

# Dielectric Material for Monolayer Black Phosphorus Transistors: A First-Principles Investigation

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**Abstract**—Using advanced parameter-free first-principles calculations, we suggested that corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) is a promising candidate of the dielectric materials for monolayer black-phosphorus (BP). Hydrogen passivated  $\text{Al}_2\text{O}_3$  is preferred to avoid metallization with monolayer BP. Clean interface is found between monolayer BP and H-terminated  $\text{Al}_2\text{O}_3$ . The valence-band offset for these systems is around 0.9eV, which is appropriate to create a reasonable carrier injection barrier. Moreover, orientation effect is found to be of great significance for these systems. Special orientation can generate an indirect band gap for monolayer BP.

**Keywords**—Black phosphorus; dielectric material; first principles calculation

## I. INTRODUCTION

Black phosphorus (BP) is a novel layered material in which individual atomic layers are stacked together by van der Waals interaction. Within each atomic layer, a phosphorus atom is covalently bounded with three neighboring atoms, forming a puckered honeycomb lattice. Such a specific geometry gives rise to attractive physical properties of BP. Recently, multi-layer BP has been extensively studied due to its suitable bandgap and high carrier mobility [1-2]. Experiments have demonstrated feasibility of fabricating BP FETs with high

driving current as well as high on/off ratio [3]. While  $\text{SiO}_2$  was used in the experimental devices, high- $\kappa$  dielectrics such as  $\text{Al}_2\text{O}_3$  or  $\text{HfO}_2$  can achieve better device performance. At present, investigations of the physical properties of high- $\kappa$   $\text{Al}_2\text{O}_3$ /BP interfaces are still lacking. In this work, we investigate the electronic properties of oxide/BP interface for future FET applications by first principles calculation.

By carefully looking into the electronic properties of three experimentally possible monolayer BP/ $\text{Al}_2\text{O}_3$  interfaces, we found that electronic properties of such systems are very sensitive to both chemical configurations and geometric orientations. Inappropriate chemical configurations, such as O-terminated or Al-terminated  $\text{Al}_2\text{O}_3$  surface, can lead to unexpected modification on the band structure of monolayer BP (MBP). H-passivated  $\text{Al}_2\text{O}_3$  appears to be a reasonable candidate that can best preserve the electronic properties of MBP. In addition, for MBP/H-passivated  $\text{Al}_2\text{O}_3$  systems, geometrical orientation is found to be of great importance to the electronic properties.

## II. METHODOLOGY

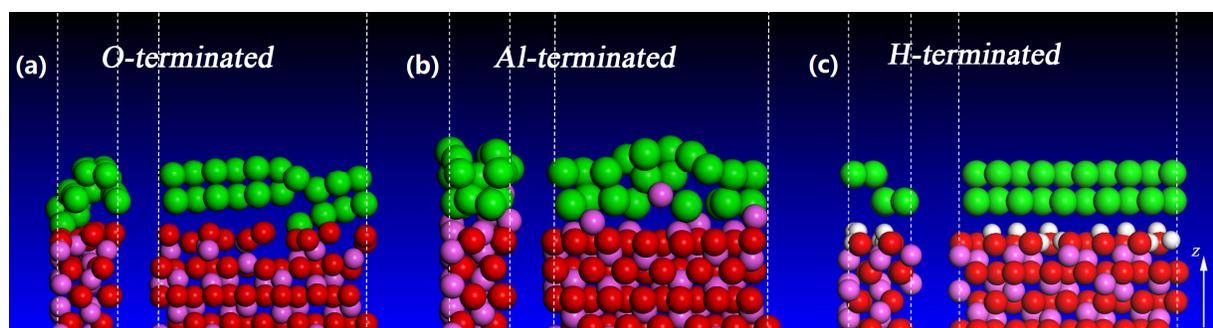


Fig. 1 Atomic structures of relaxed BP- $\text{Al}_2\text{O}_3$  supercells. The green, purple, red and white spheres denote the P, Al, O and H atoms, respectively. (a), (b) and (c) refer to O-terminated, Al-terminated and H-terminated configurations of BP- $\text{Al}_2\text{O}_3$  contacts, respectively. Side views in two different directions are shown.

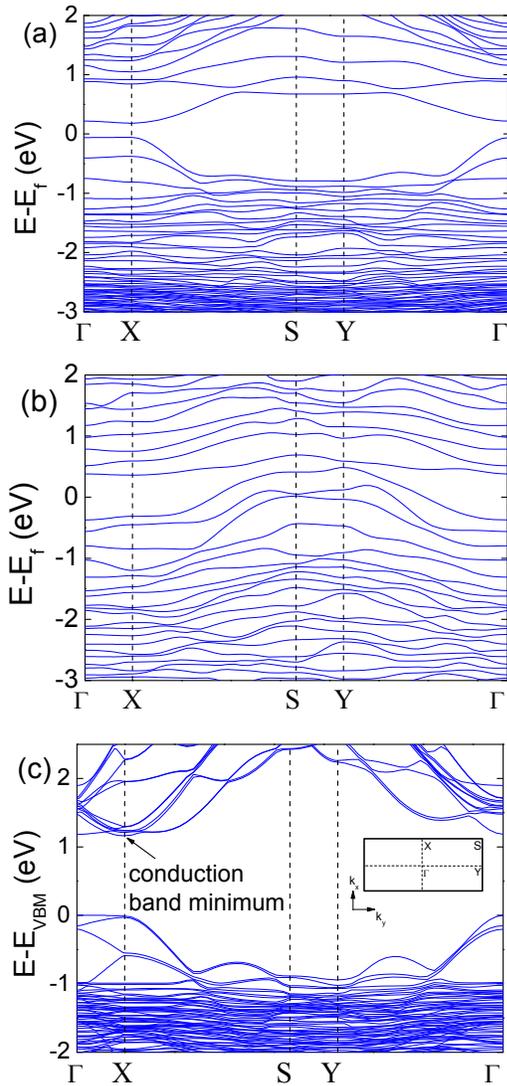


Fig. 2 Band structures of the three configurations: (a) O-terminated, (b) Al-terminated and (c) H-passivated. Band structures are plotted for a rectangular Brillouin zone. The inset in (c) shows the symmetry points across which the band structures are plotted. (a) and (b) are plotted with respect to the Fermi energy while (c) the valence band maximum.

Density functional theory (DFT) calculations are performed for three experimentally possible MBP/oxide interfaces, where the MBP is placed on top of Al-terminated  $\text{Al}_2\text{O}_3$ , O-terminated  $\text{Al}_2\text{O}_3$  or H-passivated  $\text{Al}_2\text{O}_3$  substrate, respectively (see Fig.1). Projected augmented wave (PAW) method is used to describe the atomic cores electrons and Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange correlation functional, as implemented in the Vienna Ab initio simulation package (VASP) package. The van der Waals (vdW) interaction is treated at the PBE-OPTB88 functional [4] level: vdW plays an important role for determining the geometric configurations and binding energies. In order to investigate the MBP/ $\text{Al}_2\text{O}_3$  interface, we consider

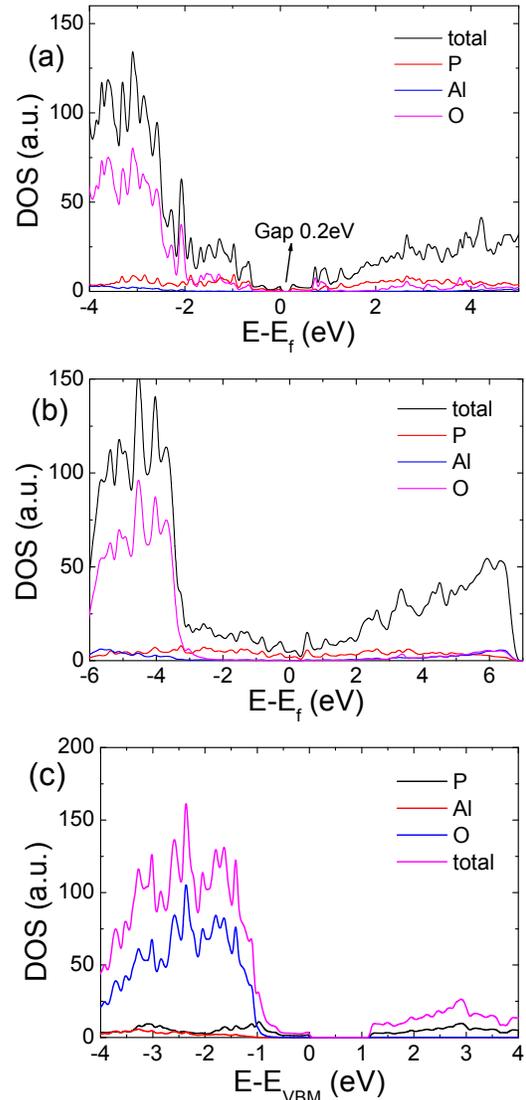


Fig. 3 PDOS of the three configurations: (a) O-terminated, (b) Al-terminated and (c) H-passivated.

the interfaces models consisting of MBP and (0001)  $\text{Al}_2\text{O}_3$  surfaces. The supercell contains 5 BP and 2  $\text{Al}_2\text{O}_3$  surface primitive cells with an acceptable lattice mismatch of  $\sim 3\%$  between them, as shown in Fig.1. We consider three  $\text{Al}_2\text{O}_3$  surfaces, O-terminated, Al-terminated and H-terminated, as shown individually in Fig.1(a), (b) and (c). The  $\text{Al}_2\text{O}_3$  surfaces is modeled by a slab containing six O layers and 12 or 11 Al layers (depending on the specific surfaces investigated) to minimize the quantum size effects. Slab surfaces that does not face BP are passivated by pseudo H atoms and a  $15\text{\AA}$  vacuum is included to isolate the slab from its periodic images. A self-consistent field dipole correction is applied to cancel spurious electric fields induced by periodic boundary condition of the interface model. In our lattice relaxation, P atoms and the top 6 layers of Al and O atoms are allowed to relax while the cell

size is kept fixed. A  $\Gamma$ -centered  $4 \times 14 \times 1$  k-point mesh is used for the relaxation calculations and the force is converged to a tolerance value of  $0.01 \text{ eV}/\text{\AA}$ . For each configuration, lattice relaxation calculations are performed for three random initial configurations to avoid local minimum. A  $6 \times 22 \times 1$  k-point mesh is used for self-consistent field calculations and  $12 \times 42 \times 1$  for density of states (DOS) calculations. The energy is converged to  $10^{-5} \text{ eV}$  for all the calculations.

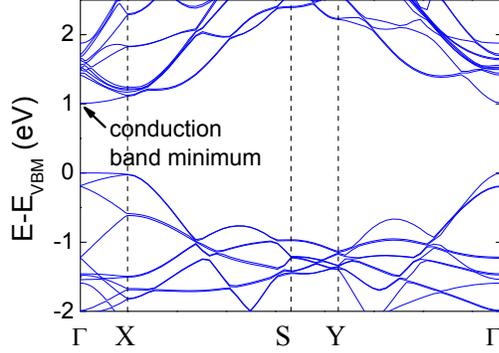


Fig. 4 Band structure of BP without oxide.

### III. RESULTS AND DISCUSSION

Fig.1 shows the relaxed atomic structure of the three systems. For each case, the three random initial configurations relax to the same final configurations. Our calculations show that except for the H-passivated interface where vdW interaction dominates interlayer interaction, MBP on both O- and Al-terminated  $\text{Al}_2\text{O}_3$  encounter strong chemical interaction with the dielectric. O-terminated  $\text{Al}_2\text{O}_3$  tends to form chemical bonds [Fig.3(a), Fig.5(a)] with the BP. Orbitals hybridization between P and O leads to a smaller gap of  $0.2 \text{ eV}$ , which is too small for practical applications in traditional MOSFET. Al-terminated  $\text{Al}_2\text{O}_3$  forms even stronger chemical bonds [Fig.3(b), Fig.5(b)] with the BP which will lead to a metallic contact property and unexpected leakage for BP transistors. Thus in order to preserve BP's electronic property, appropriate passivation on the surface dangling bonds are necessary. We choose hydrogen which is the simplest and the most widely used element for passivation (Fig.1(c)), to passivate the  $\text{Al}_2\text{O}_3$  surface. Band structure (Fig.2(c)) and DOS (Fig.3(c)) show that H-passivated  $\text{Al}_2\text{O}_3$  best preserves the geometry as well as the electronic property (compared with Fig.4). This system exhibits the best dielectric material candidate for BP. Fig.3(c) also shows that the valence-band offset for MBP/ $\text{Al}_2\text{O}_3$  system is around  $0.9 \text{ eV}$ , which is appropriate for creating a reasonable carrier injection barrier. The bounding energies for the three configurations are listed in Table I. Clearly, BP tends to form chemical bonds with O and Al. Interactions between BP and H-passivated  $\text{Al}_2\text{O}_3$  can be treated as van der Waals type, but twice as strong as that of graphene/ $\text{Al}_2\text{O}_3$  [5]. This indicates that BP is more chemically reactive than graphene and special care should be taken when choosing dielectric materials. This conclusion can also be understood by the distance between monolayer BP and  $\text{Al}_2\text{O}_3$ . Our calculations give a distance of

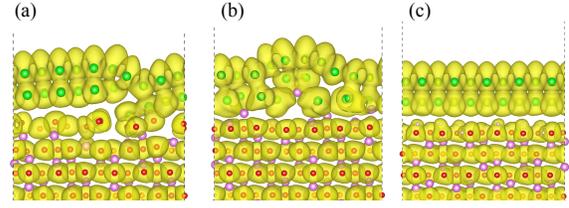


Fig. 5 Electron localization function (ELF) of the three configurations (ELF=0.5): (a) O-terminated, (b) Al-terminated and (c) H-passivated.

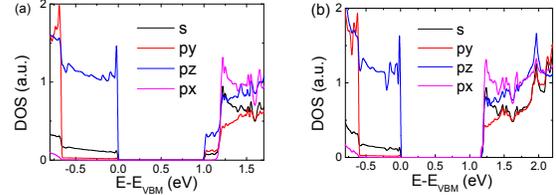


Fig. 6 DOS vs. energy. (a) Partial DOS of monolayer BP w/o oxide. (b) partial DOS of monolayer BP w/ oxide. DOS are projected on P s, px, py and pz orbitals.

$2.23 \text{\AA}$ , which is smaller than typical van der Waals interaction distance ( $\sim 3 \text{\AA}$ ).

We also observe a shift in the conduction band minimum for the H-passivated case (see Fig.2(c)). This should be accounted for as the result of inter- and intra-plane charge transfers. Fig.6(a) shows the partial DOS of MBP without  $\text{Al}_2\text{O}_3$ . We found that  $p_z$  orbital dominates states at the valence maximum and conduction minimum. When attaching BP to the  $\text{Al}_2\text{O}_3$  surface, these  $p_z$  orbitals interact with the  $\text{Al}_2\text{O}_3$  orbitals to form strong hybridization regions and thus increase the band gap. Such effects can be seen clearly by plotting the charge transfer figures. Fig.7(a) and (b) (white curve) shows the intra- and inter-plane charge transfers, respectively. A weak inter-plane charge transfer from the  $\text{Al}_2\text{O}_3$  to the BP is observed (less than  $1 \times 10^{-3} \text{ e}/\text{\AA}$ ). The intra-plane transfer appears to be more prominent (as larger as  $5 \times 10^{-3} \text{ e}/\text{\AA}$ ). Fig.7(c) shows more details on local intra-plane charge transfer. These charge transfers indicate the formation of regions where hybridizations are strong. Finally  $p_z$  orbitals energies get larger and local conduction minimum at X point becomes the conduction band minimum.

Such a shift of conduction band minimum could be detrimental for certain applications and we found it avoidable by properly manipulating the orientation of BP. Fig.8 shows the two orientations of BP: Fig.8(a), the one considered in previous calculations (denoted by config.(a)); Fig.8(b), with the BP rotated by  $\pi$  (denoted by config.(b)). Similar to the above calculation, we randomly choose three different initial positions and find that all these three give the same relaxed position as depicted in Fig.8(b). Fig.8(c) plots the band structure of the config.(b). We find that the conduction band minimum exactly locates at the  $\Gamma$  point. Based on previous discussions, this should be explained as weaker local hybridization compared to the case in Fig.8(a). We find that config.(b) gives a binding energy of  $0.0896 \text{ eV/atom}$ , which is smaller than that of the config.(a). The distance between BP and  $\text{Al}_2\text{O}_3$  is  $2.37 \text{\AA}$ , slightly larger than config.(a). We also plot the intra- and inter-plane charge transfer for config.(b). They

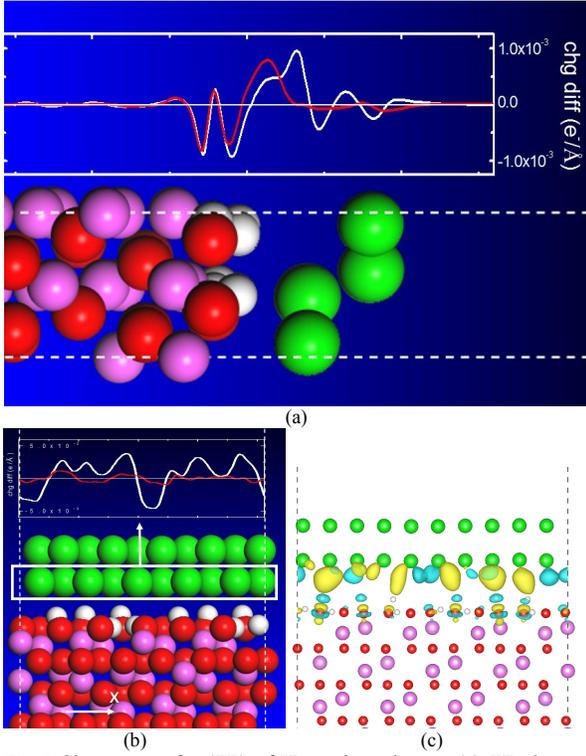


Fig. 7 Charge transfer (TF) of H-passivated case. (a) TF along  $z$  direction. (b) TF in the region specified by white box. TF is plotted along  $x$  direction. (c) The isosurface of the charge difference. The yellow indicates a positive transfer while blue a negative transfer.

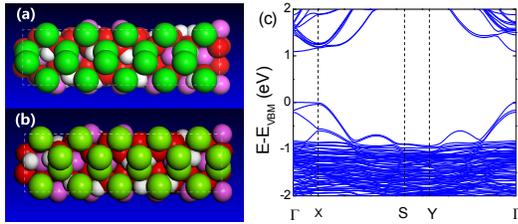


Fig. 8 Two orientations of BP. The Al<sub>2</sub>O<sub>3</sub> are fixed while BP are rotated by  $\pi$ . (a) is the configuration (config.(a)) considered in previous calculation. (b) is the new configuration (config.(b)). (c) plots the band structure of (b).

Table I: binding energies of the three configurations, unit is eV/atom.

O-terminated	0.7414
Al-terminated	1.0454
H-passivated	0.0989

are plotted in red line in Fig.7(a) and (b). Much smaller intra-plane charge transfer are observed, which should be the reason of the preservation of the conduction band minimum.

#### IV. CONCLUSION

Our calculations suggest that the H-passivated Al<sub>2</sub>O<sub>3</sub> to be the best candidate of dielectric material for BP transistors. Al-terminate Al<sub>2</sub>O<sub>3</sub> should always be avoided due to its metallic contact with BP. O-terminated Al<sub>2</sub>O<sub>3</sub> should also be avoided due to the strong interaction and hybridization with O atoms in Al<sub>2</sub>O<sub>3</sub> surface. This interaction breaks BP lattice and reduces the band gap of MBP. H-passivated Al<sub>2</sub>O<sub>3</sub> has a slight modification on BP's band structure to shift the conduction band minimum from the  $\Gamma$  point to the X point. It is believed to be caused by the in-plane charge transfer within BP induced by strong interaction with the Al<sub>2</sub>O<sub>3</sub> surface. Such a shift should be dealt with in optical and electrical applications of BP. Our calculation also suggests that this modification can be avoided by appropriate manipulation of the BP orientation.

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