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Full Length Article

Selective gas adsorption and I–V response of monolayer boron phosphide introduced by dopants: A first-principle study

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ABSTRACT

Two-dimensional (2D) materials have gained tremendous research interests for gas sensing applications because of their ultrahigh theoretical specific surface areas and unique electronic properties. Here, we investigate the adsorption of CO, SO_2, NH_3, O_2, NO and NO_2 gas molecules on pure and doped boron phosphide (BP) systems using first-principles calculations to exploit their potential in gas sensing. Our results predict that all six gas molecules show stronger adsorption interactions on impurities-doped BP over the pristine monolayer BP. Al-doped BP shows the highest sensitivity to all gas molecules, but N-doped BP is more suitable as a sensing material for SO_2, NO and NO_2 due to the feasibility of desorption. We further calculated the current–voltage (I–V) relation by mean of nonequilibrium Green's function (NEGF) formalism. The I–V curves indicate that the electronic properties of the doping systems change significantly with gas adsorption by studying the nonparamagnetic molecules NH_3 and the paramagnetic molecules NO, which can be more likely to be measured experimentally compared to graphene and phosphorene. This work explores the possibility of BP as a superior sensor through introducing the appropriate dopants.

1. Introduction

Owing to the intriguing properties in electronic applications, such as high carrier mobility, superior mechanical flexible and optical transparency [1–4], two-dimensional (2D) materials have sparked great research upsurge since the discovery of graphene [5–8]. However, the current 2D materials, including silicene [9,10], germanene [11], stanene [12], phosphorene [3,4], transition metal dichalcogenides [13,14] and so on, are either short of a band gap or instable in the atmosphere which limit their practical applications. Therefore, the work of continuing to look for more 2D materials that can lead greater improvements in composites [15], optoelectronics devices [16], spintronic devices [17] and gas sensors [18] currently becomes vital. The monolayer boron phosphide (BP), III–V binary compound semiconductor, being provided with a flat 2D honeycomb structure similar to graphene, is theoretically predicted and has aroused enormous research interests with remarkable electronic properties at the nanoscale [19,20]. Experimentally, multilayer BP films have been synthesized on silicon carbide substrate by CVD method [21]. BP possesses an in-plane Young modulus and Poisson's ratio of 135.6 N m^{-1} and 0.27, respectively, indicating that its mechanical stability is almost the same as MoS_2 and harder than graphene and monolayer BN. Besides, it also exhibits an appreciated fundamental direct band gap of 0.91 eV [19], making it a promising candidate material for the next-generation nanoelectronics.

2D materials typically show a large surface-to-volume ratio and apparent charge transfers from host materials to gas molecules, making them excellent gas sensor candidates. Sensing gas molecules play an important role in the environment monitoring, industrial, medical and agricultural applications. Graphene [22], MoS_2 [23,24], phosphorene [18] and antimonene [25] acting as sensing elements have been intensively investigated by both theoretical and experimental researches. The gas sensing mechanism is based on the changes in conductivity by the adsorption of gas molecules acting as charge donors or acceptors, thus, monitoring the conductivity changes can help to detect the concentration of gas molecules. Doping of the noble metal-free materials such as nitrogen doped carbon nanotubes [26], doped graphene [22,27–29] and metal doped boron nitride [30] have been verified to be an effective

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way to modify the electronic properties and enhance charge transfer between the host materials and reactants, and eventually lead to a higher activity. So far, there is limited number of studies on the effect of dopants on the sensing properties of BP. Hence, in the gas sensing point of view, it is worthwhile to systematically study the adsorption behavior of gas molecules on BP systems.

Herein, we firstly investigate the gas sensing properties to fully exploit the possibilities of BP as gas sensors by density functional theory (DFT) calculations. The interaction strength between the BP systems and several typical molecules, CO, SO_2, NH_3, O_2, NO and NO_2 are quantitatively evaluated based on the energetics and charge transfer. Meanwhile, we calculated the I–V relation of BP systems with and without gas molecule adsorption based on the nonequilibrium Green's function (NEGF) formalism. Doping BP by a single nitrogen or aluminum atom is premeditated for reducing complexity while perfect BP is also studied for comparison. It is found that the adsorption strength of BP systems with gas molecule is highly dependent on the amount of charge transfer. Our calculations indicate that doped BP is ingenious with the gas molecules and its electronic characteristics can be reasonably regulated through selectively adsorbing these small molecules. Furthermore, our work provides a profound insight for investigating the doped BP gas sensors at sensitive gas sensing devices and high performance catalysts and how to effectively design a selective control of the gas sensor.

2. Computational methods

In our work, first-principle calculations based on density functional theory (DFT) were performed using the $DMol^3$ package [31]. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was used to describe the exchange–correlation interaction [32]. In order to explain interaction for the noncovalent chemical functionalization of BP by gas molecules, the DFT-D2 (D2 stands for dispersion) method proposed by Grimme was employed [33,34]. Besides, the method of the all electrons for the core treatment parameter was utilized and the double numerical atomic orbital plus polarization (DNP) was chosen as the basis set with the global cutoff of 5.0 Å to ensure the high computational quality. The k-point was set to $16 \times 16 \times 1$ for the structural optimizations and $20 \times 20 \times 1$ for the accurate electronic property calculations. Moreover, the atomic positions and cell vectors were relaxed until the energy, maximum force and maximum displacement were less than 1.0×10^{-5} Ha (1 Ha = 27.2114 eV), 0.002 Ha Å^{-1}, and 0.005 Å, respectively. We have carried out a test of the adsorption energy calculations under different maximum force convergence conditions, which are summarized in Table S1 in the "Supporting Information" section, in which the tiny change confirms the accuracy of our calculation. In this study, we only consider the case of a single gas molecule adsorption on the $4 \times 4 \times 1$ supercell (16 boron atoms and 16 phosphorus atoms). Furthermore, the thickness of a vacuum region was set as 30 Å to avoid the effect of interaction deriving from the adjacent BP layers. The relaxed lattice constant and the B-P bond length of monolayer boron phosphide are 3.215 and 1.856 Å, respectively, which are in good agreement with previous theoretical studies [20,35]. We also carried out a benchmark calculation of the adsorption on phosphorene to further confirm the accuracy of our method. The adsorption energy of CO on phosphorene was calculated to be −0.312 eV, which corresponds well with reported value of −0.325 eV using the Vienna Ab Initio Simulation (VASP) package [18]. Therefore, we believe our method is reliable.

We computed the adsorption energy (E_{ad}), adsorption distance (d_{G-BP}) and charge transfer (ΔQ) in order to conduct more reliable analysis of the stability when the gas molecules are adsorbed on BP. The E_{ad} value was calculated as:

$$E_{ad} = E_{total} - E_{BP} - E_{gas} \tag{1}$$

Where E_{total}, E_{BP} and E_{gas} are the total energies with full relaxation for gas molecule on BP, isolated BP, isolated gas molecule, respectively. The d_{G-BP} is defined as the distance of nearest atoms between BP and small molecules. Charge transfers can be calculated based on the Hirshfeld charge analysis approach. The charge of each atom (atomic charge Q) is calculated by the following formula [36]:

$$Q = \int^{<MML:MROW/>} \frac{\rho_A^0(r)}{\Sigma_{A'} \rho_{A'}^0(r)} \rho(r)\, dr \tag{2}$$

Which the calculated density $\rho(r)$ and the electron density $\rho_A^0(r)$ are computed based on the isolated atom A. From this result the charge transfer (ΔQ) and adsorbate whether or not acts as an acceptor or a donor can be deduced. Moreover, the size of the charge transfer is affected for different methods calculated it.

The electronic transport properties were studied within a DFT-based real-space by the nonequilibrium Green's function (NEGF) techniques as implemented in the Atomistix ToolKit (ATK) package [37]. The electron-electron interaction is treated through the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) form [38]. A sample of $1 \times 1 \times 100$ k-points chosen by the Monkhorst-Pack method was used to describe the Brillouin zone and the mesh cutoff was chosen as 150 Ry to achieve a reasonable balance between computational efficiency and accuracy. The electron wave function was expanded using a double-ζ polarized (DZP) basis set and the solution of the Poisson equation using a fast Fourier transform 2D (FFT2D). The SG15 of the Norm-conserving Troullier–Martins pseudopotentials were used to describe the core electrons [39]. X and Z directions are used as periodic boundary conditions, while the Y direction is set as direchlet. Vacuum region of 30 Å were introduced to avoid the effect of interaction between the adjacent layers in Z direction of BP system. The electric current through the contact region is calculated using the Landauer–Buttiker formula [40,41]:

$$I(V_b) = G_0 \int_{\mu_L}^{\mu_R} T(E, V_b)\, dE \tag{3}$$

Where $G_0 = 2e^2h^{-1}$ is the unit of the quantum conductance and $T(E, V_b)$ is the electronic transport probability at energy E under the V_b applied bias voltage across the electrodes, μ_R and μ_L are the electrochemical potential of the right and left electrodes.

For simplicity, the pristine, nitrogen-doped and aluminum-doped BP are denoted as P-BP, N-BP and Al-BP, respectively, in the following.

3. Results and discussion

We investigated the effects of aluminum atom and nitrogen atom doping on BP for the following cases: (i) replacement of a boron atom with a nitrogen atom (N-BP) and (ii) substituting a boron atom with an aluminum atom (Al-BP). The above two cases can be considered as models of one-electron doping of the BP sheet. Since the formation energy of doping system for the cases of a nitrogen atom or an aluminum atom instead of a phosphorus atom is far higher than the situation mentioned above, respectively, and henceforth we ignored these two cases. We find that the dopant atom in the Al-BP surface and N-BP surface lies in the plane and does not move outward after relaxation. The Al-P bond lengths and N-P bond lengths are 2.129 Å and 1.800 Å, respectively, which are 0.273 Å longer and 0.056 Å shorter than the B-P bond of P-BP.