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

Qing Shi¹, Hong Guo¹
¹ Department of Physics, McGill University, Montréal, Canada
qing.shi2@mail.mcgill.ca

Fei Liu²
² Department of Physics, The University of Hong Kong, Pok Fu Lam, Hong Kong, China
fliu003@gmail.com

Abstract—Using advanced parameter-free first-principles calculations, we suggested that corundum (α-Al₂O₃) is a promising candidate of the dielectric materials for monolayer black-phosphorus (BP). Hydrogen passivated Al₂O₃ is preferred to avoid metallization with monolayer BP. Clean interface is found between monolayer BP and H-terminated Al₂O₃. 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 band gap 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 SiO₂ was used in the experimental devices, high-κ dielectrics such as Al₂O₃ or HfO₂ can achieve better device performance. At present, investigations of the physical properties of high-κ Al₂O₃/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/Al₂O₃ 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 Al₂O₃ surface, can lead to unexpected modification on the band structure of monolayer BP (MBP). H-passivated Al₂O₃ appears to be a reasonable candidate that can best preserve the electronic properties of MBP. In addition, for MBP/H-passivated Al₂O₃ systems, geometrical orientation is found to be of great importance to the electronic properties.

II. METHODOLOGY

Fig. 1 Atomic structures of relaxed BP-Al₂O₃ 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-Al₂O₃ contacts, respectively. Side views in two different directions are shown.
Density functional theory (DFT) calculations are performed for three experimentally possible MBP/oxide interfaces, where the MBP is placed on top of Al-terminated Al\textsubscript{2}O\textsubscript{3}, O-terminated Al\textsubscript{2}O\textsubscript{3} or H-passivated Al\textsubscript{2}O\textsubscript{3} substrate, respectively (see Fig.1). Projected augmented wave (PAW) method is used to describe the atomic core 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/Al\textsubscript{2}O\textsubscript{3} interface, we consider the interfaces models consisting of MBP and (0001) Al\textsubscript{2}O\textsubscript{3} surfaces. The supercell contains 5 BP and 2 Al\textsubscript{2}O\textsubscript{3} surface primitive cells with an acceptable lattice mismatch of \sim3\% between them, as shown in Fig.1. We consider three Al\textsubscript{2}O\textsubscript{3} surfaces, O-terminated, Al-terminated and H-terminated, as shown individually in Fig.1(a), (b) and (c). The Al\textsubscript{2}O\textsubscript{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 15Å 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

![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.](image1)

![Fig. 3 PDOS of the three configurations: (a) O-terminated, (b) Al-terminated and (c) H-passivated.](image2)
size is kept fixed. A Γ-centered 4×14×1 k-point mesh is used for the relaxation calculations and the force is converged to a tolerance value of 0.01eV/Å. For each configuration, lattice relaxation calculations are performed for three random initial configurations to avoid local minimum. A 6×22×1 k-point mesh is used for self-consistent field calculations and 12×42×1 for density of states (DOS) calculations. The energy is converged to 10⁻³ eV for all the calculations.

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 Al₂O₃ encounter strong chemical interaction with the dielectric. O-terminated Al₂O₃ 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 0.2eV, which is too small for practical applications in traditional MOSFET. Al-terminated Al₂O₃ encounters strong chemical interaction with the BP. Orbitals hybridization [Fig.3(b), Fig.5(b)] with the BP 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 Al₂O₃ surface. Band structure (Fig.2(c)) and DOS (Fig.3(c)) show that H-passivated Al₂O₃ 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/Al₂O₃ system is around 0.9eV, 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 Al₂O₃ can be treated as van der Waals type, but twice as strong as that of graphene/Al₂O₃ [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 Al₂O₃. Our calculations give a distance of 2.23Å, which is smaller than typical van der Waals interaction distance (~3Å).

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 Al₂O₃. We found that pₜ orbital dominates states at the valence maximum and conduction minimum. When attaching BP to the Al₂O₃ surface, these pₜ orbitals interact with the Al₂O₃ 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 Al₂O₃ to the BP is observed (less than 1×10⁻³e-/Å). The intra-plane transfer appears to be more prominent (as larger as 5×10⁻³e-/Å), 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, pₜ 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 π (denoted by config.(b)). Similar to the above calculation, we randomly choose three different initial positions and find that 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 Γ 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 0.0896eV/atom, which is smaller than that of the config.(a). The distance between BP and Al₂O₃ is 2.37Å, slightly larger than config.(a). We also plot the intra- and inter-plane charge transfer for config.(b).
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 Al2O3 to be the best candidate of dielectric material for BP transistors. Al-terminate Al2O3 should always be avoided due to its metallic contact with BP. O-terminated Al2O3 should also be avoided due to the strong interaction and hybridization with O atoms in Al2O3 surface. This interaction breaks BP lattice and reduces the band gap of MBP. H-passivated Al2O3 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 Al2O3 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.

ACKNOWLEDGMENT

H.G. thanks NSERC of Canada for financial support. We thank CalculQuebec and Compute-Canada for computation allocation which made this work possible. Discussions with Dr. Wei Ji are gratefully acknowledged.

REFERENCES