First-principles studies of Pb doping in graphene: stability, energy gap and spin–orbit splitting

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Abstract. Adsorption of Pb monomers (Pb-m) and Pb dimers (Pb-d) on graphene containing single vacancies was studied using density functional theory. We found that both Pb-m and Pb-d can chemically bind to graphene and turn the systems into semiconductors with moderate energy gaps. The spin–orbit (SO) splitting of the bands is significantly enhanced by Pb doping, ascribed to the large atomic SO interaction of the dopants. In addition to the in-plane spin polarization generally observed in the graphene system, considerable out-of-plane spin polarization was found in graphene with adsorbed Pb atoms. We analyze how to observe the explicit SO splitting of the systems in experiments. Our results may be helpful in finding novel spintronic applications for graphene.

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1. Introduction

Graphene, single-layered graphite, has attracted much attention since its discovery [1]. Due to its quasi-two-dimensional (quasi-2D) structure, graphene has many unusual physical and chemical properties. For example, electrons and holes at low energies can be accurately described by the Dirac equation [2], providing a way of probing quantum electrodynamics phenomena. Graphene is also a potential material for building nanodevices with certain functions, such as room temperature field-effect transistors (FETs) [3], negative differential resistance devices [4] and gas sensors [5]. Recently, many interesting phenomena related to interactions of spin–orbit (SO) coupling [6], including optical dichroism, the anomalous quantum Hall effect and the spin Hall effect, were proposed in materials. Due to the weak SO coupling of carbon atoms [7], the SO interaction in pure graphene was estimated to be very small (0.024 meV) [8]. Strong SO interactions are needed to observe experimentally the above effects in graphene.

Various strategies have been explored to enhance the SO interaction in graphene, such as by growing graphene on different kinds of metal substrates (Ni, Ag, Au, etc) [9–11], adsorbing H or F atoms on graphene [12], lattice deformations [13] or applying an external electric field [8]. Interestingly, Ertler et al [14] found that an effective random Bychkov–Rashba-like SO coupling field was induced in graphene by charged impurities and polar-optical surface phonons in the SiO$_2$ substrate. A rather large Bychkov–Rashba-type SO coupling [15, 16] on $\pi$ states ($\sim$13 meV) was detected in graphene with an intercalated Au monolayer between graphene and Ni substrate in experiments [9, 11]. In general, a large SO splitting can be produced in graphene if a strong asymmetry of the potentials on the two sides of the graphene plane appears [11, 12], induced by heavy atoms of substrates or dopants [9, 10]. Comparing Ni and Ag substrates, Li et al [11] further pointed out that heavy atoms may not always produce large SO splitting in graphene. It depends sensitively on whether the graphene $p_z$ states hybridize effectively with d bands of substrates [11]. In addition to the out-of-plane potential gradient, the in-plane potential gradient may also lead to large spin splitting of the bands [17]. It was, however, not explored much in graphene.

In this paper, the electronic structures and SO splitting of defective graphene with adsorbed heavy Pb atoms are studied. Both theoretical and experimental reports have shown that heavy atoms such as Au, Ag, Pb and Bi are always weakly physisorbed on perfect graphene [18–21]. The binding energy of Pb adsorbed on perfect graphene is only about 0.2 eV [18]. To achieve Pb–graphene systems with high structural stability, we remove one of the carbon atoms from the graphene and then dope the Pb atoms (single atom or dimer) around the vacancy. Recently, by irradiating with electron or ion beams, single vacancies in nanostructured carbon materials were generated [22]. Atomic-scale vacancies in carbon nanotube and graphene were also created by Rodríguez-Manzo et al [23] by using an electron beam in a scanning transmission electron microscope. More importantly, they could further trap the metal atoms in the vacancies with almost atomic precision. Using high-resolution transmission electron microscopy (HRTEM), Gan et al [24] provided direct experimental evidence that Au and Pt heavy metal atoms can be substitutionally doped into a thin graphitic layer. These experimental reports indicate that defective graphene with adsorbed Pb can be fabricated in experiments with current techniques. We find that both Pb monomers (Pb-m) and Pb dimers (Pb-d) can chemically bind to graphene and turn the systems into semiconductors with moderate energy gaps. Very large Bychkov–Rashba-type SO splitting of graphene $\pi$-derived bands is
Figure 1. The most stable structures of Pb-m (a) and Pb-d (b). Panels (c) and (d) show the charge density differences for the systems of panels (a) and (b), respectively. Yellow regions indicate gain of charge, while blue regions indicate loss of charge. The inset shows the initial positions considered for Pb dopants (see text). The carbon vacancy is at the blue site 1.

obtained. The in-plane potential gradient is found to induce detectable spin splitting around the K point.

2. Computational method and model

The calculations were performed with the projector-augmented wave (PAW) formalism based on density functional theory (DFT), as implemented in the Vienna \textit{ab initio} simulation (VASP) program \cite{25–27}. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) \cite{28} was adopted to represent the exchange and correlation potential. The C 2s and 2p and Pb 6s and 6p electrons were treated as valence electrons and the test calculations show that the calculations including the Pb 5d electrons yield essentially the same results. Plane waves with a cut-off energy of 550 eV were used for the expansion of the Kohn–Sham orbitals. The SO coupling effect can be included by solving the generalized Kohn–Sham equations in the relativistic DFT \cite{29}.

To minimize the lateral interactions between the adatoms, a large supercell ((5 × 5) or (4 × 4)) was used to simulate the 2D structures (figures 1(a) and (b)). In the direction perpendicular to the graphene, the distance between two adjacent layers is about 15 Å to avoid interactions between the layers. The Brillouin zone integrations were performed by using Monkhorst–Pack grids of (9 × 9 × 1) \cite{30}. Structure optimizations were performed till the Hellmann–Feynman force on each atom was less than 0.02 eV Å\(^{-1}\). The binding energy \(E_b\) (eV) is defined as \(E_b = nE_M + E_{Gr} - E_{tot}\), where \(E_M\), \(E_{Gr}\) and \(E_{tot}\) represent the total energies of a single gas phase adatom, the graphene with a C atom removed and the corresponding
Table 1. The calculated physical quantities of the studied systems in the most stable configuration: binding energy ($E_b$), average bond length between the metal adatom and its nearest C atoms ($d_{MC}$), bond length of Pb-d ($d_{MM}$), vertical distance from the adatom to the graphene plane ($h_M$), average up-moving distance of the C atoms nearest to the adatom with respect to the graphene plane ($h_C$), net charge transfer from the metal atoms to graphene ($\delta q$) and the Bychkov–Rashba parameter ($\alpha_R$). The former and latter values for some cases in Pb-d refer to the Pb$^1$ and Pb$^2$ atoms, respectively.

|       | $E_b$ (eV) | $d_{MC}/d_{MM}$ (Å) | $h_M$ (Å) | $h_C$ (Å) | $\delta q$ (e) | $\alpha_R$ (eV Å) |
|-------|------------|---------------------|-----------|-----------|----------------|------------------|
| Pb-m (5 × 5) | 3.40       | 2.30                | 2.33      | 0.69      | 1.89           | 0.09             |
| Pb-d (5 × 5) | 5.04       | 2.34, 2.50/3.00    | 2.41, 2.94| 0.67      | 1.71, 1.30     | –                |
| Pb-m (4 × 4) | 3.41       | 2.30                | 2.22      | 0.56      | 1.89           | 0.14             |
| Sn-m (5 × 5) | 4.44       | 2.15                | 2.12      | 0.70      | 2.24           | 0.02             |

complex, respectively; $n$ denotes the number of doped atoms in one unit cell. As a benchmark calculation, we predicted the SO splitting around the Dirac point of graphene with adsorbed Au to be $\sim 5$ meV, in good agreement with the results ($\sim 8$ meV) of [13].

Note that in our DFT calculations, the adsorbed atoms are periodic and ordered, while they may be disordered in the experimental samples. Since the distance between two neighboring adsorbed atoms or vacancies is long ($\sim 12.3$ Å), the interactions between them are negligible. Thus, our models should be reasonable to describe the experimental samples with impurities and vacancies at certain concentrations. A supercell of similar size has also been employed in previous works to study the interaction of metal atoms and defective graphene [19, 31, 32]. Actually, there are many DFT-based studies with the supercell method on graphene [21, 33], which can generally produce very consistent results compared to experiments.

3. Results and discussion

To obtain the most stable configurations, structural relaxations for various initial sites were performed for the adsorption of Pb-m and Pb-d on graphene. As shown in the inset of figure 1, three typical sites, 1, 2 and 3, were considered for the adsorption of single Pb atoms, which finally converged to the same configuration as illustrated in figure 1(a), with the binding energy of 3.40 eV (table 1). In this stable configuration (figure 1(a)), the Pb atom just sits above the carbon vacancy and the distances between the Pb atom and its three nearest C atoms are all about 2.3 Å, indicating chemical bonding. The adsorption modifies the structure of defective graphene. The three nearest C atoms rise above the graphene plane of 0.69 Å. For Pb-d, two kinds of adsorption configurations are considered: the dimer axis lies parallel or perpendicular to the graphene plane. For the former, the following combinations are adopted: 1–4, 1–7, 1–8, 1–9, 1–10, 1–11, 2–5, 2–6 and 3–5; and for the latter, the sites of 1, 2, 4 and 5 are employed. The most stable structure for Pb-d is presented in figure 1(b), where Pb$^1$ sits above the vacancy, whereas Pb$^2$ is above one of the C–C bonds closest to the C vacancy. Due to the existence of Pb$^2$, the bond lengths between Pb$^1$ and the three neighboring C atoms are not identical any more. As listed in table 1, the two Pb–C bond lengths are still about 2.3 Å, the same as that in the stable structure of Pb-m, but the third one is elongated to 2.5 Å. Pb$^2$ is bonded to Pb$^1$ (3.0 Å)
The calculated binding energy for this configuration is 5.0 eV. The adsorption stability is found to be mainly caused by the effective interaction between 6p (6s) of Pb atoms and 2p of the neighboring C atoms. In the following, we only focus on the most stable structures of Pb-m and Pb-d systems.

To understand the interaction between the dopant and the graphene, we calculated the charge density differences according to \( \Delta \rho = \rho_{total} - \rho_{Pb} - \rho_{Gr} \), where \( \rho_{total} \), \( \rho_{Pb} \) and \( \rho_{Gr} \) are the total charge densities of Pb-m (or Pb-d), the Pb single atom (or dimer) and the rest of the whole complex, respectively. The result of the charge density differences for Pb-m is shown in figure 1(c). There is a significant negative region around the Pb atom. Thus, there exists a large amount of charge transfer from the Pb to C atoms. This trend is in agreement with the result of Bader charge analysis \[34\], whereby 1.89 electrons have been transferred between them. For the C atoms around the vacancy and the Pb dopant, obvious charge transfer between them also occurs and the Pb atom has been slightly polarized. The charge transfer in Pb-d is somewhat complex: Pb\textsubscript{1} and Pb\textsubscript{2} have lost 1.71 and 1.30 electrons, respectively. There is electron depletion between the two Pb atoms (figure 1(d)). The characteristics of charge transfer and charge density differences in graphene with doped Pb attribute an ionic character to the bonding between Pb and the defective graphene. Similarly to the case of Pb-m, only the charge among the C atoms near dopants is redistributed much, indicating localization of the influence of Pb dopants. The localized nature of Pb states hints at the strong SO effects to be induced in the system. The essential charge transfer between Pb and the neighboring C atoms reflects strong interactions between them, which can give rise to a large SO effect in graphene-derived bands.

Next we investigate the influence of Pb doping on electronic structures. For bare graphene, it is a nonmagnetic semimetal and the density of states is zero at the Fermi level \( (E_F) \). As shown in figure 2, the doping of Pb atoms in graphene can drastically modify the band structures of graphene. Pb-m and Pb-d display semiconductor character with band gaps of 0.26 and 0.21 eV, respectively. Since the gaps produced by using GGA are generally underestimated, the opened band gaps in the system are moderate and can benefit the fabrication of graphene-based nanoelectronic and nanophotonic devices, such as the FET. The charge density analyses for the valance and conduction bands near the \( E_F \) of Pb-m demonstrate that the valence bands mainly display the \( p_x \) and \( p_y \) character of the adatom and its neighboring C atoms; for the latter, the \( p_z \) states of the adatoms and graphene are dominant. In the Pb-d case, in addition to the above behavior, the robust \( p_x \) states from Pb\textsubscript{2} show up in both the valance and conduction bands near \( E_F \). Substitutional Bi atoms make the system metallic \[19\]. This can be understood by considering that the Bi atom has one valence electron more than the Pb atom.
The band structures without and with SO interactions for Pb-m are shown in figures 3(a) and (b), respectively. Upon substitution of the Pb atoms, the SO effect is significantly enhanced. The SO splitting for the valance band at the K point is as large as 116.6 meV. The charge density isosurface of this state indicates significant p$_x$ and p$_y$ character of the adatom (the middle panel of figure 3(c)). Dong et al [12] found that the SO coupling-induced splitting of the band of fluorinated graphene can reach 27.4 meV, ascribed to the large intrinsic SO coupling of the F atom. The SO interaction parameter for the Pb atom is up to 0.91 eV [35]. Thus, it is reasonable that the substitution of the Pb atom can induce a large SO splitting in the state, dominated by p$_x$ and p$_y$ of the adatoms. The SO splitting for the conduction band around the $\Gamma$ point is more intriguing. The size of splitting is linear as a function of the wave vector and the spin polarization ($P$) lies in the 2D surface Brillouin zone and perpendicular to the direction of the wave vector (the bottom panel of figure 3(c)). These suggest that the SO splitting is of Bychkov–Rashba type [15], which results from the out-of-plane gradient of the crystal potential due to Pb doping. As shown in the top panel of figure 3(c), the wave function composition of the states at the $\Gamma$ point in the band is contributed by p$_z$ states of graphene and the Pb atom. The strong interaction between the doped Pb and the graphene p$_z$ states leads to a large asymmetrical potential distribution perpendicular to the graphene plane. An explicit Bychkov–Rashba effect around the $\Gamma$ point is consequently formed. The calculated Bychkov–Rashba parameter, $\alpha_R$, is 0.09 eV Å and the splitting can reach 13 meV, close to that induced by an Au monolayer between graphene and Ni(111) substrate [9].

Interestingly, in addition to the in-plane spin polarization, the out-of-plane $P$ component also appears in the system and gradually increases along the $\Gamma$–K direction, while it decreases...
Figure 4. The band structures for Pb-d without (a) and with (b) SO interactions. In (c), the top (bottom) panel shows the charge density isosurface for the bottom of the conduction bands (the top of the valence bands), indicated by the blue arrows in (a).

along the K–M direction (the bottom panel of figure 3(c)). Note that along the Γ–K and K–M directions, the in-plane and out-of-plane $P$ components coexist. The occurrence of the out-of-plane $P$ component, obtained for the first time to the best of our knowledge, must result from the in-plane potential gradient [15], probably due to the very low coverage of Pb doping in the graphene plane. A large out-of-plane $P$ component has been reported by Ast et al [17] in Bi/Ag(111) alloy with one-third of a monolayer of Bi atoms in both experiments and theories.

To explore the origin of the SO effect in the bands, we study the case of graphene with doped single Sn atoms. Sn atoms have the same $s^2p^2$ electronic configuration. However, the atom SO parameter (0.27 eV) is $\sim 3$ times smaller than that for Pb atoms [35]. Our calculations show that Sn monomer doping has similar band structures as that of Pb-m and that the calculated Bychkov–Rashba parameter, $\alpha_R$, is $\sim 5$ times lower than that for Pb doping (table 1), indicating the direct influence of the atomic SO interaction of the dopants on the SO effect of the graphene bands. The trend is different from that found in graphene grown on Ni and Ag due to the different interaction behavior [11].

For the Pb-d system, the band structures without and with SOC are presented in figures 4(a) and (b), respectively. The magnitudes of the SO splitting for the top of the valence band and the bottom of the conduction band are 81.5 and 50.2 meV, respectively. As mentioned before, in addition to the robust Pb$^2$ $p_x$ states, the valence (conduction) band around $E_F$ also has contributions from certain in-plane states ($p_x$ and $p_y$) and out-of-plane states ($p_z$) of atoms (figure 4(c)). Comparing figures 3(a) and (b), $p_x$ states of Pb$^2$ decrease the SO splitting of the valence band near $E_F$, while they increase the SO splitting of the conduction band near $E_F$, which can be ascribed to different orbital features of the two bands.

The band structures for the system with high doping concentration are investigated, that is, for the system in which one Pb atom replaces one C atom in a (4 × 4) supercell instead of a (5 × 5) one. The band structures with SO interactions are shown in figure 5(a). The Bychkov–Rashba parameter, $\alpha_R$, in the conduction band near $E_F$ around the $\Gamma$ point is about 0.14 eV Å (table 1) and the SO splitting can reach 40 meV. The enhanced SO splitting in a
(4 × 4) supercell can be rationalized by the greater contribution of Pb states to the graphene bands through charge transfer between them. Since photoemission spectra [9] are usually available for the occupied states, to measure this Bychkov–Rashba splitting in experiments, we need to shift the $E_F$ position up in energy. To carry out this goal, we inject one electron into the (4 × 4) supercell, leading to crossing of the ‘conduction band’ with $E_F$ (figure 5(b)). Importantly, the Bychkov–Rashba splitting is not varied by the additional electrons added to the system. It is consequently possible to apply the photoemission spectra to observe the Bychkov–Rashba SO splitting induced by Pb atom doping in graphene. The SO splitting in graphene can also be monitored in spin relaxation experiments [14, 36, 37]. Generally, the stronger the SO interaction, the shorter the spin relaxation time. For example, Pi et al [36] explored the influence of Au doping on the spin lifetime in the graphene system in experiments. Ertler et al [14] predicted in theory that Au adatoms on graphene could cause the spin lifetime of graphene to decrease significantly (shorter than nanoseconds) due to the large SO interaction induced by the adatoms. Our results indicate that the spin lifetime of graphene with Pb doping may not be very long.

4. Conclusion

In conclusion, we have studied the structural stability, electronic structures and SO effects in graphene with doped Pb single atom and dimer. The results show that Pb single atoms and dimers can both chemically bind to graphene with vacancies. The substitutional doping with either single Pb atoms or dimers turns the systems into semiconductors. The SO splitting in the graphene bands around $E_F$ can be significantly enhanced due to the large atomic SO interaction of the Pb dopant and the effective interaction between Pb and the neighboring C atoms. Both the in-plane and out-of-plane potential gradients are found to contribute to the SO effect in the system. The obvious Bychkov–Rashba splitting may be detected through photoemission spectra in experiments by injecting electrons into the system. Our findings may kindle more experimental and theoretical work in this direction.
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