General approach to understanding the electronic structure of graphene on metals

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Abstract

This manuscript presents the general approach to the understanding of the connection between bonding mechanism and electronic structure of graphene on metals. To demonstrate its validity, two limiting cases of ‘weakly’ and ‘strongly’ bonded graphene on Al(111) and Ni(111) are considered, where the Dirac cone is preserved or fully destroyed, respectively. Furthermore, the electronic structure, i.e. doping level, hybridization effects, as well as a gap formation at the Dirac point of the intermediate system, graphene/Cu(111), is fully understood in the framework of the proposed approach. This work summarises the long-term debates regarding connection of the bonding strength and the valence band modification in the graphene/metal systems and paves a way for the effective control of the electronic states of graphene in the vicinity of the Fermi level.

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The recent demonstration of the unique transport properties of graphene [1, 2], a two-dimensional allotrope form of carbon, opens a door in the world where strict 2D circuits built on the basis of graphene can be fabricated and used [3]. However, all these applications require that at some point the graphene-based device is contacted by metal. Considering graphene on metal one can expect, in the general case, a strong modification of its valence band electronic structure. Presently, with respect to such changes, graphene on metal is described either as ‘strongly’ or ‘weakly’ bonded to metal. In the first case graphene is always \( n \)-doped and the overlap of the valence band states of graphene and metal at relatively short distance between
them (in the range of 2 - 2.3 Å) completely destroys the linear dispersion of the graphene $\pi$ states around the Fermi level ($E_F$) [4–9]. For the ‘weakly’ interacting system (graphene can be $n$- or $p$-doped) a linear dispersion of $\pi$ states around $E_F$ is preserved [10–14].

Here it is worth mentioning that DFT calculations with different functionals, in most cases giving very good agreement with experiment regarding the electronic structure, predict the bonding energy of graphene to metals in the range of 50 - 150 meV/C-atom with the higher value for ‘strongly’ bonded graphene [15]. This value is far below the lower limit of $\approx -500$ meV atom$^{-1}$ which is usually taken for the description of the strong chemical adsorption on the metallic surfaces, allowing one to conclude that the interaction between graphene and metal is of physical nature in all studied cases.

At the same time, the recent angle-resolved photoemission experiments on graphene/Cu and graphene/Au show that despite the linear behaviour of the graphene-derived $\pi$ states around $E_F$, there is a clear hybridization between graphene $\pi$ and metal $d$ valence band states [16, 17]. These experiments also reveal the pronounced energy gap at the Dirac point ($E_D$) [13, 17]. The idea that this gap is due to the broken sublattice symmetry and that the width of the energy gap depends on the doping level of graphene is not supported by other experiments or calculations [14, 18–20].

In this manuscript, basing on the analysis of a large amount of experimentally and computationally obtained band structures, we propose a universal model that allows one to describe qualitatively any graphene/metal system. All experimental observations such as doping, hybridization of the valence band states of graphene and metal, and gap formation are considered and explained in the framework of this approach. The validity of our model is supported by the results of DFT calculations for several representative examples.

Let us consider graphene on the close-packed metallic substrate, as shown in figure 1. Without loss of generality (see supplementary material, available at stacks.iop.org/MRX/1/035603/mmedia for details) we take a lattice-matched case of graphene on the (111) surface of close-packed metal. In such a system two carbon atoms from different sublattices occupy inequivalent adsorption positions of the metallic surface. They are called $\text{top}$, $\text{fcc}$, and $\text{hcp}$ if carbon atom is placed either above M(S) atom or above the corresponding hollow site of the metallic slab, respectively (figure 1(a)). Usually in the ground-state structure one of the carbon atoms occupies $\text{top}$ position and the second one is placed above $\text{fcc}$ or $\text{hcp}$ position (see [15] and reference therein; [21]). In this case one can expect that the sublattice symmetry is broken if the interaction strength between graphene and metal is strongly varied along the graphene lattice. However, as the bonding energy between graphene and metal is quite small (in the range of 50 - 150 meV/C-atom) and graphene is bonded to the metallic surface only via van der Waals (vdW) forces, the difference in the adsorption position cannot lead to the strong variation of the interaction strength between carbon atoms and the metallic substrate. Therefore the mechanism of the gap opening for the $\pi$ band around the Dirac point due to the violation of the sublattice symmetry in the graphene unit cell can be fully ruled out.

First, let us consider a ‘trivial’ case when graphene is placed on $sp$-metal (figure 2(a)). Here the mobile $sp$ electrons fill the unoccupied $\pi^*$ states of graphene yielding the shift of $E_D$ below $E_F$ ($n$-doped graphene). The equilibrium distance as well as the doping level of graphene depends on the difference of the work functions of graphene and metallic surface [22, 23]. The localization of the electron density on the graphene-derived $\pi$-orbitals at the graphene/metal interface leads to the increase of the attraction between graphene and metal. In the electronic structure of graphene the energy shift of $\pi$ and $\sigma$ states is equal. This description is valid for the
graphene/alkali-metals [19] and graphene/Al [14] interfaces, where simple $n$-doping of graphene is observed without any modification of the Dirac cone. In the case of $p$-doped graphene (the electrons are transferred from graphene to metal), the Dirac cone is shifted upwards. Opposite to the former situation, the electron density depletion at the graphene/metal interface leads to the decrease of the vdW interaction at the interface as the dipole moment becomes smaller. Though $p$-doping is hardly possible when dealing with simple $sp$-metals, its formal reference here is needed for further discussion.

If the underlying metal has an open $d$-shell, its interaction with graphene is more complicated (figure 2(b)). At first, analogously to the case of $sp$-metals, the mobile $sp$ electrons of metal will define the initial doping of a graphene layer. In all existing cases doping of graphene leads to the positioning of $E_D$ within the $d$ band. Due to the existence of the $d$-orbitals with out-of-plane components ($d_{xz}$, $d_{yz}$, $d_{z^2}$), several, so-called, hybrid states are formed around the K-point (figure 2(b)) from the corresponding $d$-states of metal and graphene-derived $\pi$-states. Here, several conditions for the hybridization are fulfilled, energy-, real-space-, and $k$-space-overlapping of the initial orbitals.

The effect of the $\pi$-$d$ hybridization leads to the violation of the sublattice symmetry in the graphene unit cell. Considering a graphene layer on top of the close-packed (111) surface of metal in the top-fcc arrangement (figure 1(b)) [15], one can see that the $p_z$ orbital of the C-top atom overlaps with $d_{z^2}$ orbital of the metal atom in the surface layer, M(S), forming the

![Figure 1](image_url)
Similarly, the $p_z$ orbital of C-fcc atom overlaps with $d_{x^2-y^2}$ orbitals of M(S), forming the \( p_z^{C-fcc} - d_{x^2-y^2} \)-hybrid. Generally, for the free-standing graphene, the electronic states from both carbon atoms are degenerate at the K point. In the case of graphene adsorbed on metal, such degeneracy is lifted up via gap opening at K because the effect of hybridization described earlier leads to the formation of two hybrid states of different symmetry which cannot exist simultaneously at the same energy at the K point.

All reasonings given above for graphene on the $sp$ and open $d$-shell metals can be generalized for graphene on the closed $d$-shell metal (figure 2(c)). Initial doping of graphene is governed by the mobile $sp$ electrons of metal. If $d$ band of metal is filled then it is located far below $E_D$ of the doped graphene. However, as was discussed earlier, the energy-, real-space-, and k-space-overlap of the metal $d$- and graphene-derived $\pi$-orbitals leads to the formation of the hybrid states and opening of the energy gaps according to the avoided-crossing mechanism in the energy and k-vector ranges where $\pi$ band is crossed by the $d$ bands. Such interaction, accompanied by the formation of $p_z^{C-top} - d_{z^2}$ and $p_z^{C-fcc} - d_{x^2-y^2}$ hybrid states of different orbital symmetry, leads to the violation of the symmetry of the electronic states at the K point and opens the energy gap at $E_D$ of graphene.

Figure 2. Energy schemes demonstrating the discussed model. (a) Graphene/sp-metal: doping of graphene, the characteristic linear dispersion near the Dirac point is largely preserved. (b) Graphene/open-$d$-shell-metal: after initial doping, formation of \( \pi - d \) hybrid states with a massive rearrangement of bands. (c) Graphene/closed-$d$-shell-metal: after initial doping, formation of hybrid states in the energy range far below $E_D$ and the opening of a band gap at $E_D$. For further details, see text.
Thus, the effect of hybridization between graphene-derived π-states and filled shell d states of metal, which exists in the energy range and for k-vector values far off the Dirac point, leads to the opening of the energy gap directly at $E_D$ due to the lifting of the degeneracy of the electronic states for two carbon sublattices: the π states of carbon atoms from different sublattices hybridize with d states of the different symmetries of the same interface metal atom, M(S) (figures 1(b) and 2(c)).

Now we demonstrate the validity of our model with several representative examples. DFT calculations (see Supplementary material [20] for details) for free-standing graphene give a linear dispersion of the π states in the vicinity of $E_F$ around the K point (figure 3(a)). Adsorption of graphene on Al(111) (sp metal) yields the n-doping of graphene via transfer of the mobile $s^2p^1$ electrons on the unoccupied π* graphene states and $E_D$ is placed at $E - E_F = -0.7$ eV (figure 3(b)). This situation is described by the scheme shown in figure 2(a). The obtained results are in very good agreement with experimental data for the graphene/Al/Ni(111) system [14], where simple doping of graphene without gap formation was observed. Similar results were experimentally found for other graphene/sp-metal systems [18–20, 24].

The electronic structure of graphene on Ni(111) (open d shell metal) is shown in figure 3(c). Here doping of graphene by 4s electrons places $E_D$ below $E_F$ so it energetically overlaps with the Ni 3d bands. Electrostatic interaction decreases the distance between graphene and Ni that increases the space overlap of the Cpz and Ni 3d orbitals. As a result of the energy-, real-space-, and k-space-overlap of the valence band states of graphene and metal, the Dirac cone of graphene is fully destroyed and several hybrid states are formed. Hybridization yields further decreasing of the distance between graphene and Ni(111) to the equilibrium value of 2.08 Å. This situation is described by the scheme in figure 2(b). These results are in very good agreement with our model with several representative examples.
agreement with experimental data for graphene/Ni(111) as well as for other ‘strongly’ interacting graphene/metal systems [7, 9, 15, 18, 25].

The most interesting situation is observed for graphene/Cu(111) (figure 3(d)), where graphene is n-doped due to the s electrons transfer from Cu, and $E_D$ is at $E - E_F = -0.45$ eV. Similar to graphene/Ni(111), doping of graphene decreases the distance between graphene and Cu(111). This effect allows one to satisfy three necessary conditions for the hybridization of the Cu3$d$ and graphene $\pi$ states (space-, energy-, and $k$-vector conservation during hybridization) and the hybridization in this system is detected in the energy range of $E - E_F \approx -2...4.5$ eV (figure 3(d)).

Further analysis of the calculated band structure of graphene/Cu(111) shows that the energy gap of 18 meV is opened directly at $E_D$ (figure 4(a)). Decomposition of the bands around $E_D$ shows that the obtained picture is fully identical to the scheme presented in figure 2(c). The hybridization discussed earlier leads to the appearance of the hybrid states formed by the $p_z$ states of the two carbon atoms from different sublattices of the graphene layer and 3$d$ states of different symmetry of the same top Cu atom: $p_z^{C-top}$$d_{z^2}^{Cu(S)}$-hybrid and $p_z^{C-fcc}$$d_{xz,yz}^{Cu(S)}$-hybrid.

**Figure 4.** (a,b) Decomposition of the electronic structure of graphene/Cu(111) in the vicinity of the energy gap at the K point. The weight of the corresponding states is proportional to the width of the coloured line. (c) and (d) Dependencies of the gap width on the doping level of graphene and on the graphene-Cu(111) distance, respectively. Relative Cu 3$d$ weight is plotted on the corresponding panels. The solid lines are eye-guides.
Formation of these two states leads to the lifting of the initial degeneracy at $E_D$, characteristic for the free-standing or doped graphene, and opening of the symmetry band gap.

Following the above discussion, one can expect that the width of the gap will further depend on the relative energy positions of the unperturbed Dirac cone and the metal $d$-band due to the increased partial weight of the metal $d$ states in the energy band: the closer the cone to the $d$-band the larger the gap at the Dirac point. A similar effect is expected if the distance between a graphene layer and Cu(111) is decreased due to increase of the space overlap of $p_z$ and $d$ orbitals.

In order to follow this effect we simulated the artificial doping of the graphene/Cu(111) system via adsorbing the Li atoms above the graphene layer. As expected the energy gap is increased and the results for the doping level of $E - E_F = -1.33$ eV and the energy gap of 46 meV are presented in figure 4(b), respectively. Further increase of the doping level leads to the widening of the energy gap as shown in the plot in figure 4(c), where the relative Cu 3$d$ weight in the lower-energy branch at the K point is also presented (for the corresponding band structures, see the supplementary material, figure S2 [20]). A similar effect is also observed if the distance between graphene and Cu(111) is varied: lessening the distance leads to the stronger space overlap of graphene $\pi$ and Cu 3$d$ orbitals increasing the partial $d$ weight of the band and consequently further widening the energy gap for the $\pi$ states at the K point (figure 4(d) (for the corresponding band structures, see the supplementary material, figures S3 and S4 [20]). The calculated doping level for all distances from figure 4(d) is below the maximum doping obtained in figure 4(c) as it is defined by the more mobile 4$s$ electrons. From these data we can conclude that the energy overlap of the graphene $\pi$ and Cu 3$d$ states plays a dominant role on the width of the band gap around $E_D$ of graphene.

It is interesting to note that appearance of the energy gap for the graphene-derived $\pi$ states and its width is caused by the mixing of the graphene and metal valence band states and it changes the band dispersion close to the border of the Brillouin zone drastically. As can be seen from figure 4 this leads to the violation of the linear dispersion of the $\pi$ states around the K point with the increase of the effective mass of carriers. This effect can drastically change the transport properties of the graphene-based devices where graphene/metal interfaces are implemented.

The presented model describes the appearance of the energy gap at $E_D$ of graphene on metal on the qualitative level and predicts its behaviour as a function of the doping level of graphene in this system, that correlates with available experimental data. The doping of graphene alone cannot cause any sizeable gap in the electronic structure of graphene around $E_D$.

The three different cases considered in the present work are related to the $n$-doped graphene on metal. The situation is slightly different for the $p$-doped graphene on metal. Here the electron-transfer from graphene to metal reduces the polarization of the graphene layer that might lead to the reduction of the vdW attraction in the system that reduces the possible space overlapping of the graphene $p_z$ and metal $d$ orbitals. However, as shown in the experiment [13, 26], the doping of these systems can shift $E_D$ closer to the $d$ states of metal thus widening the energy gap in the electronic structure of graphene.

In conclusion, we have built an universal model for the description of the electronic structure of graphene on any metallic surface. Our model takes into account initial doping of a graphene layer by mobile $sp$ electrons, which depends on the work functions of graphene and metallic surface. Further modification of the electronic structure of graphene on $d$ metals is determined by the position of the Dirac point with respect of the $d$-band of metal. Such
interaction leads either, in the case of the open $d$ shell metals, to the complete destruction of the Dirac cone around the K point or, in the case of the closed $d$ shell metals, to opening the energy gap in the electronic structure of graphene directly at the Dirac point. Both effects are connected with the overlap of the graphene $p_z$ orbitals of two carbon atoms in the graphene unit cell with $d$ orbitals of the interface metal atom of different symmetries. Our funding explains all observed effects on the qualitative level and allows predicting the behaviour of the electronic states of graphene upon formation of the graphene/metal contacts in future devices.

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References

[1] Novoselov K, Geim A, Morozov S, Jiang D, Katsnelson M, Grigorieva I, Dubonos S and Firsov A 2005 Nature 438 197
[2] Zhang Y, Tan Y, Stormer H and Kim P 2005 Nature 438 201
[3] Novoselov K S, Fal’ko V I, Colombo L, Gellert P R, Schwab M G and Kim K 2013 Nature 490 192
[4] Bertoni G, Calmels L, Altibelli A and Serin V 2004 Phys. Rev. B 71 075402
[5] Karpan V M, Khomyakov P A, Starikov A A, Giovannetti G, Zwierzycki M, Talanana M, Brocks G, van den Brink J and Kelly P J 2008 Phys. Rev. B 78 195419
[6] Weser M, Voloshina E N, Horn K and Dedkov Y S 2011 Phys. Chem. Chem. Phys. 13 7534
[7] Dedkov Y S and Fonin M 2010 New J. Phys. 12 125004
[8] Varykhalov A and Rader O 2009 Phys. Rev. B 80 035437
[9] Brugger T, Guenther S, Wang B, Dil J H, Bocquet M-L, Osterwalder J, Wintterlin J and Greber T 2009 Phys. Rev. B 79 045407
[10] Dedkov Y S, Shikin A M, Adamchuk V K, Molodtsov S L, Laubschat C, Bauer A and Kaindl G 2001 Phys. Rev. B 64 035405
[11] Pletikosić I, Kralj M, Pervan P, Brako R, Coraux J, N’diaye A, Busse C and Michely T 2009 Phys. Rev. Lett. 102 056808
[12] Sutter P, Sadowski J and Sutter E 2009 Phys. Rev. B 80 245411
[13] Varykhalov A, Scholz M, Kim T and Rader O 2010 Phys. Rev. B 82 121101
[14] Voloshina E N, Generalov A, Weser M, Böttcher S, Horn K and Dedkov Y S 2011 New J. Phys. 13 113028
[15] Voloshina E and Dedkov Y 2012 Phys. Chem. Chem. Phys. 14 13502
[16] Shikin A M, Rybkin A G, Marchenko D, Rybkina A A, Scholz M R, Rader O and Varykhalov A 2013 New J. Phys. 15 013016
[17] Vita H, Boettcher S, Horn K, Voloshina E, Ovcharenko R, Kampen Th and Thiessen A 2014 Sci. Rep. 4 5704
[18] Grünéis A and Vyalikh D 2008 Phys. Rev. B 77 193401
[19] Petrović M et al 2013 Nat. Commun. 4 2772
[20] Fedorov A V et al 2014 Nat. Commun. 5 3257
[21] Gamo Y, Nagashima A, Wakabayashi M, Terai M and Oshima C 1997 Surf. Sci. 374 61
[22] Giovannetti G, Khomyakov P A, Brocks G, Karpan V M, van den Brink J and Kelly P J 2008 Phys. Rev. Lett. 101 026803
[23] Khomyakov P A, Giovannetti G, Rusu P C, Brocks G, van den Brink J and Kelly P J 2009 Phys. Rev. B 79 195425
[24] Bianchi M, Rienks E D L, Lizzit S, Baraldi A, Balog R, Hornekaer L and Hofmann P 2010 Phys. Rev. B 81 041403
[25] Pacilé D et al 2013 Phys. Rev. B 87 035420
[26] Enderlein C, Kim Y S, Bostwick A, Rotenberg E and Horn K 2010 New J. Phys. 12 033014