Embedded ribbons of graphene allotropes: an extended defect perspective

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Abstract. Four fundamental dimer manipulations can be used to produce a variety of localized and extended defect structures in graphene. Two-dimensional templates result in graphene allotropes, here viewed as extended defects, which can exhibit either metallic or semiconducting electrical character. Embedded allotropic ribbons—i.e. thin swaths of the new allotropes—can also be created within graphene. We examined these ribbons and found that they maintain the electrical character of their parent allotrope even when only a few atoms in width. Such extended defects may facilitate the construction of single atomic layer carbon circuitry.

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1. Introduction

The presence of defects in condensed matter has a dramatic influence on electrical character. Extended defects such as dislocations, grain boundaries and phase interfaces, for instance, tend to have a deleterious effect on electron mobility and can serve as unwanted recombination sites in photovoltaic materials. The introduction of localized dopant defects to tune electronic structure, on the other hand, is a mainstay of the semiconductor industry. Whether unavoidably present or intentionally introduced, localized and extended defects tend to be statistically distributed. The precise placement of defects, however, offers a mechanism for the architecture of materials.

Graphene offers a particularly attractive setting for such defect engineering. Its two-dimensional geometry implies that the entire domain is accessible to external manipulation. Although such manipulations may seek to modify the thermal, mechanical or chemical character, our current focus is to provide a means of creating single atomic layer, carbon logic circuitry. This requires that it be possible to create conductors, semiconductors and charge confinement structures. In addition, composite systems must be structurally stable and should not unduly modify individual character. Charge may then be introduced, confined, gated and routed within a single sheet.

Our approach is in contrast to a number of other strategies that are being explored to manipulate the electronic structure of graphene. Those tend to focus on the use of external agencies to distort graphene so that it exhibits a band gap. Such external agencies include the use of strongly interacting substrates [1]–[3] or the application of electric fields in graphene bilayers [1, 4, 5]. Quantum confinement effects can also be exploited in carbon nano-ribbons (CNRs) [6]–[8] or carbon nano-meshes [9]. Another approach for tailoring graphene is chemical modification. For instance, hydrogen can be introduced so as to change the bonding from sp-2 to sp-3 for creating the corrugated insulator graphane [10]. Similarly, a graphene oxide insulator can be created via bonding with hydroxyl groups [11]. The external agency can also appear in the form of neighboring regions of foreign material as in composite two-dimensional structures that harbor domains of graphene [12]. However, we consider an intrinsic approach to modification, where defects are introduced into graphene in order to endow it with new electronic properties. Several other researchers in the field are also exploring such defect modifications [13].

In a series of earlier works, we have identified simple defects from which a variety of localized and extended structures can be fabricated [14]–[17]. Our perspective is now that the design space is best described as four basic operations that can be performed on a single carbon dimer. These are shown in figure 1. The first is the identity operation in which an existing carbon dimer is left unchanged. The second is the familiar Stone–Thrower–Wales (STW) defect consisting of a rotation of a carbon dimer. Addition of a dimer constitutes the third configuration and results in an inverse Stone–Thrower–Wales (ISTW) defect [14, 18]. Conversely, removal of a carbon dimer results in a di-vacancy (DV) defect, the fourth letter in our alphabet. All structures to be considered can be reduced to a weighted sum of these basic building blocks. Even when distinct from the actual synthesis routes, the analytical fabrication of structures as a sequence of dimer additions, subtractions, rotations and preservations lends a new type of insight into form and function.

All elements of this defect alphabet have been experimentally observed [19]–[24]. STW defects have been extensively studied in both graphene [19, 25, 26] and CNTs [27, 28], and
Figure 1. A four-letter alphabet for defect creation: (a) identity operation leaving the dimer as is; (b) dimer rotation to create an STW defect; (c) dimer addition to create an ISTW defect; (d) dimer removal to create a DV defect; (e) extended defect, an embedded semiconducting ribbon created with a combination of dimer rotations and dimer removals.

they can be created by scanning tunneling microscopy (STM) [29] or atomic force microscopy (AFM) [30]. DV defects can be created via irradiation or electron bombardment [21, 23]. Recently, an electron irradiation beam focused to 1 Å was shown to be capable of precisely creating vacancies in CNTs [20]. DVs have also been considered theoretically within a CNT setting, where molecular dynamics annealing causes them to reconstruct into 5-8-5 defects [31, 32]. A series of ad-dimer ISTW defects has been experimentally achieved [24] by focusing on the interatomic spacing of the defect rather than on physically depositing a dimer on the graphene. High-resolution transmission electron microscopy was also used to identity a collection of pentagon and heptagon defects that amount to an STW and an ISTW defect in close proximity, as shown in figure 3(i) [33]. Direct dimer addition may be another avenue for achieving the ISTW defect as advances in experimental methods of graphene manipulation are now approaching atomic fidelity using STM [29] and AFM [30] and via novel inventions such as the one proposed by Allis and Drexler [34].

In this work, we focus on patterned defect structures obtained by replication of a defect unit, a combination of the basic alphabet members. For instance, ad-dimers can be used to create nonplanar blisters by adding STW defects to either side as shown in figures 2(a) and (b). Larger blisters can also be created using additional ISTW defects, and graphene islands can

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Figure 2. A metacrystal created by patterning a localized defect structure: (a) an ISTW defect with STW defects on either shoulder relaxes into a non-planar blister; (b) perspective view of the blister shown in (a); (c) patterning of blisters results in a metacrystal. Blisters with both positive polarity (red) and negative polarity (yellow) are possible. (Panel (c) has been reproduced with permission from [14]. Copyright 2008 by The American Physical Society.)

even be made to bubble up when corralled by a loop of the ad-dimers [14]. Replication of localized blisters results in the metacrystal shown in figure 2(c). However, even closer packing can result in planar allotropes of graphene [15]. These allotropes may be either conducting or semiconducting; they merit a brief review because they are a starting point for the embedded defect ribbons that we have in mind, i.e. thin strips of an allotrope existing within a parent graphene sheet, e.g. as shown in figure 1(e). These ribbons are the monolithic analogue of graphene nanoribbons [7], but their electronic character is intrinsic and not due to the presence of free boundaries. We will show that both conducting and semiconducting ribbons can be constructed within a completely planar setting.

The electrical, and most likely magnetic, properties of graphene allotropes are attributable not to any one of the fundamental dimer operations but rather to the type, arrangement and misfit distortion of the carbon rings that result. For instance, octagonal rings can be created with differing combinations of dimer operations so as to give differing types of neighbor rings. Adjacent STW defects can create an octagon surrounded by pentagons, hexagons and heptagons, as illustrated in figure 3(a). An octagon can also be created when a DV pinches in at left and right, as shown in figure 3(b). Here the resulting octagon is encircled with only pentagons and hexagons. However, the addition of STW defects on either side results in a periphery of only hexagons (figure 3(c)). On the other hand, two adjacent STW defects create an octagon surrounded by alternating pentagons and heptagons, and two ISTW defects create an octagon between them with a new arrangement of pentagons and heptagons (figure 3(d)) [16]. This variety of octagonal defect combinations has recently resulted in the prediction of a number of new graphene allotropes [35, 36].

Our computational approach is outlined in section 2, where we also provide comparative checks against previously obtained computational and experimental data. In section 3, we
Figure 3. Octagonal structures can be created using any of the fundamental defect building blocks: (a) DV; (b) DV with two STW defects; (c) two STW defects; (d) two ISTW defects. The structures shown in (a), (b) and (c) are planar, while that shown in (d) is nonplanar.

consider the construction and electronic structure of metallic and semiconducting graphene allotropes. Section 4 focuses on the creation and analysis of thin, embedded ribbons of these allotropes within graphene to establish their structural stability and electronic character. Finally, in section 5, we conclude.

2. Methodology and the formation energies of fundamental defect structures

Density functional theory (DFT) is employed throughout this work to estimate ground state structures and predict their electronic character. A real-space numerical atomic orbital code [37] was used to initially relax the structures until the energy change was less than $2.7 \times 10^{-4}$ eV. A double numeric polarized basis set was employed and the Perdew–Wang generalized gradient approximation was used to account for electron exchange and correlation energy [38]. This computational setting has been shown to accurately predict the defect geometries and energies associated with graphene structures [14]–[16].

In order to more thoroughly examine the band structure (BS) of a semiconducting allotrope, a second DFT implementation was also used that employs a plane-wave basis set [39]–[42]. There a projector augmented wave [43, 44] approach with an energy cut-off of 400 eV was used within a generalized gradient approximation [45] and a $24 \times 24 \times 1$, $\Gamma$-centered $k$-space grid was used to compute the BS and density of states (DOS). The methodology was also extended to account for quasiparticle effects, within a $G_0W_0$ approximation [46], because DFT typically underestimates the band gap of periodic structures [47].

An STW defect was estimated to have a formation energy of 5.08 eV when embedded within a 144-atom graphene supercell; this compares well with an estimate of 4.8 eV from the
Table 1. Defect formation energies.

| Defect | eV  | Number of atoms in the supercell |
|--------|-----|----------------------------------|
| STW    | 5.1 | 144                              |
| ISTW   | 6.2 | 200                              |
| DV     | 7.6 | 200                              |

Figure 4. Representative members of graphene allotrope families: (a) pentaheptite, (b) haeckelite, (c) dimerite and (d) octite.

literature [25]. The formation energy required to create an ISTW defect, calculated using a 200-atom supercell, was found to be 6.20 eV [14]. The energy required to create a DV in a 200-atom periodic supercell was 7.6 eV, in agreement with previous DFT estimates of 8.7 eV [48] and 7.5 eV [27]. These formation energies are tabulated in table 1.

3. Graphene allotropes from templated defects

Even before the experimental realization of graphene in 2004 [49], planar allotropes had been predicted with properties distinct from graphitic sheets. Motivated by a desire to find a pure carbon allotrope with a high DOS at the Fermi level, Crespi suggested that graphene allotropes with zero net curvature could form periodic, two-dimensional crystals [50] and proposed the pentaheptite structure shown in figure 4. A family of planar allotropes of carbon created from combinations of five-, six- and seven-sided rings was proposed shortly thereafter [51]. Dubbed haeckelites, these sheets were predicted, using tight-binding calculations, to have metallic character. The two lowest energy structures are shown in figure 4.

More recently, a link between allotropes and defects was established by showing that pentaheptite and all haeckelites can be constructed using STW and ISTW defects [15]. This led to the prediction of a new family of graphene allotropes named dimerites because of their exclusive dependence on only the ad-dimer ISTW defect. The lowest energy dimerite is shown in figure 4. Although generally having higher energy than the haeckelite allotropes, dimerites are promising structures for synthesis because they can be made entirely from ad-dimers.
Table 2. Carbon allotropes listed according to energy. The total energy of graphene was taken as $-1037.229 \text{ eV atom}^{-1}$ as computed using a 144-atom supercell.

| Allotrope       | meV atom$^{-1}$ above graphene energy | Atoms in unit cell | Defect composition |
|-----------------|---------------------------------------|-------------------|--------------------|
| Graphene        | 0                                     | 2                 | 0                  |
| Octite M1       | 193                                   | 20                | 2 STW + 2 ISTW     |
| Octite M2       | 205                                   | 20                | 2 ISTW             |
| Octite M3       | 208                                   | 34                | 2 STW + 2 ISTW     |
| Haeckelite H$_{567}$ | 233                               | 16                | 1 STW + 1 ISTW     |
| Dimerite I      | 284                                   | 16                | 1 ISTW             |
| Octite SC       | 318                                   | 28                | 2 STW + 1 DV       |
| Dimerite II     | 330                                   | 40                | 2 ISTW             |
| Octite M4       | 357                                   | 8                 | 1 STW              |
| Haeckelite O$_{567}$ | 364                               | 12                | 1 STW              |
| Dimerite III    | 366                                   | 30                | 3 ISTW             |
| Haeckelite R$_{57}$ | 372                               | 16                | 2 STW              |
| Buckeyball C$_{60}$ | 372                               | 60                | –                  |

Figure 5. DOS of graphene, pentaheptite, haeckelite H$_{567}$, dimerite I and octite M2. All four allotropes are metallic. A (12, 6, 12) Monkhorst–Pack grid was employed along with a linear interpolation grid size of 0.05 eV.

A subsequent focus on defect arrangements resulting in octagons led to the prediction of a new family of allotropes called octites [35, 36], the name reflecting the presence of eight-member rings. The octite family includes three metallic allotropes of lower energy than any haeckelite and an intrinsic semiconducting graphene allotrope. We use ‘M’ or ‘SC’ to indicate metallic or semiconducting character (table 2).

The pentaheptite, haeckelites and dimerites are predicted to be conductors as shown in the DOS summaries of figure 5. All of these can be constructed by patterning of STW and ISTW
defects. Similarly, metallic octites are composed of STW and ISTW defects. This apparent correlation motivated us to search for a new type of defect-building block that would lead to a semiconducting carbon sheet. The result was the addition of the DV defect as a third basic building block [36].

Of particular interest is a new semiconducting allotrope, octite SC, which can be constructed from a combination of STW and DV defects. It amounts to a patterning of the defect assemblies shown in figures 3(a) and (b). To see this, consider the 170-atom carbon sheet of figure 6(a). The edges are passivated with hydrogen to maintain sp-2 bonding for all carbon atoms and a single DV defect is introduced. Two bond rotation defects are subsequently imposed (figures 6(b) and (c)). The result is then replicated periodically so as to create an array of octagonal defects. Octagons surrounded by hexagons result from DV and STW defects, while smaller octagons surrounded by alternating pentagons and hexagons derive from STW defects (figure 6(d)). The planar arrangement of atoms with three nearest neighbors suggests sp-2 bonding, although variations in bond length (1.40 to 1.54 Å) indicate that the threefold symmetry of graphene bonding is no longer present. For the sake of comparison, sp-2 bond lengths in graphene are 1.42 Å, while the sp-3 bond lengths of diamond are 1.54 Å.

The stand-alone form of this semiconductor is shown in figure 7. It has a primitive cell of 28 atoms arranged in pentagons, hexagons and octagons. The planar density is 0.364 atoms per Å²,
Figure 7. A computationally created semiconducting allotropic of graphene resulting from patterned defects. The planar structure is only 313 meV atom$^{-1}$ above that of graphene, comparable to 233 meV atom$^{-1}$ for haeclelite $H_{567}$, a metallic graphene allotropic previously theorized [51]. Left: four unit cells showing the arrangement of rings around a central octagon; right: perspective view making clear that this allotrope is planar.

comparable to 0.380 atoms per Å$^2$ for graphene. The central geometrical feature is an octagon completely surrounded by hexagons. The cell geometry is square with p4/MMM symmetry. A Hessian linear vibrational analysis showed the structure to be a local energy minimum. Room temperature quantum molecular dynamics simulations were also used to confirm its stability.

The semiconducitor of figure 7 was first geometrically optimized without allowing the lattice parameters to change. The lattice parameter was subsequently optimized as well. The energy per atom of the non-optimized lattice was 366 meV atom$^{-1}$ as compared with 313 meV atom$^{-1}$ for the optimized lattice. The lattice parameter changed from 9.030 to 8.767 Å. The band gap for these two limiting cases differed by only 0.1 eV as estimated using DFT under a generalized gradient approximation. In addition, the qualitative character of the BSs was the same. This has made us conclude that the band gap is very stable with respect to lattice strains.

The ground state structure was verified using a second DFT implementation that employs a plane-wave basis set [39]–[42]. The wave function energy cut-off was set as 400 eV, and a conjugate gradient method employing a $4 \times 4 \times 2$ Monkhorst–Pack grid resulted in the same ground state structure but with a lattice constant of 8.674 Å. The plane-wave DFT code was used to predict both the BS and DOS. A $24 \times 24 \times 1$, $\Gamma$-centered k-space grid was used for calculating the electronic properties. The BS and DOS diagrams are shown in figure 8. The material possesses a 0.2 eV direct band gap at the $\Gamma$ point. Consistent with the stability of the band gap in response to geometric optimization, we found that a band gap of 0.3 eV persists even if the lattice is dilated to the density of graphene. As in graphene, all carbon atoms bond with three nearest neighbors, but the symmetry of the in-plane sp-2 character has been disrupted by the varying bond angles and bond lengths.

DFT typically underestimates the band gap of periodic structures [47], so the 0.2 eV gap should be viewed as a lower bound. Many-body perturbation theory, within the $G_0W_0$ approximation [46], was therefore used to provide a more accurate estimate of the electronic structure. As expected, the inclusion of quasiparticle effects widens the band gap, providing an estimate for the direct, $\Gamma$ point gap of 1.1 eV. The $G_0W_0$ BS is shown with its DFT counterpart.
Figure 8. Electronic structure of the octite semiconductor. (a) The BS and DOS for a semiconducting graphene allotrope. Both DFT and \( G_0W_0 \) predictions are shown. The DOS plot is from the DFT calculation. (b) Perspective view of the BS over the entire two-dimensional k-space.

Three iterations towards self-consistency (\( GW_0 \) approximation) opened the band gap slightly to 1.2 eV.

Metallic allotropes can also be composed of octagonal rings, and three have been computationally predicted to have lower ground state energies than any previous allotrope [35]. One of them, octite M1, has an energy only 194 meV atom\(^{-1}\) above that of graphene—lower than the 233 meV atom\(^{-1}\) calculated for the lowest energy haeckelite or the 284 meV atom\(^{-1}\) for the lowest energy dimerite. This structure is important because it is expected to be the most stable of any predicted graphene derivative, which therefore makes it a likely candidate for experimental realization. In all of the metallic octites, octagonal rings are built exclusively from ISTW and STW defects. This is in contrast to the semiconducting octite wherein DVs are employed to build octagons with different local environments within the carbon sheet.

From the perspective of defect engineering, the octite M1 can be constructed from a template composed of two STW defects and two ISTW defects as shown in figure 9. This synthesis route was carried out computationally on a rectangular supercell of graphene measuring 21.34 Å by 12.32 Å. The intermediate steps were geometrically optimized DFT
Figure 9. Defect engineering a patch of octite M1 within graphene: (a) graphene with highlight on the atoms to be manipulated; (b) two STW bond rotations; (c) the first ISTW ad-dimer; (d) the second ISTW ad-dimer.

Figure 10. A $2 \times 2$ supercell of the lowest energy octite M1: (a) top view and (b) perspective view.

ground states after each defect was introduced, but the lattice was not allowed to dilate. The initial zero energy state is graphene with two dimers at infinity. Two STW bond rotations (b) raise the energy to $9.1 \text{ eV}$ but dimer addition through ISTW defects lowers the energy to $1.6 \text{ eV}$ (c) and finally to $-6.8 \text{ eV}$.

The resulting octite M1, shown in figure 10, is completely flat and contains 20 atoms in the primitive unit cell. The energy minimum was verified via a Hessian vibrational matrix. Quantum molecular dynamics simulations were also utilized, at 300 and 500 K, to ensure that the structure is indeed stable.

DOS calculations were performed using a Monkhorst–Pack [52] grid size of $12 \times 12 \times 4$ which was then interpolated into a grid of $200 \times 200 \times 200$ points. The use of four K points in association with the out-of-plane direction does not offer any greater accuracy than a single K point, but it was necessary in order to perform this interpolation using our existing code. A slight broadening of $0.05 \text{ eV}$ was applied for a more physical representation of the DOS in a large system. Figure 11 shows that octite M1 is a good conductor with approximately 2 electrons $\text{eV}^{-1}$ at the Fermi level.
Figure 11. The BS and total DOS for the lowest energy graphene allotrope, octite M1. The DOS is dominated by the p-state contribution.

Figure 12. Minimal ribbon of octite M2 within graphene: (a) perspective view of the extended defect; (b) DOS exhibiting good conduction with 20 meV interpolative instrument broadening [55]; (c) valence band edge state; (d) conduction band edge state. Isosurfaces are for 0.03 electrons Å$^{-3}$. Green and brown colors distinguish regions for which the orbital wave function has positive and negative phases. The orbitals of (c) and (d) have been constructed using a Γ-point (k = 0) spatial frequency.

4. Embedded ribbons of graphene allotropes

The link between defects and allotropes provides the design guidance needed to create both localized and extended regions of semiconducting and/or conducting material within graphene. We take up this issue by investigating embedded allotrope ribbons, i.e. a thin strip of one allotrope embedded within another. These are distinguished from nanoribbons, which are
thin strips of material with free boundaries. Nanoribbons have been promoted as a means of endowing graphene with a tunable band gap, and the approach requires that a thin strip of graphene be precisely cut to a prescribed chirality and width. Lateral confinement of the charge carriers creates a band gap [53]. Computational studies have determined that nanoribbons can be conductive or insulating depending on the shape of their edges [7]. Embedded allotropic ribbons offer an alternative strategy wherein both conducting and semiconducting pathways can be created on a single, planar sheet of carbon. We examine both types of ribbons embedded within a graphene sheet.

A minimal ribbon of a conducting octite (figures 4 and 5) within graphene is shown in figure 12(a). Within this setting, the extended defect amounts to an alternating sequence of octagons and paired pentagons. The relaxed, planar ground state structure is a conductor (figure 12(b)) with band edge states consistent with that previously determined for isolated ISTW defects [16]. Specifically, the tops of the ad-dimers repel additional electrons, while the shoulders of the extended defect actually attract additional electrons. This is made clear in figures 12(c) and (d), which show the highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO). These orbitals are constructed using a Γ-point ($k = 0$) spatial frequency, i.e. by setting the Bloch function wave number to zero and relying on linear combinations of atomic orbitals to describe the electronic structure. These band edge states are both localized along the ribbon, and the ribbon itself endows the composite with a high DOS at the Fermi level, similar to vacancy localization effects found in bilayer graphene [54]. The composite structure is a conductor as shown in figure 12(b).

The conducting nature of the composite is presumably due to electron transport along the extended defect. This is supported by plots of the electrostatic potential provided in figure 13.

**Figure 13.** Electrostatic field of the minimal ribbon of octite M2 shown in figure 12(a): (a) isosurface of 0.27 V; (b) cross-section at 1.7 Å above surface, ranging from 0.0 V (red) to 0.93 V (blue); (c) side view of isosurface, showing spatial orientation of the cross-sectional plot.
Figure 14. Ni(111) surface (nickel lattice shown in blue) was used to grow flakes of graphene centered on either threefold (yellow carbon atoms) or hollow (red carbon atoms) sites. The extended defect where dissimilar flakes meet is the minimal ribbon of metallic octite shown in figure 12(a).

Figure 15. Experimentally realized ribbon of octite M2, courtesy of [24]. Reproduced with permission. Copyright 2010 Nature Publishing Group. The structure is identical to the minimal ribbon of octite shown in figure 12: (a) perspective view showing the extended defect; (b) close-up view of the region marked by white lines in (a), with overlay schematic of the lattice structure.

The isosurface shown in figure 13(a) indicates that the defect has a positive potential and thus attracts additional charge, while figure 13(b) shows potential contours in a plane that intersects the isosurface.

Importantly, this metallic defect ribbon has recently been experimentally synthesized [17, 24, 35]. Graphene was grown epitaxially on the (111) surface of nickel, where graphene...
may be aligned in one of two nearly energetically equivalent ways: one-half of the carbon atoms may lie over either threefold or hollow sites as shown in figure 14. The mismatch in carbon atoms at the interface of dissimilar graphene flakes results in the extended defect structure of figure 12. The nickel can be subsequently removed, resulting in a stand-alone sheet of graphene with a minimal ribbon of dimerite. Although not measured experimentally, DFT analysis performed by Batzill et al [24] in the localized density approximation suggested that these ribbons are metallic, consistent with our own DFT studies using a generalized gradient approximation. The experimental result is shown in figure 15 [24]. This suggests that the realization of more complex defect designs is only a matter of time.

Embedded ribbons of semiconducting octite (figure 7) were subsequently investigated. The dimensions of the periodic cell were fixed to simulate a constraining lattice of graphene, and DFT was used to obtain the planar, ground state structure shown in figure 16(a). The DOS plot of figure 16(b) indicates that the ribbon endows the graphene with a 0.17 eV band gap, only slightly smaller than the 0.2 eV band gap of the octite SC itself. Unlike the metallic ribbon, the HOMO and LUMO states are not confined to the ribbon, although they do have contributions from orbitals along the interfaces between the two allotropes (figure 16(c) and (d)). Localized states appear along the edge of zigzag nanoribbons [56], and interestingly, the LUMO+1 state is highly localized within the ribbon as shown in figure 16(e).

The electronic structure of the semiconducting ribbon is further analyzed by plotting the electrostatic field. As shown in figure 17, potential isosurfaces tend to be more localized on the
Figure 17. Electrostatic field of octite SC within graphene: (a) isosurface of 0.27 V; (b) cross-section at 1.7 Å above surface, ranging from 0.0 V (red) to 0.73 V (blue).

Figure 18. (a) Embedded ribbons of semiconducting octite form a network partitioning graphene into diamond-shaped islands. (b) DOS with 10 meV interpolative instrument broadening [55] shows that the ribbons disrupt electron conduction. (c) Valence band edge state; (d) conduction band edge state. Isosurfaces are for 0.01 electron Å$^{-3}$. Green and brown colors distinguish regions for which the orbital wave function has positive and negative phases. The orbitals of (c) and (d) have been constructed using a Γ-point ($k = 0$) spatial frequency.
Figure 19. Electrostatic field of octite SC forming a patterned arrangement of diamond-shaped islands of graphene: (a) isosurface of 0.27 V; (b) cross-section at 1.5 Å above surface, ranging from 0.0 V (red) to 0.54 V (blue).

ribbon as the distance above the sheet increases. These potential surfaces are positive, indicating that additional charge will be attracted to the semiconducting ribbons.

Embedded ribbons may be constructed with a variety of chiralities, and this can be exploited to create junctions and ribbon networks. Two examples of such semiconductor networks are considered. The first is shown in figure 18(a), where the enforcement of periodic boundary conditions gives graphene islands in the shape of diamonds. For this orientation of ribbons, the DOS plot indicates that the sheet still maintains a small band gap (0.05 eV). The HOMO state is localized within the ribbons with the exception of the ribbon junction, while the LUMO state shows that the first excited state will tend to avoid the junction completely.

The electrostatic potential of the patterned arrangement of diamond-shaped islands of graphene is shown in figure 19. Consistent with the results for isolated allotrope interfaces, potential surfaces lying furthest above the sheet are positive and localized on the ribbon network. Higher energy excited electrons should therefore be attracted to these conduction channels.

Perhaps not surprisingly, the orientation of intersecting ribbons impacts the electronic structure of the sheet. This is made clear by considering a second network of semiconducting ribbons that now partitions the graphene into rectangular islands. Figure 20(a) shows the planar, ground state geometry. The DOS of this system (figure 20(b)) indicates that the band gap is essentially lost. The HOMO state is now localized along the horizontal semiconducting ribbon (figure 20(c)), but the two states of immediately lower energy do not show localization along
Figure 20. (a) Embedded ribbons of semiconducting octite form a network partitioning graphene into rectangular domains. (b) DOS with 10 meV interpolative instrument broadening \( [55] \) shows that the ribbons disrupt electron conduction. (c) Valence band edge state; (d) conduction band edge state. Isosurfaces are for 0.015 electron Å\(^{-3}\). Green and brown colors distinguish regions for which the orbital wave function has positive and negative phases. The orbitals of (c) and (d) have been constructed using a \( \Gamma \)-point \( (k = 0) \) spatial frequency.

either ribbon orientation. This suggests that the two orientations have fundamentally different electronic properties, which likely extends to their respective electron mobilities.

The electrostatic potential of the rectangular network, shown in figure 21, is very similar to that of the diamond networked sheet. Once again, potential surfaces lying furthest above the sheet are positive and localized on the ribbon network. Higher-energy excited electrons should therefore be attracted to these conduction channels. The electrostatic contours of figure 21(c), however, show that the horizontal ribbon attracts electrons more strongly at a fixed height above the sheet.

5. Conclusions

Defect engineering offers a means of changing the electronic character of graphene without the need to introduce new atomic elements. An algebraic framework has been identified for the modification of lattices and is based on four basic actions that can be performed with a carbon dimer: bond rotation (STW defect); dimer addition (ISTW defect); dimer removal (DV defect); and no action (standard graphene dimer). These dimer actions can be combined to build a variety of localized defect structures; this work has focused on the templating of elements to create extended defects. Two-dimensional templates can be used to create graphene allotropes.

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Figure 21. Electrostatic field of octite SC forming a patterned arrangement of rectangular-shaped islands of graphene: (a) isosurface of 0.27 V; (b) cross-section at 1.5 Å above surface, ranging from 0.0 V (red) to 0.54 V (blue).

While most of these are good conductors, we have identified a defect structure that opens up a band gap of 1.2 eV. These allotropes can be created as conducting and semiconducting ribbons within graphene, extended one-dimensional defect structures. Their electronic character is largely preserved even for the narrowest ribbons, which offers the prospect of designing electronic components crafted entirely out of carbon.

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