First-principles study of Bi and Sb intercalated graphene on SiC(0001) substrate

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The atomic structures and electronic properties of antimony and bismuth intercalated graphene on SiC(0001) substrate were investigated using first-principles calculations. The results show that, at Bi and Sb coverages of 1 ML, the Dirac cones were preserved. The π and π* bands of the graphene are barely split by extrinsic spin–orbit interaction from metal layers. At 2/3 ML, the Bi and Sb metal layers form a honeycomb structure, and the Dirac cones remain intact. Furthermore, a notable band splitting at the M point contributed from metal layers was found at 1 ML, whereas a similar splitting at the K point was found at 2/3 ML. Finally, our results show that these two metal intercalations lead to n-type doping of graphene.

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1. Introduction

Graphene is a gapless semiconductor with a linear band dispersion near the Fermi level where electrons behave as massless fermions. The unique electronic properties of graphene make it useful for investigating a wide range of phenomena in fundamental science, since it offers an accessible platform for testing predictions of relativistic quantum mechanics in table-top experiments [1]. While many of the fundamental science experiments have been done with exfoliated graphene layers, epitaxial growth of high-mobility graphene is essential for technological applications. Both metallic and insulating substrates have been used to successfully grow large-area epitaxial layers, with the SiC(0001) and SiC(00001) substrates being of particular interest [2–8]. Existence of a bulk bandgap is one of the main advantages of SiC in comparison with metallic substrates, since it is difficult to single out the dispersive band connecting valance bands and conduction bands for the latter [9,10].

While exfoliated graphene commonly behaves as an isolated graphene layer, interaction with the supporting substrate plays an important role in epitaxial graphene. In fact, transfer of graphene films to weakly interacting substrates is often necessary to restore the intrinsic electronic band structure for experimental studies. Recently, decoupling of graphene from the substrate has been achieved by inserting atomic buffer layers between the graphene and SiC(0001) substrates. Numerous studies [7,11–27] have aimed to understand the resulting multi-layers and their effect on the electronic structure of graphene. On the other hand, the intercalated metal layer may also be used to induce extrinsic spin–orbit coupling in graphene and therefore serve as a convenient tool for tailoring the electronic properties for spintronic applications [21,28–30].

Enhancement of spin–orbit coupling (SOC) effects in graphene can be achieved by introducing defects such as impurities, vacancies, and adatoms [31]. However, these types of defects induce Rashba-type splittings of the σ bands of graphene instead of splitting the linear conical dispersion in addition. Varykhalov et al. [32,33] showed that spin–orbit coupling can be introduced by growing graphene on magnetic metal substrates. Similar layered structures may be formed on semiconducting substrates [34]. Motivated by the earlier experimental studies [7,19] in which Bi, Sb, and Au were deposited over epitaxial graphene on SiC(0001), we focus on the Bi and Sb intercalations since their intercalated structures are not yet established and their effects on the spin–orbit coupling in graphene are not yet known. In addition, other studies have shown that Bi and Sb exhibit a strong Rashba spin–orbit effect in surface alloys on Si(111) and Ge(111) [35–39]. Most recently, strained single Bi(111) and Sb(111) bilayers regarded as a buckled honeycombs were found to be two dimensional topological insulators [40,41]. Therefore, it is highly desirable to predict a proper buffer layer on the semiconductor SiC(0001) substrate which can both preserve the linear dispersive bands near the K point and enhance the strength of spin-orbit coupling in graphene.

In this study, we explore Bi and Sb intercalations using first-principles density-functional theory (DFT) calculations. We show that at metal coverage of 1 monolayer (ML) the π and π* bands of the graphene exhibit spin–orbit (SO) splitting, and the splitting of the conical energy spectrum near the K point, ΔSO(π), is around 5.0 and 2.5 meV for Bi and Sb buffer layers, respectively. A notable band splitting at the
2. Computational methods

The calculations were carried out within the generalized gradient approximation (GGA) [42] to the density-functional theory (DFT) [43] using the projector-augmented-wave (PAW) method [44] as implemented in the highly efficient Vienna Ab-initio Simulation Package (VASP) [45]. The Bi pseudopotential version that we used treats the 3d-states as core electrons, while the standard version is used for the other elements (Sb, Si, C, and H). As in previous studies [5,6,13,20,21], a \( \sqrt{3} \times \sqrt{3} \) supercell of SiC(0001) is used to match the \( 2 \times 2 \) supercell of graphene. The coverage of deposited metals was previously defined as the ratio of the number of metal atoms with respect to the number of C atoms in a \( 2 \times 2 \) supercell of graphene [20,21]. There are eight carbon atoms in the \( 2 \times 2 \) supercell. However, it corresponds to three topmost Si atoms for SiC(0001) \( \sqrt{3} \times \sqrt{3} \). Therefore, two and three metal atoms within SiC(0001) \( \sqrt{3} \times \sqrt{3} \), respectively, are equal to 2/8 ML and 3/8 ML. In contrast, the coverages will be 2/3 and 3/3 ML with respect to the SiC(0001) \( \sqrt{3} \times \sqrt{3} \) supercell. We use the latter definition for the entire article.

Four 4H–SiC(0001) bilayers were used as the substrate throughout our study. A vacuum layer of 12 Å is included in the supercell. The bottom carbon atoms were passivated by H atoms. Except for the bottom hydrogens and the bottom bilayer, all other atoms were relaxed until the residual force on each atom was smaller than 0.01 eV/Å. The kinetic cutoff energy is set to 400 eV. The dispersive van der Waals (vdW) forces were treated using the vdW functional proposed in Refs. [46,47]. A 12 \( \times 12 \times 1 \) k point grid was used for structural relaxations. The criteria for the electronic self-consistency without SOC is set to \( 10^{-6} \) eV change in the total energy. After the lowest energy structures are determined, spin–orbit coupling (SOC) effects are subsequently included in the band structure calculation using complex spinor wave functions and the second variational method. Moreover, a Gamma-centered \( 12 \times 12 \times 1 \) Monkhorst–Pack k point sampling was used and the convergence criteria for the electronic self-consistency in the calculation with SOC was also set to \( 10^{-6} \) eV.

Different initial magnetic moments for the metal layer were assigned to locate the lowest-energy spin orientation.

3. Results and discussion

The possible atomic structures of the metal-intercalated graphene on SiC(0001) at a coverage of 1 ML are shown in Fig. 1 based on our earlier results for noble metal intercalations [21]. The metal atoms can occupy the T1, H3, or T4 sites, as indicated in Fig. 1(g)–(i). We adopted the nomenclature used for the Si(111) surface, since SiC(0001) is of similar bilayer structure. The atop T1 site is above the topmost Si atom, the 4-fold coordinate T4 site is above the second layer C atom, and the 3-fold hollow H3 site is on top of the center of the honeycomb from the first bilayer and above the C of the second bilayer. If the metal atoms do not bond to the Si atom (such as in the T4 site), they can form a buckled layer due to strong interactions between the metal atoms and the inability to fit them within the surface unit cell of SiC(0001). We label the resulting structure as T4’, in which one metal atom is higher than the other two [see Fig. 1(j), where the atom at the higher position is colored red]. We examined the energetics for each element in all of the atomic configurations shown in Fig. 1(g), (h), and (i), provided that the graphene is on top of the metal layer in the way shown in either Fig. 1(b) or (c) [10,20,21]. For Fig. 1(b), two metal atoms are right below the carbon atoms, while for Fig. 1(c), the metal M point is also found. At 2/3 ML, the Bi and Sb metal layers form the honeycomb structure and their band structures exhibit notable split-tings at the K point. Our results suggest that the layered structure plays a key role in manipulating the behavior of electron spins.

Fig. 1. (a) The blue dashed lines and black solid lines indicate the Brillouin zones of the \( 1 \times 1 \) unit cell and \( 2 \times 2 \) supercell of graphene, respectively, while the red solid lines indicated the \( 1 \times 1 \) unit cell of SiC(0001). The \( \sqrt{3} \times \sqrt{3} \) supercell of SiC(0001) is identical to \( 2 \times 2 \) supercell of graphene. Specific k-points are labeled. (b) and (c) are the top views of graphene on metal layer for Top and Bridge sites at metal coverage of 1 ML. (d) and (e) are the top views derived from (b) by manipulating one metal atom in the supercell, while (f) is top view derived from (c) by manipulating one metal in the supercell. (g), (h), and (i) are the side views of the atomic models that the metals are, respectively, at T1, H3, and T4 sites. For illustration purpose, the graphene is at the position shown in (b). (j) is the side view of the atomic model for T4’ site. The graphene, for illustration purpose, is at the position shown in (d).
Table 1
The site where the metal adsors and the position of the graphene, G. The relative energy, \( \Delta E \), to the lowest energy model of the same metal coverage. The distance, \( d_{C-M} \), between the graphene and the metal layers and the vertical distance, \( d_{M-M} \), within the metal layers as illustrated in Fig. 1(j). The Dirac point (\( E_D \)) of graphene which is defined as the position of Dirac point relative to the Fermi level. \( \Delta E_{SOC} \) is the relative energy after inclusion of SOC. \( \Delta E_{SOC} \) is the vertical splitting of the conical energy spectrum near the K point due to SOC.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Model</th>
<th>Site</th>
<th>G</th>
<th>( \Delta E ) (eV/cell)</th>
<th>( d_{C-M} ) (Å)</th>
<th>( d_{M-M} ) (Å)</th>
<th>( E_D ) (meV)</th>
<th>( \Delta E_{SOC} ) (meV)</th>
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<tr>
<td>Bi</td>
<td>T1 – Top</td>
<td>T1</td>
<td>1(g)</td>
<td>0.000</td>
<td>3.616</td>
<td>0.00</td>
<td>-586</td>
<td>0.000</td>
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<tr>
<td></td>
<td>T1 – Bridge</td>
<td>T1</td>
<td>1(g)</td>
<td>0.000</td>
<td>3.613</td>
<td>0.00</td>
<td>-593</td>
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<tr>
<td></td>
<td>H3 – Top</td>
<td>H3</td>
<td>1(h)</td>
<td>1.550</td>
<td>3.656</td>
<td>0.03</td>
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<td></td>
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<tr>
<td></td>
<td>H3 – Bridge</td>
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<td>1(h)</td>
<td>1.541</td>
<td>3.638</td>
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<tr>
<td></td>
<td>T4 – Top</td>
<td>T4</td>
<td>1(i)</td>
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<td>3.129</td>
<td>-0.19</td>
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<td>1(j)</td>
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<td>3.365</td>
<td>1.023</td>
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<td>Sb</td>
<td>T1 – Top</td>
<td>T1</td>
<td>1(g)</td>
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<tr>
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<td>T4 – Bridge</td>
<td>T4</td>
<td>1(i)</td>
<td>3.343</td>
<td>3.206</td>
<td>0.00</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>T4′ – Top</td>
<td>T4′</td>
<td>1(j)</td>
<td>2.888</td>
<td>3.365</td>
<td>1.023</td>
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</table>

atoms are below the three carbon–carbon bonds. For brevity, Fig. 1(b) is regarded as the Top site, while Fig. 1(c) is regarded as the Bridge site. Thus, a total combination of six structural models were derived. For example, the T1 – Top model has the metals at the T1 site [Fig. 1(g)] and the relative position of graphene on top of the metal layer is at the Top site [Fig. 1(b)]. The exact coordinates used for Bi intercalated graphene on these sites can be found as supplementary material (online publication). In addition, for metals at the T4′ site, as shown in Fig. 1(j), the graphene can be in one out of three positions indicated in Fig. 1(d), (e), or (f). In total, nine different initial surface structures were considered for each type of buffer layer (Bi and Sb); these structures were fully relaxed. Buckled metal layers at the T1 and H3 sites were also examined. For the T1 site, the metal layer relaxed back to the planar configuration, while for the H3 site, the buckled and unbuckled models are both energetically higher than the lowest-energy T1 – Top model. Furthermore, the energies of the models where the deposited Bi and Sb layers sit above the epitaxial graphene at 1 ML are higher than those of the aforementioned intercalated T1 and H3 models. In short, for both antimony and bismuth intercalations, the layered structures have the lowest energies when the intercalated metal is at the T1 site [Fig. 1(g)]. Since the models with the same coverage have the same number of atoms, the total energy of the most stable model was reset to zero, and the total energies of the other models are positive, i.e., the relative energy is defined as the total energy of a model minus the total energy of the most stable model. The energy differences between different graphene positions are rather small. The calculated data for all studied structural models is summarized in Table 1.

Even though an earlier study [7] did not provide direct experimental evidence that Bi, Sb, and Au intercalate between the graphene and the Si(0001) substrate, a subsequent study [19] showed that intercalation indeed occurs for Au. The same outcome is expected for Bi and Sb. Our calculations show that the Bi and Sb intercalated models are, respectively, energetically more favorable than the deposited models at 1 ML by around 2.7 and 3.5 eV per cell. Thus, the Bi and Sb metals should be able to intercalate at elevated temperatures. As for the kinetic process on how Bi and Sb go underneath the graphene and break the Si–C bond, a direct diffusion of Bi or Sb through the graphene may not be a favorable path. Due to the comparatively large atomic sizes of Bi and Sb, intercalation via a defect-mediated process is more reasonable [16]. Another possible intercalation path goes through the edge of graphene via the side-diffusion process, which has been widely discussed for graphene on transition metal substrates.

Next, we analyze the band structures of the two lowest-energy structures (T1 – Top and T1 – Bridge) listed in Table 1. Different initial magnetic moments of the metal atoms were assigned to understand the magnetic anisotropy energies. Our result show that the spin configuration without a net magnetic moment has the lowest energy. Other orientations of the magnetic moment, such as in-plane and out-of-plane, were found to be higher by tens of \( \mu \text{eV} \) than that with a zero net magnetic moment.

In addition to energetic degeneracy, we also found that the band structures are very similar when metals are at the T1 sites regardless of the graphene position. Thus, only the band structures of T1 – Top for Bi and Sb intercalations are shown in Fig. 2(a) and (b), respectively. The band structures including SOC along the \( M'–K'–\Gamma–M' \) line are

![Fig. 2](image-url)
plotted in order to observe possible Rashba SO splitting effects at high-symmetry points. Since the path is along the k_x axis, the m_y component of spinor was used to identify the spin helicity. The red crosses and blue circles indicate the positive and negative signs of the m_y component, respectively. Overall, we find that the band dispersions are similar since Bi and Sb are in the same group of the Periodic Table. The splitting for Bi is more pronounced than that for Sb.

In addition to the conical bands from the graphene, additional cone-like dispersive split bands with predominantly Bi and Sb characters are centered between K' and Γ. These bands are indicated by the red arrows as shown in Fig. 2(a) and (b). Moreover, the bands contributed from the intercalated Bi and Sb layers exhibit Rashba spin–orbit splittings around the Γ point as pointed out by the blue arrows in Fig. 2(a) and (b). Also, at the M point, we noticed a SO splitting of 379 meV and 178 meV for Bi and Sb intercalations, respectively.

The linear dispersive π and π* bands contributed from the graphene are colored in green in Fig. 2(a) and (b). These two metal intercalations lead to n-type doping of graphene. We found that the small band splitting of π and π* are 5.0 and 5.2 meV for T1–Top and T1–Bridge models of Bi intercalation, respectively, as listed in Table 1. In fact, we also note that the SO splitting seems to extend to the π and π* bands.

The equilibrium distances between the graphene and metal layers are 3.62 Å in Bi and Sb, respectively. The carbon atoms within the graphene sheet are at the same height. We also considered an idealized case of a layered (sandwiched) structure where additional buffer layers have been deposited on top of graphene to tune the spacing between the graphene and the underlying Bi metal layer.

This will give us an indication of how the metal layer affects the band structure of graphene. The T1–Top model of Bi intercalation was used for this demonstration. The distance, d_C–Bi, was gradually reduced from 3.62 Å to 2.87 Å. The carbon atoms are maintained at the same vertical distance to the metal layer. The magnified energy dispersions of the π and π* bands at K point with different spacings are plotted in Fig. 3. We found that, as the distance approached 2.87 Å, the SO splitting reached as high as 50 meV, as shown in Fig. 3(d).

Next, a three dimensional plot of the energy dispersion of the case at 2.87 Å [Fig. 3(d)] is shown in Fig. 3(e), calculated on an equivalent 2712 × 2712 × 1 k-point grid. To understand the spin texture, an energy isosurface is chosen. Fig. 3(f) shows the interpolated contour lines of spin–orbit split π band at energy of −0.80 eV from Figure (d). The arrows in the Figure (f) are to indicate the spin helicity at these points.

Fig. 3. The SO splitting of Dirac cone near K point for the spacing, d_C–Bi, of (a) 3.62, (b) 3.37, (c) 3.12 and (d) 2.87 Å between the graphene and the Bi metal layer. (e) is the three dimensional energy dispersion plot of π and π* bands around the K point of Figure (d). (f) is the interpolated contour lines of spin–orbit split π band at energy of −0.80 eV from Figure (d). The arrows in the Figure (f) are to indicate the spin helicity at these points.

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from the zone boundary. The shift of the Dirac cone can be explained by the symmetry-perturbing effect of the metal layer, as shown in Fig. 1(c). Since the metal atoms are under the three edges of the honeycomb, this results in inequivalent C–C bonds within the graphene sheet. A tight-binding model for graphene with inequivalent nearest-neighbor hopping energies can easily reproduce the cone shifting observed in our DFT calculations. These results show that care must be taken when drawing conclusions about the existence of a conical dispersion based on a traditional choice of k-point path in band structure calculations or angle-resolved photoemission spectroscopy (ARPES) measurements. Indeed, structural perturbations in the graphene layer due to interactions with the substrate may move the position of the Dirac cone away from the three-fold symmetric K point, and as a result one may find a large induced gap at the K point if the measurements or calculations are confined to the Γ–K–M line.

Finally, we studied the structural models at 2/3 ML. The structural models were created by removing one metal atom from the stable 1 ML models. By taking the symmetry into account, there are three inequivalent positions of graphene on top of the metal layer. The first two models, as shown in Fig. 1(d) and (e), are derived from the 1 ML model in Fig. 1(b), while the third model, shown in Fig. 1(f), is derived from the 1 ML model in Fig. 1(c). Note that the atom colored in red is removed and the metal layer forms the honeycomb structure [41].

Our calculations show that, at Bi and Sb coverages of 1 ML, the stable intercalated structural model has metal atoms at the T1 sites, while the relative position of graphene is at the Top site. It is energetically unfavorable for the metal to be above the graphene sheet. Band structure calculations show that the Dirac cones are preserved. In addition, the n and n′ bands of the graphene are found to exhibit strong SO splitting along the Γ–K line and around the K point. A splitting of 368 meV at the K point is attributed to the perturbation from SiC(0001) substrate. Therefore, the bands contributed from the Bi atoms also show strong SO splitting as the coverage of Bi is reduced to 2/3 ML. In short, the metal layer exhibits bandgap opening due to the inclusion of SOC and the band spin–orbit splitting due to charge gradient at the interface as well as perturbation from the SiC(0001). Lastly, compared to free-standing graphene which has the Fermi level at the Dirac cone, the metal layers introduce n-type doping of graphene (i.e., charge is transferred from the metal to the graphene).

4. Conclusions

We demonstrated that appropriately designed layered structures can preserve the Dirac cones and enhance the extrinsic spin–orbit coupling in graphene. As the spacing between the graphene and the Bi layer is reduced, the n and n′ bands of the graphene are found to exhibit strong SO splitting, which extends to the conical energy spectrum near the K point. The Dirac cone is split. At 2/3 ML, the Bi and Sb metal layers form a honeycomb structure and the Dirac cones are also preserved. Similarly, the intercalated models are energetically more favorable than the as-deposited models with the metal on top of the graphene layer. A notable band splitting at the M point contributed from the Bi honeycomb. To understand the cause of the gap opening, we calculated the free-standing Bi and Sb honeycomb structure and it exhibits the same bandgap opening [41] when we include spin–orbit coupling in the calculation. Furthermore, the bands contributed from the Bi atoms also show strong SO splitting along the Γ–K line and around the K point. A splitting of 368 meV at the K point is attributed to the perturbation from SiC(0001) substrate, since it was not observed in the free-standing case. Moreover, the n and n′ bands from the graphene show no SO splitting as the coverage of Bi is reduced to 2/3 ML. In short, the metal layer exhibits bandgap opening due to the inclusion of SOC and the band spin–orbit splitting due to charge gradient at the interface as well as perturbation from the SiC(0001).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.susc.2013.06.002.

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