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Sublattice-induced symmetry breaking and band-gap formation in graphene

Ralph Skomski, P. A. Dowben, M. Sky Driver and Jeffry A. Kelber

A reduction of symmetry from $C_{6v}$ to $C_{3v}$ leads to the opening of a band gap in the otherwise gapless semiconductor graphene. Simple models provide a fairly complete picture of this mechanism for opening a band gap and in fact can be discussed in terms of the tight-binding approximation, accurately resolving the wave-vector space to a very high accuracy. This picture is consistent with experiments that yield a band gap due to A and B graphene-site symmetry breaking due to substrate interactions.

A. Introduction

There are various widely publicized approaches to engineering a band gap in graphene, such as strain engineering, spatial restriction, for example via graphene nanoribbon fabrication, controlling the density of electrons as in adsorbate hybridization, and symmetry breaking, typically as a result of substrate interactions. All have major flaws when the goal is retention of the unique properties of graphene while opening a band gap.

The creation of a band gap with strain has been investigated both theoretically and experimentally. Theoretical models are pretty consistent in showing that a band gap will open in graphene for some types of uniaxial strain but not for isotropic (affine) strain. The effective mass ($m_{\text{eff}}$) for uniaxially strained graphene, which is really the key parameter, in addition to the band gap, has sadly not been realistically considered in many of the model calculations of the strain-induced graphene band gap, with only a few exceptions. It is the large increase in $m_{\text{eff}}$ that diminishes the value of opening a band gap in graphene, as this increase is usually considerable. For graphene nanoribbons the situation is worse: not only is there a huge increase in $m_{\text{eff}}$, but edge scattering will be significant, further diminishing an already lack-luster carrier mobility. Recent transport measurements, for graphene nanoribbons of 40 nm width, have shown impressive mobilities, of $10^5$ to $10^7$ cm$^2$ V$^{-1}$ s$^{-1}$. This suggests that edge...
scatter may not always be a dominant factors for some graphene nanoribbon widths, but these nanoribbons were grown on SiC, where heavy n-doping is likely\textsuperscript{26,40,47,53,54} and a band gap with the chemical potential placed mid gap is unlikely. This leaves adsorbate or substrate induced band gaps as a more promising avenue for band gap engineering of graphene.

When considering a substrate induced modification of the gapless graphene, a band gap of zero\textsuperscript{22} to 0.16 eV (ref. 23) has been predicted for the single layer graphene between boron nitride layers while a band gap of 0.35 eV was predicted for graphene placed epitaxial registry on SiO\textsubscript{2},\textsuperscript{24} generally larger band gaps in graphene than the band gap of about 53 meV predicted for graphene on BN\textsuperscript{25} resulting from symmetry breaking, Obviously charge disorder or breaking of the A and B site symmetry matters.

A band gap of 0.26 eV has been experimentally determined for graphene on SiC,\textsuperscript{26,40} attributed to A and B site symmetry breaking, but is not a true band gap as the graphene is heavy n-type doped and the chemical potential (Fermi level) does not fall in the gap. Not just substrate symmetry breaking, but Bernal stacking, and the charge gradient due to substrate interactions, are expected to open a band gap for a trilayer graphene on SiC,\textsuperscript{35} but again, this is not a true band gap as the graphene is heavy n-type doped and the chemical potential (Fermi level) does not fall in the gap. Scanning tunneling microscopy spectroscopy finds a 100 meV gap, at zero bias,\textsuperscript{36} suggesting Fermi level placement midgap. In fact, both experimental band mapping and the scanning tunneling microscopy results for graphene on SiC may not be indicative of a band gap at all. Similar band structure mappings,\textsuperscript{55,56} attributed the distortions in the band structure near the Dirac point to electron-plasmon scattering\textsuperscript{41,53,57,58} and lateral scattering\textsuperscript{53,59} not a direct result of A and B site symmetry breaking.

An even larger band gap approximately 0.5–1 eV, is found for graphene on MgO, where again the band gap is believed to be a result of symmetry breaking\textsuperscript{29–31} in the graphene. This band gap for graphene on MgO, of order of 1/2 eV in experiment,\textsuperscript{31,32} is found to be larger than predicted by theory.\textsuperscript{33,34} Importantly, a band gap of about 180 meV has been predicted for graphene on the Al-terminated Al\textsubscript{2}O\textsubscript{3}(0001) surface, with an increase in electron effective mass of about $8 \times 10^{-3}$ $m_e$.\textsuperscript{35} Experimental studies of graphene grown directly on Al\textsubscript{2}O\textsubscript{3}(0001), however, revealed no evidence of a room temperature band gap.\textsuperscript{60} Thus theory does not always predict a smaller band gap than observed in experiment.

Other extrinsic breaking of symmetry is also possible. For Bernal-stacked bilayer graphene, carriers occupy the non-stacked sites of the two layers equally, in the absence of a perpendicular electric field, leading to the degeneracy of the conduction and valence bands at the charge neutrality (Dirac) point.\textsuperscript{61} As with the predictions applied to graphene on SiC,\textsuperscript{41,54,55} the application of a perpendicular electric field opens a band gap up to 0.25 eV and renders the transport insulating.\textsuperscript{36,39,41} For single layer graphene between boron nitride layers, application of an electric field also leads to an increased band gap in the range of 0.23 eV (ref. 22) to 0.34 eV.\textsuperscript{23}

In some sense, almost all approaches to opening a band gap in graphene also result in symmetry breaking, but all schemes involving sublattice modification seem to involve this mechanism. Our goal here is to provide an overall explanation of the effect, based on the chemical inequivalence of the A and B sites of graphene: breaking the AB sublattice symmetry of the graphene and reducing the symmetry from $C_{6v}$ to $C_{3v}$.

**B. Graphene on h-BN(0001)**

Density functional theory calculations for isolated graphene/BN bilayers,\textsuperscript{35} indicated that the most stable configuration for graphene on BN places the C atoms above N atoms and the center of BN rings (Fig. 1). Such a configuration manifestly breaks the chemical equivalence of graphene A and B lattice sites, resulting in a predicted band gap of 0.053 eV (53 meV).\textsuperscript{25} Consistent with

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other theory, changing the on-site potential difference between the carbon atoms in graphene, and the boron and nitrogen atoms in the h-BN, has been predicted to increase the induced gap, if the graphene is in registry with the boron nitride.

Experimental formation of graphene/BN bilayers has involved a number of approaches including physical transfer of graphene to BN crystallites and direct growth by CVD of graphene on BN deposited by atomic layer deposition (ALD). Studies involving physically transferred graphene generally have not investigated the relative orientation of the bilayers, and revealed no evidence of a band gap in the graphene. For graphene not precisely in registry with the hexagonal boron nitride, the expectation is that a gap may be induced at the graphene “Dirac point” while a new superlattice of Dirac points develop at finite energy, yet such graphene overlayers exhibit very high mobilities of 25 000 cm² V⁻¹ s⁻¹ (ref. 62) to 37 000 cm² V⁻¹ s⁻¹ (ref. 67) and above, consistent with little or no band gap.

Graphene/BN bilayers with graphene and BN in registry with each other can be formed by direct growth on transition metal substrates. Typically the BN moiety consists of a monolayer resulting from self-limiting pyrolysis of borazine or similar precursors. However, graphene has been directly grown on BN(0001) nanoflakes by various methods. Graphene/BN bilayers formed by direct growth on Ni(111) (ref. 65) or Ru(0001) (ref. 65) do indicate that the graphene and BN sheets are in registry with each other, consistent with Fig. 1 and expectations, although the precise relative coordination of the two layers was not determined from the reported LEED data.

The metallic substrate can influence the BN electronic structure. This is manifest from a close inspection of the data in Fig. 2. The photoemission/inverse photoemission data (Fig. 2a) and the STM dI/dV data (Fig. 2b) show no evidence of a band gap in the (room temperature) density of states for graphene/h-BN/Ru(0001). but again substrate effects are difficult to completely exclude. The direct growth of graphene on multilayer BN may be expected to diminish the effects of the metal substrate interactions with the first BN overlayer, and afford a clearer understanding of graphene/BN interactions and large-area h-BN(0001) multilayers have been fabricated by atomic layer deposition.

Consistent with the very small predicted band gap of 0.053 eV (53 meV) for graphene on boron nitride, the combined photoemission/inverse photoemission data (Fig. 2a) and the STM dI/dV data (Fig. 2b) show no evidence of a band gap in the (room temperature) density of states for graphene/h-BN/Ru(0001). but again substrate effects are difficult to completely exclude. The direct growth of graphene on multilayer BN may be expected to diminish the effects of the metal substrate interactions with the first BN overlayer, and afford a clearer understanding of graphene/BN interactions and large-area h-BN(0001) multilayers have been fabricated by atomic layer deposition.

Misalignment of the graphene with a substrate, even a substrate like h-BN, can result from the graphene placement with respect to the substrate lattice. For graphene not grown in registry with the h-BN lattice, a Moiré pattern results as the crystallographic directions of the graphene rotated with respect to the substrate. In terms of electronic structure, this causes a folding of the graphene band structure in momentum space, potentially resulting in the replication of multiple Dirac points at symmetric densities away from the zero energy Dirac point. Worse yet, graphene bilayers, misaligned from one another might well result in something akin to a 2 dimensional electron gas. These misaligned graphene to h-BN or graphene to graphene bilayers represent weak van der Waals interactions, but strong interactions are also deleterious to formation of any band gap, such as introduced by a partial transition metal layer
in close proximity to graphene,\textsuperscript{29,30} which leads to a density of states at the Fermi level.

### C. Graphene on MgO(111)

It is not enough to simply open a band gap in graphene, as shown with graphene on SiC:\textsuperscript{28,30,31} as noted above, the chemical potential need not fall midgap as adsorbates or substrate interactions may also dope the graphene. More promising in this regard has been graphene on oxides (although not Al\textsubscript{2}O\textsubscript{3} \cite{ref. 60}) but where with the correct surface termination or oxide surface reconstruction, the graphene is no longer a gapless semiconductor, but an insulator.\textsuperscript{29,30,34,35} The low energy electron diffraction (LEED) data, in Fig. 3, indicates that graphene growth on the reconstructed surface of MgO(111) leads to a 1 monolayer (ML) graphene film that is actually of $C_{3v}$ symmetry rather than six-fold symmetry \cite{fig:3a}.\textsuperscript{29,30,32} This indicates that in the first layer, the chemical equivalence of the graphene A sites and B sites has been lifted, apparently due to interactions with the MgO substrate. This pattern of 3-fold symmetry is also observed for few-layer graphene on MgO(111),\textsuperscript{29,30,32} as seen in Fig. 3b. The formation of an oxidized carbon component coinciding with the onset of long-range order and a $C_{3v}$ LEED pattern strongly indicate that the graphene/MgO interface is commensurate and involves both an interfacial reconstruction and chemical reactions. Since the O–O nearest-neighbor distance in bulk-terminated MgO(111) is about 2.8 Å,\textsuperscript{33} an incommensurate graphene/oxide interface will result if the oxide surface does not reconstruct. Carbon A sites and B sites would thus experience an ensemble of different substrate environments, resulting in the same average environment at both A and B sites. Instead, the 3-fold symmetry observed for single and few-layer films,\textsuperscript{30} coincident with the formation of an oxidized carbon peak carbon 1s X-ray photoemission peak strongly suggests significant carbon and/or oxide reconstruction at the interface.\textsuperscript{30,32} Indeed, this first layer may not be pure “graphene”, but a partially oxidized, albeit ordered, form.

A band gap is evident in the combined photoemission and inverse photoemission,\textsuperscript{28,30,32} as seen in Fig. 2, for graphene on MgO(111), and although heavily p-doped by the oxide interface, this graphene is insulating. Charge transport data\textsuperscript{30,32} for a single layer C(111) film (produced by PVD) on MgO(111) are also shown in Fig. 4. Fig. 5 shows a logarithmic plot of the resistance as a function of reciprocal temperature, which is linear and exhibits the negative magnetoresistance characteristic of a nonmetal. The transport data yield a carrier-hopping activation energy of 0.64 (±0.05) eV,\textsuperscript{30,32} consistent with a band gap of 0.5 eV or greater that is estimated from the combined photoemission/inverse photoemission.\textsuperscript{31,32} Given that this picture is also evident in model calculations for single layer graphene between boron nitride layers,\textsuperscript{23} graphene on BN,\textsuperscript{25,27} SiO\textsubscript{2},\textsuperscript{24} Al\textsubscript{2}O\textsubscript{3}(0001) \cite{ref. 35} and MgO,\textsuperscript{14} and the possibly controversial\textsuperscript{34,35,91} experimental band gap for graphene on SiC,\textsuperscript{28,40} charge disorder or breaking of the A and B site symmetry matters.

Other oxides should be considered in the future, but identifying a suitable surface where there is an interface lattice match with graphene, as in the case of MgO(111), is a challenge. For graphene grown on Co\textsubscript{3}O\textsubscript{4}(111), there is no evidence of a band gap, and extensive p-doping of the graphene is likely.\textsuperscript{22,93} Chromia, i.e. Cr\textsubscript{2}O\textsubscript{3}, has potential to be more effective than MgO(111) if the interface is stable and suitably terminated. The
attraction with chromia is the voltage controlled high surface polarization. Both the graphene Co$_3$O$_4$(111) and Cr$_2$O$_3$(001) to graphene interfaces are incommensurate, that is say that while graphene is aligned with the substrate when grown directly on Co$_3$O$_4$(111), the graphene lattice period is not identical with the substrate, at the interface. This makes symmetry reduction through different chemical interactions the graphene A and B sites more complex, if not more difficult. Cr$_2$O$_3$(001) is also attractive as having a less polar surface than MgO(111), thus less likely to p-dope the adjacent graphene layer extensively. As emphasized by Ballhausen as well as others, crystal-field and chemical effects are equivalent as far as symmetry-breaking is concerned, and the difference between the present theory and a more complete description of the electronic structure is the same as between Bethe-level crystal-field theory and ligand-field theory. For the theoretical background and the tight-binding calculation, see ref. 41 and references therein.

Fig. 5 shows the considered structure, distinguishing between the two sublattices in graphene. The bright (A) and dark (B) atoms sit on top of crystallographically nonequivalent sites of the substrate, so that the orbital or “on-site” energies of the p$_z$ electrons are different. Ignoring a physically unimportant zero-point energy, the on-site energies for the A and B atoms are $E_{AB} = \pm V_{CF}/2$. Here the crystal-field parameter $V_{CF}$ increases with decreasing distance between graphene layer and substrate. The corresponding tight-binding Hamiltonian is

$$\mathcal{H} = \begin{pmatrix} \frac{+V_{CF}/2}{T} & T \\ -V_{CF}/2 & \frac{-V_{CF}/2}{T} \end{pmatrix}$$

where $T = t \sum \exp(ik \cdot R_{AB})$ describes the interatomic hopping between the A and B sites.

D. Band-gap formation in graphene through sublattice modification

The reduction of symmetry, by breaking the chemical equivalency of the graphene A and B sites, leads to a reduction in symmetry from $C_{6v}$ point group to the $C_{3v}$ point group. In the $C_{3v}$ point group, away from $\Gamma$ the center of the Brillouin zone, there is no mirror plane symmetry in the Brillouin zone line to $K$, the edge of the graphene Brillouin zone, about which the Dirac cone is centered. With the loss of mirror plane symmetry at $K$, the $\pi$ band may not retain pure p$_z$ character, particularly if the graphene does not remain fiat in the x-y plane as a result of the symmetry reduction. It should be recognized, as throughout surface science, there is an interplay between the energy cost or strain energy for a surface (and in this case graphene) structural reconstructions and reduction in energy opening up a band gap. More importantly, when a reduction of the symmetry is allowed, graphene can lower the total free energy of the system and a band gap will open at the Dirac point.

To explain how symmetry breaking substrates affect the band structure of graphene, we have modeled the substrate as a crystal-field source and treated the graphene as a tight-binding p$_z$-electron system. As emphasized by Ballhausen as well as others, electrostatic crystal-field and quantum-mechanical ligand-field theories are equivalent as far as symmetry-breaking is concerned, and the difference between the present theory and a more complete description of the electronic structure is the same as between Bethe-level crystal-field theory and ligand-field theory. For the theoretical background and the tight-binding calculation, see ref. 41 and references therein.

Fig. 6 shows the considered structure, distinguishing between the two sublattices in graphene. The bright (A) and dark (B) atoms sit on top of crystallographically nonequivalent sites of the substrate, so that the orbital or “on-site” energies of the p$_z$ electrons are different. Ignoring a physically unimportant zero-point energy, the on-site energies for the A and B atoms are $E_{AB} = \pm V_{CF}/2$. Here the crystal-field parameter $V_{CF}$ increases with decreasing distance between graphene layer and substrate. The corresponding tight-binding Hamiltonian is

$$\mathcal{H} = \begin{pmatrix} \frac{+V_{CF}/2}{T} & T \\ -V_{CF}/2 & \frac{-V_{CF}/2}{T} \end{pmatrix}$$

where $T = t \sum \exp(ik \cdot R_{AB})$ describes the interatomic hopping between the A and B sites.
\[ T = t(\exp(ik,a) + 2 \exp(-ik,a/2)\cos(\sqrt{3}k,a/2)) \]  

(2)

The appearance of \( T^* \) in the bottom left corner of the Hamiltonian of eqn (1) is mandated by hermiticity, but it can also be interpreted in terms of interchanged sublattices (\( R_{BA} = -R_{AB} \)).

The solution of eqn (1) is trivial and yields two energy branches

\[ E_{\pm}(k) = \pm \sqrt{V_{CF}^2/4 + T^*(k)T(k)} \]  

(3)

where \( V_{CF} \) can be shown to equal the band gap. This is evident from Fig. 7, which compares the familiar “spider legs” of the graphene Brillouin-zone boundary dispersion relation \( E_i(k) \) without (a) and with (b) symmetry breaking. For \( V_{CF} = 0 \), the legs have needle-shaped feet which touch the Dirac points (dots), indicating linear dispersion near the Dirac point and zero effective mass. In the presence of the symmetry-breaking potential \( \pm V_{CF}/2 \), a gap of width \( V_{CF} \) opens and the ends of the legs become curved, corresponding to a non-zero effective mass.

Near any of the Dirac points \( (k_x, k_y) \), the energy can be expanded in terms of the small wave-vector difference \( \mathbf{q} = (k_x - K_x, k_y - K_y) \). This leads to \( T^*T = 3a^2q^2t^2/4 \) where \( q = (q_x^2 + q_y^2)^{1/2} \), and the corresponding dispersion relation, \( E_i = V_{CF}/2 + 3a^2q^2t^2/4V_{CF} \), yields the effective mass \( m^* = 2\hbar^2V_{CF}a^2 \). Since the lattice parameter \( a \) does not vary very much from system to system, the effective mass is essentially determined by the band gap \( V_{CF} \). It is convenient to consider the ratio \( m^*/m = 4V_{CF}E_{\text{cap}}a^2/3t^2a^2 \), where \( m \) is the electron mass, \( E_{\text{cap}} = 13.6 \) eV, and \( a_0 = 0.529 \) Å. Taking \( V_{CF} = 0.5 \) eV, \( t = 2.7 \) eV, and \( a = 2.46 \) Å yields \( m^*/m = 0.058 \), which can be regarded as a typical value for the effective mass. This is a smaller effective mass than is the case when the band gap is opened by uniaxial strain.4

Note that the gap is the same for all Dirac points (Fig. 8), that is, all spider legs have the same length. The difference between the A and B sites appears in the wave functions \( \psi_{\pm}(r) \) corresponding to the two energy branches of eqn (3): at the Dirac points, the wave functions are entirely of the A type \( (\psi_+) \) or of the B type \( (\psi_-) \). For example, n-doping means that only A sites are occupied. In the absence of currents in the graphene sheet, the wave functions must be real. At the Dirac points, this can be achieved by superposing solutions for \( \mathbf{K} \) and \( -\mathbf{K} \), exploiting that \( \exp(\mathbf{K} \cdot \mathbf{R}_A) + \exp(-\mathbf{K} \cdot \mathbf{R}_A) = 2 \cos(\mathbf{K} \cdot \mathbf{R}_A) \). Fig. 8 shows typical \( p_z \) electron density that might be possible for graphene, as induced by the substrate. For n-doped graphene and positive \( V_{CF} \), the extra electrons occupies the A sites, and the electron density of the dark blue atoms is 4 times higher that of the bright blue atoms. For p-doped graphene, the same argument would of course apply to hole carriers.

For the derivation and interpretation of Fig. 8, it is convenient to use \( \mathbf{K} = (4\pi/3\sqrt{3}a, 0) \). The horizontal distance between columns of atoms, \( \Delta = \sqrt{3}a/2 \), then corresponds to a phase

Fig. 7 The energy dispersion \( E_i(k_x, k_y) \) for (a) perfect graphene \( (V_{CF} = 0) \) and (b) graphene on a symmetry-breaking substrate \( (V_{CF} = 2V_0 = 0.8 t) \).

Fig. 8 Schematic real-space electron density (top view of \( p_z \) electrons) for n-doped graphene and positive \( V_{CF} \).

Fig. 9 The relationship of the band gap near the Dirac point and the relative on-site energies of the A and B sites by \( \pm V_{CF}/2 \).
shift of $2\pi/3 = 120^\circ$. This means a shift by $3\Delta$ or $360^\circ$ reproduces the original charge density. It should be noted that opening the band gap does result in an increase in carrier effective mass, and the greater the band gap, the greater the effective mass, as summarized in Fig. 9.

E. Conclusions

Band gap engineering of graphene is certainly possible, and this opens up the possibility of devices in very strict 2 dimensional conduction channels, but at the cost of increased effective mass. Effective mobilities for graphene on MgO have not been reported, but for graphene without a band gap (or at least a very nearly negligible band gap), transferred to various substrates, room temperature mobilities above ~20 000 cm$^2$ V$^{-1}$ s$^{-1}$ (ref. 62, 63 and 101) are possible, but more often below 3000 cm$^2$ V$^{-1}$ s$^{-1}$ are reported. While such mobility limitations are for the most part due to factors other than band structure, the introduction of a band gap can only further decrease carrier mobilities (Fig. 8 and 9).

It is important to realize that extrinsic mechanisms like adsorbate or substrate interactions may also dope the graphene. If the advantages accrued by converting graphene from a gapless semiconductor to a band gap semiconductor, it is important that the graphene then not be over-doped to imitate a degeneratively doped semiconductor. We note that there are flaws in estimating the band gap in graphene with density-functional theory (DFT): on the one hand, DFT is notorious for underestimating band gaps due to correlations, but on the other hand, wave-vector sampling techniques might not sample the density of states with a sufficient wave-vector grid and therefore overestimate a band gap. While correlation effects in graphene are debatable, our present approach explains band-gap openings in graphene with very high $k$-space accuracy.

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Notes and references