAs and hole doped with *p*-GaAs. It also suggests that selective area doping in GaAs could lead to similar doping patterns in graphene. We expect the band structure of bilayers and multilayers to be similar to free-standing films, although the effect of the surface dipole might be to open a gap in the bilayer case.

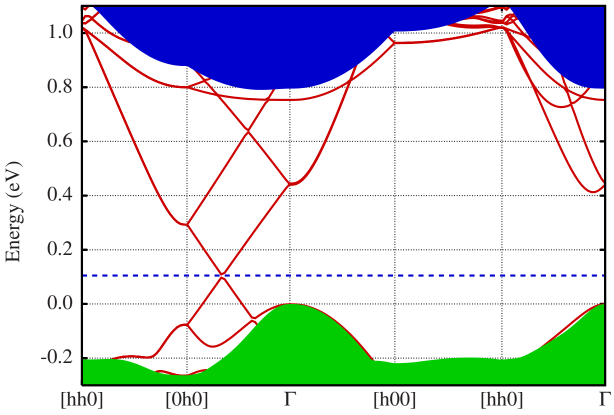

FIG. 6. (Color online) Band structure of graphene on top of the (110) surface of GaAs. The green/light gray lightly shaded region is occupied by surface and bulk filled bands of GaAs, while the blue/dark gray heavily shaded region denotes surface and bulk empty bands of GaAs. The red/gray (full) lines denote the band structure of the surface graphene. The Fermi level is shown as a dotted horizontal line and lies in the gap and the vertical axis is in eV.

It is interesting to see if these results can be explained from studying the ionization energies and electron affinities of the isolated constituents. The work function and electron affinity of graphene are both thought to be about 4.5 eV.[7] The ionization energy of GaAs is 5.5 eV.[24] Thus electron transfer between *n*-GaAs (work function of 4.0 eV) and graphene (electron affinity of 4.5 eV) is expected. In addition, electron transfer between graphene and *p*-GaAs would occur as the work function of graphene at 4.5 eV is less than the electron affinity of *p*-GaAs at 5.5 eV. That this is so supports the calculations showing that electron transfer from graphene to *p*-GaAs, as well as from *n*-GaAs to graphene, is possible on energy grounds.

However this argument does not apply to C_{60}. To explain the absence of electron transfer from C_{60} to *p*-GaAs in terms of the work functions and electron affinities of the isolated constituents, we would require the work function of C_{60} [4.6 eV (Ref. 3)] to be greater than the affinity of *p*-GaAs (5.5 eV). This is not the case. Moreover, for *n*-GaAs, electron transfer from GaAs to C_{60} would be explained if the work function of *n*-GaAs, ∼4 eV, is less than the electron affinity of C_{60}, which is estimated to be 2.9 eV from the difference in its ionization energy of 4.6 eV and its band gap of 1.75 eV. Again this is not the case. Thus to account for the experimental results, the ionization energy and electron affinity of C_{60} have to be increased by about 1 eV. It is possible that this is caused by changes in the surface dipole of GaAs in the presence of C_{60}. Such a shift is consistent with the theory given here, which shows that the occupied levels of C_{60} lie below the valence band of GaAs and the unoccupied levels of C_{60} lie below the conduction band of the semiconductor. This implies that the surface dipole on GaAs is strongly affected by the adsorbed layer of C_{60}. We can estimate an upper value to the density of holes in the graphene in *p*-GaAs assuming effective screening as follows: The integrated density of states within an energy E of the Dirac point may be accurately approximated by $0.026E^2$ per C atom within a few tenths of an eV. This gives a hole concentration in the graphene of about 10^{12} cm^{-2} for the case where the Dirac point lies about 0.1 eV above the valence band of GaAs (Fig. 5). This is comparable to the changes in hole concentration caused by adsorbed NO_2.[25] For *n*-GaAs, the same analysis suggests a density of electrons transferred to graphene would be a factor ∼10 or more greater. However, in this case, the screening effect of the transferred charge would have to be considered.

In conclusion, the use of *n*-GaAs and *p*-GaAs substrates to epitaxially deposited graphene offers a means of doping graphene in a simple way. Similar effects are expected in other III–V materials.

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[1] C. E. Nebel, B. Rezek, D. Shin, H. Watanabe, and T. Yamamoto, J. Appl. Phys. **99**, 033711 (2006).

[2] J. P. Goss, B. Hourahine, R. Jones, M. I. Heggie, and P. R. Briddon, J. Phys.: Condens. Matter **13**, 8973 (2001).

[3] S. J. Sque, R. Jones, J. P. Goss, P. R. Briddon, and S. Öberg, J. Phys.: Condens. Matter **17**, L21 (2005).

[4] P. Strobel, J. Ristein, L. Ley, K. Seppelt, I. V. Goldt, and O. Boltalina, Diamond Relat. Mater. **15**, 720 (2006).

[5] J. P. Goss, R. J. Eyre, and P. R. Briddon, Phys. Status Solidi A **204**, 2903 (2007).

[6] S. J. Sque, R. Jones, S. Öberg, and P. R. Briddon, Phys. Rev. B **75**, 115328 (2007).

[7] S. J. Sque, R. Jones, and P. R. Briddon, Phys. Status Solidi A **204**, 3078 (2007).

[8] J. Chen, C. Klinke, A. Afzali, and P. Avouris, Appl. Phys. Lett. **86**, 123108 (2005).

[9] E. L. Sceats and J. C. Green, Phys. Rev. B **75**, 245441 (2007).

[10] W. Chen, S. Chen, D. C. Qi, X. Y. Gao, and A. T. S. Wee, J. Am. Chem. Soc. **129**, 10418 (2007).

[11] T. R. Ohno, Y. Chen, S. E. Harvry, G. H. Kroll, and J. H. Weaver, Phys. Rev. B **44**, 13747 (1991).

[12] M. Krüger, I. Widmer, T. Nussbaumer, M. Buitelaar, and C. Schönenberger, New J. Phys. **5**, 138 (2003).

[13] S. Y. Zhou, G.-H. Gweon, A. V. Fedorov, P. N. First, W. A. De Heer, D.-H. Lee, F. Guinea, A. H. Castro Neto, and A. Lanzara, Nat. Mater. **6**, 770 (2007).

[14] A. L. Vazquez de Parga, F. Calleja, B. Borca, M. C. G. Passeggi, J. J. Hinarejos, F. Guinea, and R. Miranda, Phys. Rev. Lett. **100**, 056807 (2008).

[15] G. Bertoni, L. Calmels, A. Altibelli, and V. Serin, Phys. Rev. B **71**, 075402 (2005).

[16] J. Coutinho, R. Jones, P. R. Briddon, and S. Öberg, Phys. Rev. B **62**, 10824 (2000).

[17] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).

[18] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[19] J. Coutinho, R. Jones, M. J. Shaw, P. R. Briddon, and S. Öberg, Appl. Phys. Lett. **84**, 1683 (2004).

[20] G. X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **37**, 1303 (1988).

[21] X. Zhu, S. B. Zhang, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **63**, 2112 (1989).

[22] A. Huijser and J. von Laar, Surf. Sci. **52**, 202 (1975).

[23] D. Straub, M. Skibowski, and F. J. Himpsel, Phys. Rev. B **32**, 5237 (1985).

[24] G. W. Gobeli and F. G. Allen, Phys. Rev. **137**, A245 (1965).

[25] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, Nat. Mater. **6**, 652 (2007).