Metal adsorption on monolayer blue phosphorene: A first principles study

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ABSTRACT

We investigated the electronic structure, adsorption energies, magnetic properties, dipole moment and work function of metal adatoms (Mg, Cr, Mo, Pd, Pt, and Au) adsorption on a blue phosphorene monolayer. For Mg, Pt and Au metals, the most stable state was found in hollow site while for Cr, Mo and Pd metals we found an adsorption in valley site. We suggest that the Pd and Pt atoms prefer 2D growth mode while the Mg, Cr, Mo and Au atoms prefer 3D island growth mode on monolayer phosphorene. The electronic band structures and magnetic properties were dependent on the doping site and dopant materials. For instance, the semiconducting features were preserved in Mg, Pd, Pt, and Au doped systems. However, the Cr and Mo doped systems displayed half-metallic band structures. The total magnetic moment of 4.05, 2.0 and 0.77 μ_B/impurity atom were obtained in Cr, Mo and Au doped systems whereas the Mg, Pd and Pt doped systems remained nonmagnetic. We also investigated the magnetic interaction between two transition metal impurities. We observed ferromagnetic coupling between two transition metal impurities in Cr and Mo doped systems while the Au doped system displayed almost degenerated magnetic state. For Mg, Cr, and Mo adsorptions, we found relatively large values of dipole moments compared to those in the Pd, Pt and Au adsorptions. This resulted in a significant suppression of the work function in Mg, Cr and Mo adsorptions. Overall, adsorption can tune the physical and magnetic properties of phosphorene monolayer.

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1. Introduction

Two-dimensional (2D) materials are receiving an extensive research interest due to their unique properties, not found in bulk structures. So far, various types of 2D materials are extensively studied; graphene, hexagonal boron nitride (h-BN), transition metal oxides, transition metal dichalcogenides and phosphorene for different potential applications [1–6]. Among them, the graphene is one of the most interesting materials because of its excellent optical, thermal, electrical and mechanical properties [7–9]. However, the graphene has no intrinsic band gap and this limits its use for transistor device applications.

For various device applications, it is highly desirable to fabricate a material which has a finite band gap with a high mobility. In this regard, the black phosphorene is a very interesting material because it possesses an intrinsic band gap with high enough electrical mobility. Thus, the black phosphorene receives tremendous research interests ever since its discovery in 2014. Indeed, it has been shown that the phosphorene-based field effect transistor exhibits high mobility and on/off ratio. Moreover, the electrical transport and optical properties of phosphorene are anisotropic. These features may bring potential optoelectronic device applications [10–14]. Along with the anisotropic electrical and optical properties, it will be an interesting issue to explore the magnetic property for spintronics applications. However, the phosphorene layer consists of non-magnetic element phosphorous atoms and this results in non-magnetic characteristic in the pristine phosphorene layer. Thus, the manipulation of a magnetic state is necessary for its use in spintronics. The adsorption of transition metal (TM) on the surface of a 2D material is one of the common ways to control or to modify its various properties; structure, bonding, charge transfer mechanism or magnetic ground state. For example, the effect of a single impurity adsorption or substitution on the graphene was extensively studied [15–17]. Previously, we also investigated the physical properties of transition metal adatom and dimer on the black phosphorene monolayer [18,19]. In addition to the black phosphorene, there exists another allotrope called the blue phosphorene. The blue phosphorene has a different structure from that of black phosphorene [20]. The black phosphorene has an orthorhombic primitive cell with four *P* atoms per unit cell while the blue phosphorene has a hexagonal structure with two *P*

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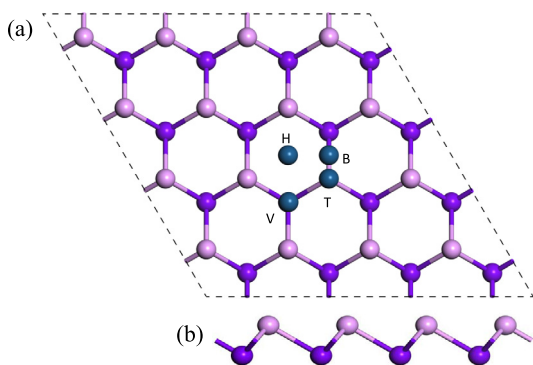*E-mail address:* hongj@pknu.ac.kr (J. Hong).

Fig. 1. Schematic illustration of (a) top view of adatom on monolayer phosphorene and (b) side view of pristine phosphorene monolayer.

atoms per unit cell. Due to this difference in their structures, both could have different physical and magnetic properties. Therefore, in our work, we will explore the electronic and magnetic properties of metal adatom (Mg, Cr, Mo, Pd, Pt, and Au) adsorbed blue phosphorene using first principles density functional calculations.

2. Numerical methods

In order to study the structural, electronic and magnetic properties of metal adatom on monolayer blue phosphorene, we performed the spin-polarized calculations within the framework of generalized gradient approximation (GGA) of Perdew–Burke–Enzerhof [21]. The Vienna ab initio Simulation Package (VASP) [22, 23] was used with a plane wave basis set and an energy cut-off of 500 eV was employed in our calculations. The pristine blue phosphorene has a hexagonal primitive cell with two phosphorous atoms per cell and a lattice constant of $a = b = 3.28$ Å. This crystal structure belongs to the space group of $P-3M1$ in which the phosphorous atom is residing on 2d site with a buckling height of 1.24 Å. To study the metal adatom adsorption, we considered a (4×4) supercell containing 32 phosphorous atoms with one metal adatom and this corresponds to a doping concentration of 3.125%. A vacuum distance of more than 16 Å was used in order to avoid the artificial interaction from the neighboring cell. In order to determine the magnetic coupling between two impurities, we doubled the previous supercell of phosphorene in x-direction and doped two metal adatoms keeping the same doping concentration like in a single impurity case. The energy convergence criteria in all systems were set to 10^{-5} eV. The self-consistent calculations were performed using a $(7 \times 7 \times 1)$ Monkhorst pack k-mesh for single metal adatom systems while $(5 \times 10 \times 1)$ for two metal adatom systems [24]. Furthermore, the ferromagnetic (FM) and antiferromagnetic (AFM) spin configurations between two adatoms were also taken in to account to find the stable magnetic ground state.

3. Numerical results

To find the most stable metal adsorption site on the phosphorene layer, we considered four different adsorption sites such as hollow (H), bridge (B), top (T) and valley (V) site. Fig. 1 (a) shows the schematic illustration of the top view of adatom on phosphorene layer while Fig. 1 (b) shows the side view of pristine blue phosphorene. The pink and purple spheres represent the phosphorous atoms in upper and lower half layer while the blue sphere represents the impurity atom. Table 1 shows the total energy difference in each site for a specific impurity atom. We found that the most stable adsorption site was dependent on the impurity atom. For instance, the Mg, Pt and Au metal adatoms preferred the hollow site while the Cr, Mo and Pd metal adatoms preferred the

Table 1
Calculated total energy differences (in eV/cell) for top, bridge, hollow and valley sites.

Adatom/Doping site	Top	Bridge	Hollow	Valley
Mg	0.14	0.11	0	0.04
Cr	0.71	0.54	0.22	0
Mo	1.47	1.20	0.84	0
Pd	0.49	0.46	0.02	0
Pt	0.35	0.46	0	0.01
Au	0.20	0.19	0	0.28

Table 2
Adsorption energy (E_a), vertical height (h) of adatom, magnetic moment of adsorbant and band gap for metal adatom on most stable adsorption site.

Adatom	E_a (eV/atom)	h (Å)	m (μ_B)	Band gap (eV)
Mg	0.20	2.240	0	0.32
Cr	1.45	1.390	4.05	Half metal
Mo	2.29	1.328	2	Half metal
Pd	2.89	1.410	0	1.45
Pt	3.86	1.435	0	1.15
Au	1.43	1.772	0.77	0.10

valley site. For Mg, Pt and Au impurity atoms, our results agree with the previously reported study [25].

We also calculated the adsorption energy in the most stable adsorption site using the following relation

$$E_a = E_P + E_M - E_{MP} \qquad (1)$$

where E_P, E_M and E_{MP} represent the total energies of the pristine phosphorene layer, the isolated metal atom, and the adatom adsorbed phosphorene. Table 2 shows the results. The lowest adsorption energy was found in Mg adsorption while the Pt had the highest adsorption energy. Compared with the metal adsorption energy on the graphene [15], we obtained very high values of the adsorption energy on the blue phosphorene and this suggests a strong interaction between metal adatom and the blue phosphorene sheet. To understand the growth morphology or growth mode of metal atom on phosphorene, i.e. whether metal elements will have two-dimensional (2D) or three-dimensional (3D) growth morphology, it is necessary to investigate several factors; the ratio of the adsorption energy to the bulk cohesive energy, the diffusion barrier energy or thermal stability. Here, we also calculated these quantities. The experimental bulk cohesive energies of metals elements were taken from the ref. [26]. For a large ratio of the adsorption energy to the bulk cohesive energy, the metal adatom may prefer 2D growth mode on a substrate and will stick to the substrate instead of making an island formation while the 3D island growth mode is more favorable for a small value. Fig. 2 (a) shows the calculated results. A relatively larger value was found for Pd and Pt while the ratio was rather small for Mg, Cr, Mo, and Au. This indicates that the Pd and Pt may prefer 2D growth mode while Mg, Cr, Mo, and Au can prefer 3D island growth mode.

In addition, the diffusion barrier energy determines how fast an adatom can join to an existing island before making a new island with other adatoms. Therefore, this is an important factor which affects the metal island density and size. The diffusion barrier was estimated by assuming that the diffusion path between favorable sites would be through the high symmetry directions. Fig. 2 (b) shows the results. A very low diffusion barrier was found for all the metal adatoms except Mo impurity. Thus, we expect large size metal islands to be formed on the phosphorene surface. Comparatively high value of diffusion barrier for Mo could be due to the reduced vertical height of Mo from phosphorene. Our diffusion barriers for Au is in agreement with the previous study [25]. Another important factor is the thermal stability of the metal island on the substrate. The thermal stability can be controlled by the