Defect in Phosphorene

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Defects are inevitably present in materials and always can affect their properties. Here, first-principles calculations are performed to study the stability, structural and electronic properties of typical point defects in semiconducting phosphorene, including the Stone-Wales (SW) defect, single and double vacancy (SV5566, DV585, DV555777 and DV4104) defects. We find that these defects are all much easily created in phosphorene with higher areal density compared with graphene and silicene. Furthermore, these defects are easy distinguish each other and correlate with their defective atomic structures with simulated scanning tunneling microscopy images at positive bias. Interestingly, the SW, DV555777 and DV4104 defects have little effect on phosphorene’s electronic properties and defective phosphorene monolayers still show semiconducting with similar band gap values to perfect phosphorene. But, the SV5566 defect can induce hole doping in phosphorene and the DV585 defect can introduce two unoccupied localized states into the fundamental bandgap of phosphorene.

I. INTRODUCTION

Two-dimensional (2D) ultrathin materials, such as graphene,\textsuperscript{1,2} silicene,\textsuperscript{3,4} hexagonal boron nitride,\textsuperscript{5,6} graphitic carbon nitride\textsuperscript{7,8} and molybdenum disulphide,\textsuperscript{9,10} have received considerable interest recently owing to their outstanding properties and potential applications. Graphene,\textsuperscript{2} a 2D sp\textsuperscript{2}-hybridized carbon monolayer, is known to have remarkable electronic properties, such as a high carrier mobility, but the absence of a bandgap limits its applications of large-off current and high on-off ratio for graphene-based electronic devices. The same problem also exists in silicene, another well-known single silicon monolayer, which has most similar remarkable electronic properties to graphene but with buckled honeycomb structures.\textsuperscript{4}

Most recently, a new 2D material, namely, phosphorene,\textsuperscript{11–15} has been isolated in the experiments through mechanical exfoliation from bulk black phosphorus and has immediately received considerable attention. Phosphorene also shows some remarkable electronic properties superior to graphene and silicene. For example, phosphorene is a semiconductor with a direct bandgap of about 1 eV,\textsuperscript{12} showing the drain current modulation up to $10^5$ and carrier mobility up to $10^5 \text{ cm}^2/(\text{Vs})$ in nanoelectronics.\textsuperscript{13–15} Furthermore, up to now, besides graphene, phosphorene is the only stable elemental 2D material which can be mechanically exfoliated in the experiments.\textsuperscript{15} Therefore, introduced as an alternative to graphene,\textsuperscript{16,17} phosphorene may lead to faster semiconductor electronics in the future.

On the other hand, the properties of these 2D ultrathin materials are always affected by the presence of defects. Typical point defects in graphene and silicene include Stone-Wales (SW) defect, single and double vacancy (SV and DV) defects.\textsuperscript{18–22} Generally, both graphene and silicene have two kinds of SVs (SV59 and SV5566) and DVs (DV585 and DV555777), respectively. These defects are inevitably present in graphene and silicene and severely affect the electronic properties of graphene\textsuperscript{20} and silicene,\textsuperscript{21} thus alter their applications.\textsuperscript{23–25}

In the present work, we systematically study the stability and electronic structures of typical point defects in semiconducting phosphorene using the density functional theory calculations. We find that these defects are all much easily created in phosphorene with regard to graphene and silicene and they are easy distinguish each other and correlate with their defective atomic structures with simulated scanning tunneling microscopy images at positive bias. Interestingly, the SW, DV555777 and DV4104 defects have little effect on phosphorene’s electronic properties. But, the SV5566 defect can induce hole doping in phosphorene and the DV585 defect can introduce two unoccupied localized states into the fundamental bandgap of phosphorene.

II. THEORETICAL METHODS AND MODELS

First-principles calculations are based on the density functional theory (DFT) implemented in the VASP package.\textsuperscript{26} The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)\textsuperscript{27} is chosen due to its good description of electronic structures of phosphorene,\textsuperscript{12} graphene,\textsuperscript{21} and silicene.\textsuperscript{24} All the geometry structures are fully relaxed until energy and forces are converged to $10^{-5}$ eV and 0.01 eV/Å, respec-
tively. The energy cutoff is set to be 500 eV. The lattice parameters of phosphorene calculated to setup unit cell are \( a(P) = 4.62 \, \text{Å} \) and \( b(P) = 3.30 \, \text{Å} \). A large \( 5 \times 7 \) supercell of phosphorene with a vacuum space about 15 Å in the Z direction is adopted to study the effect of various local defects in phosphorene. The surface Brillouin zone is sampled with a \( 3 \times 3 \) regular mesh.

FIG. 1: (Color online) Geometric structures of (a) perfect and defective phosphorene in the \( 5 \times 7 \) supercell, including the (b) SW, (c) SV5566, (d) DV585, (e) DV555777 and (f) DV4104 defects. The violet and yellow balls denote unaffected and affected phosphorus atoms, respectively.

III. RESULTS AND DISCUSSION

We first check the geometric properties of defects in phosphorene as shown in Figure 1. Typical point defects of SW, SV5566, DV585 and DV555777 in graphene\(^{20}\) and silicene\(^{21}\) also can be formed in phosphorene. But, the SV59 defect is proved to be unstable in phosphorene, which is the only stable SV in graphene\(^{20}\) and also is metastable (5566 is most stable SV defect) SV in silicene,\(^{21}\) and can automatically translate into the SV5566 defect in phosphorene after structural optimization. Interestingly, we find a new stable structure of DV defect, namely 4|10|4, as shown in Figure 1(f), which does not exit in both graphene and silicene.

To help recognize the defects in future experiments, the scanning tunneling microscopy (STM) images of perfect and defective phosphorene are simulated at \(+1.0\) and \(-1.0\) V bias as shown in Figure 2. At positive bias \(+1.0\) V, the STM images of these defects are easy to understand and correlate with their defective atomic structures. But at negative bias \(-1.0\) V, the STM images of perfect and defective phosphorene are difficult to distinguish each other due to a direct consequence of height variation for the buckling of phosphorene.

FIG. 2: (Color online) Simulated STM images (+1.0 and -1.0 V) of (a) perfect and defective phosphorene, including including the (b) SW, (c) SV5566, (d) DV585, (e) DV555777 and (f) DV4104 defects.

Then, we study the stability of defects in phosphorene. To characterize the stability of a defect in phosphorene, we define its formation energy as

\[
E_f = E_{\text{Phosphorene}} - N_p \star E_P
\]

where \( E_{\text{Phosphorene}} \) represents the total energy of defective phosphorene, \( E_P \) is the energy per phosphorus atom in a perfect phosphorene sheet and \( N_p \) corresponds to the number of phosphorus atoms in phosphorene. Notice that for perfect phosphorene, \( E_f(\text{Phosphorene}) = 0 \) eV. In addition, the stability of perfect and defective phosphorene can also be predicted via its cohesive energy, given by

\[
E_c = \mu_p - E_{\text{Phosphorene}}/N_p
\]

where \( E_{\text{Phosphorene}} \) represents the total energy of the phosphorene system, \( \mu_p \) is the chemical potentials of phosphorus atoms and \( N_p \) corresponds to the number of phosphorus atoms in the system. The calculated stability of formation and cohesive energy of perfect and defective phosphorene, graphene and silicene are summarized in
TABLE I: Calculated stability and electronic properties of perfect and defective phosphorene, including the cohesive energy $E_c$ (eV/atom), formation energy $E_f$ (eV), total magnetic moment $\mu$ ($\mu_B$) and band gap $E_g$ (eV).

|       | $E_c$  | $E_f$  | $\mu$  | $E_g$  |
|-------|-------|-------|--------|-------|
| Perfect | 3.477 | 0.000 | 0.963  |       |
| SW    | 3.469 | 1.012 | 0.989  |       |
| SV5566| 3.462 | 2.025 | 0.000  | 0.963 |
| DV585 | 3.455 | 3.041 | 0.559  |       |
| DV555777| 3.458| 3.041 | 2.613  | 1.042 |
| DV4104| 3.461 | 2.137 | 0.000  | 1.002 |

Table II: Comparison results of cohesive energy $E_c$ (eV/atom) of perfect phosphorene, graphene and silicene with corresponding various defects’ formation energy $E_f$ (eV).

| Reference | Phosphorene | Graphene | Silicene |
|-----------|-------------|----------|----------|
| $E_c$ (Perfect) | 3.48       | 7.90     | 3.96     |
| $E_f$ (SW)    | 1.01       | 4.50     | 2.09     |
| $E_f$ (SV5566) | 2.03     | 7.80     | 3.77     |
| $E_f$ (DV585) | 3.04       | 7.52     | 3.70     |
| $E_f$ (DV555777) | 2.61      | 6.40     | 2.84     |
| $E_f$ (DV4104) | 2.13       |          |          |

Table I and Table II. Perfect phosphorene shows less stable with a smaller cohesive energy of 3.48 eV/atom compared with graphene (7.90 eV/atom) and silicene (3.96 eV/atom). We find that the SW defect is most easily formed in phosphorene with the smallest formation energy of 1.01 eV among various defects similar to graphene and silicene. But, there is only one SV defect (5566) in phosphorene with a small formation energy of 2.03 eV. For DVs, the 585 and 555777 defects are also stable in phosphorene similar to graphene and silicene. Interestingly, we find the most stable DV in phosphorene is 4104 with a smaller formation energy of 2.13 eV, but which can not formed in graphene and silicene. Notice that defective phosphorene monolayers all have smaller formation energy compared with defective graphene and silicene with the same types of defects as summarized in Table I.

At finite temperature $T$, defects’ areal density $N_{\text{Defect}}$ (m$^{-2}$) in 2D materials follows the Arrhenius equation

$$N_{\text{Defect}} = N_{\text{Perfect}} \exp\left(-\frac{E_f}{k_B T}\right)$$

where $N_{\text{Perfect}}$ is the areal density of atoms in perfect 2D materials, $E_f$ is the formation energy of a defect formed in materials and $k_B$ is the Boltzmann constant. For perfect phosphorene, graphene and silicene, their areal densities are $N_{\text{Perfect}}$(Phosphorene) = 2.62 × 10$^{19}$ m$^{-2}$, $N_{\text{Perfect}}$(Graphene) = 3.79 × 10$^{19}$ m$^{-2}$ and $N_{\text{Perfect}}$(Silicene) = 1.55 × 10$^{19}$ m$^{-2}$, respectively. The temperature-dependence areal density of defects in phosphorene, graphene and silicene is calculated and plotted in Figure 3. The results show that these defects have much higher areal density and they are much easily created in phosphorene compared with graphene and silicene.

Electronic band structures of perfect and defective phosphorene are shown in Figure 4. Monolayer phosphorene is semiconducting with a direct band gap of 0.96 eV (Figure 2b), which agrees well with previous theoretical studies. We find that all these defective phosphorene monolayers are not magnetic similar to silicene. Furthermore, the SW, DV555777 and DV4104 defects have little effect on phosphorene’s electronic properties, still showing semiconducting with similar band gap values for defective phosphorene, different from graphene and silicene. But, defective phosphorene with the DV585 defect is also a semiconductor but with a reduced band gap of 0.56 eV due to two unoccupied localized states introduced into phosphorene’s fundamental band gap as shown in Figure 4(d). Specifically, the only stable SV defect (5566) in phosphorene can induce hole doping as shown in Figure 4(c), which can increase the hole carrier concentration of semiconducting phosphorene. Notice that phosphorene has a high areal density (1 × 10$^{-6}$ m$^{-2}$ at $T = 400$ K) for the SV5566 defect, agreeing well with a high hole mobility observed in phosphorene in recent experiments.
IV. CONCLUSIONS

In summary, we systematically study the stability, structural and electronic properties of typical point defects in semiconducting phosphorene using the density functional theory calculations. We find that these defects are all much easily created in phosphorene with higher areal density compared with graphene and silicene. Furthermore, these defects are easy distinguish each other and correlate with their defective atomic structures with simulated scanning tunneling microscopy images at positive bias. Interestingly, the SW, DV555777 and DV4104 defects have little effect on phosphorene’s electronic properties and defective phosphorene monolayers still show semiconducting with similar band gap values to perfect phosphorene. But, the SV5566 defect can induce hole doping in phosphorene and the DV585 defect can introduce two unoccupied localized states into the fundamental bandgap of phosphorene. The resent theoretical results provide valuable insights into the identification of defects in the experiments and the understanding their effects on the properties and applications of phosphorene.

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FIG. 4: (Color online) Electronic band structures of (a) perfect and defective phosphorene, including the (b) SW, (c) SV5566, (d) DV585, (e) DV555777 and (f) DV4104 defects. The Fermi level is marked by green dotted lines and the vacuum level is set to zero.
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