



Swansea University
Prifysgol Abertawe



Cronfa - Swansea University Open Access Repository

This is an author produced version of a paper published in :
Microelectronic Engineering

Cronfa URL for this paper:
<http://cronfa.swan.ac.uk/Record/cronfa33643>

Paper:

Guo, Y. & Robertson, J. (2017). Band offsets and metal contacts in monolayer black phosphorus. *Microelectronic Engineering*
<http://dx.doi.org/10.1016/j.mee.2017.05.010>

This article is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Authors are personally responsible for adhering to publisher restrictions or conditions. When uploading content they are required to comply with their publisher agreement and the SHERPA RoMEO database to judge whether or not it is copyright safe to add this version of the paper to this repository.
<http://www.swansea.ac.uk/iss/researchsupport/cronfa-support/>

Accepted Manuscript

Band offsets and metal contacts in monolayer black phosphorus

Yuzheng Guo, John Robertson

PII: S0167-9317(17)30207-1
DOI: doi: [10.1016/j.mee.2017.05.010](https://doi.org/10.1016/j.mee.2017.05.010)
Reference: MEE 10563

To appear in: *Microelectronic Engineering*

Received date: 20 February 2017
Revised date: 7 May 2017
Accepted date: 8 May 2017

Please cite this article as: Yuzheng Guo, John Robertson , Band offsets and metal contacts in monolayer black phosphorus, *Microelectronic Engineering* (2017), doi: [10.1016/j.mee.2017.05.010](https://doi.org/10.1016/j.mee.2017.05.010)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Band Offsets and Metal Contacts in Monolayer Black Phosphorus

Yuzheng Guo^{1*}, and John Robertson²

1 College of Engineering, Swansea University, Swansea, SA1 8EN

2 Engineering Department, Cambridge University, Cambridge, CB2 1PZ, UK

E-mail address of corresponding author: yuzheng.guo@swansea.ac.uk

Abstract: Black phosphorus(b-P) is a new member of 2D materials for field effect transistor(FET) application due to its atomic monolayer structure and high electron/hole mobility. The FET application requires the knowledge of b-P interface with high-k oxide and metal electrodes. In this work, the band offsets for gate insulators such as HfO₂ on black phosphorus (b-P) are calculated using density functional theory(DFT). It is confirmed that HfO₂ can provide good band alignment for both conduction and valence band. The Schottky barrier heights(SBH) are also calculated for the monolayer and bulk using the supercell model, for the perfect interface with no defects in the b-P. A strong p-type Fermi level pinning has been observed due to strong metal-P bonding.

1. Introduction

The 2D materials have received a lot of attention since the discovery of graphene [1]. However, there is no simple way to open a band gap in graphene without significantly lowering its performance. The discovery of first semiconducting 2D material, the transition metal dichalcogenides (TMDs) like MoS₂, opens up the way to fabricate FETs with atomically thin materials [2-4]. However, the carrier mobility in the TMDs is limited by their d-like band edge character [4,5]. The semi-local d electrons contribute much to both the valence band and conduction band edges so that both the electron and hole mobilities are affected in all TMDs. The strong Fermi level pinning and intrinsic defects in TMD also hinders further application in FET [6-9]. Therefore, people are still searching for different semiconducting 2D materials with higher mobility.

Recently the black phosphorus (b-P) based devices have been fabricated [10-25]. B-P has a buckled layer structure with 3-fold covalent bonding within each layer and van der Waals bonding between each layer. Each monolayer has top and bottom P atoms labelled as light and dark atoms in Figure 1(a). Compared to graphene, the lower symmetry gives b-P a band gap. There is a direct band gap in few-layer b-P. The monolayer has a direct band gap of 1.5eV while the bulk band gap is about 0.3eV [10,11]. Its band edges are purely p-type so that the carrier mobility is much higher than that of MoS₂ because p states are less sensitive to disorder and localisation than d states [12-13]. Field effect mobilities as high as 1000-2000 cm²V⁻¹s⁻¹ have been reported by various experimental groups [10-14]. Theoretical predictions of upper limit are up to 10,000 cm² V⁻¹ s⁻¹ [15-18]. In our previous works, we have discussed the intrinsic defects and possible doping strategies of monolayer black phosphorous

and other TMDs [25-28]. However, the interface between 2D materials and electrodes/gate oxide is also critical in FET applications.

In this work, we further examine the band alignment of b-P with other oxides and 2D materials for heterostructure applications such as tunnel FET (TFET) and defect-free interfaces between b-P and several metals. It is found that HfO_2 is a good high-k oxide for both monolayer and bulk b-P. Just like the TMD monolayers, there is strong p-type Fermi level pinning for both monolayer and bulk b-P. The pinning factor is calculated to be 0.11 for monolayer and 0.10 for bulk. This indicates that it is even more difficult to control the Schottky barrier height by electrode in b-P than in TMDs. But it is easy to make p-type Ohmic contact on b-P using common metals.

2. Methods

All simulations in this work are carried out using the plane-wave pseudo potential code CASTEP [29]. The general gradient approximation (GGA) functional suffers from the well-known band gap error and thus cannot give correct band alignment for semiconductors and insulators. Critically, GGA gives a negative band gap for bulk b-P. The screened exchange (SX) hybrid functional is known to be able to correct the band error in both bulk and 2D materials [26, 27]. SX is applied in the calculation of band offsets of various 2D materials. The same pseudopotentials and parameters are used as in our previous works in 2D materials. The band gap of few layer and bulk b-P is shown in Figure 2(b), consistent with experimental values and other simulations with LDA and GGA methods [22,25,30]. The hybrid functional is too resource consuming for large supercell of metal:b-P models. Therefore, the PBE-style GGA is used for geometry relaxation of the Schottky barrier height supercell calculations in this work.

A 6-layer b-P is used to represent bulk b-P during the SBH calculation. The b-P primitive cell is first relaxed to compare the lattice constants with experimental values, as shown in Table 1. The difference is less than 3%. During the fabrication process, the metal gate is usually evaporated or sputtered onto the surface of b-P in vacuum. Thus, the b-P few-layer is first presented and the metal atoms are later added. The metal part could be amorphous especially near the interface. Therefore, the supercell lattice constant is set to that of b-P and the strain is applied purely in metal part. The supercell parameters are summarized in Table 2. The same strategy has been applied to other 2D materials and has given satisfied results compared with experiments [28]. The strain is below 5% in all our models. For reciprocal space integration, we take the Γ point scheme for the defect model due to the large supercell. The cut off energy of 480eV is chosen in all GGA based calculations. For the electrodes, we use the metals Sc, Al, Cr, Ru, Co, Ni, Pd, and Pt, to cover a wide range of work functions for the test of Fermi level pinning. The (0001) surface is used for hexagonal close packed (HCP) metals and (100) surface is used for face centred cubic (FCC) metals when constructing the supercell models. The atomic structures for

HCP and FCC structure metal/b-P used in this work are shown in Figure 2 for Sc and Pt respectively. The work functions of the metals range from 3.5eV (Sc) to 5.65eV (Pt). The experimental work functions are taken from Michaelson [30]. The strong van der Waals interaction has been confirmed in many 2D materials. In our simulation, the TS scheme is used to include van der Waals correction empirically in all the supercell calculation with a metal:b-P interface[31].

The charge neutrality level(CNL) is where the Fermi level would be if a new surface is cleaved from bulk without any structure reconstruction. According to metal induced gap state theory, the contact metal's work function would match the semiconductor's CNL at the interface. It can be calculated from the density of states $N(E)$, as shown in Figure 1 (c), as the energy at which the Greens function is zero,

$$G(E) = \int \frac{N(E') \cdot dE'}{E - E'} = 0 \quad (1)$$

All the DOS enters this equation. This gives a CNL energy of 0.36 eV above the valence band in the monolayer. We also use the CNL to calculate the band offsets of different semiconductors.

The SBHs are extracted as the energy difference from the top of the valence band to the metal Fermi energy. The valence band top is difficult to identify in the supercell density of states or surface band structure. We use instead the theoretical analogue of the Kraut's photoemission method [32] and choose the P 3s core level as a reference level to compare the valence band top in the isolated case to the metal supercell case. The s orbital is 13-15eV below the Fermi level, deep in the valence band.

3. Results

Figure 3 shows the band offsets of monolayer b-P and bulk b-P with HfO_2 and other 2D materials aligned with CNL. The band offsets between both b-P for conduction band and valence band are larger than 1eV [33,34], which is large enough to stop the leakage current for gate oxide. Therefore, HfO_2 is a good candidate as high-k oxide for mono-layer or few-layer b-P [33,34].

Another important strategy for band engineering in 2D materials is by stacking different layers of 2D materials together. The van der Waals gap between different materials can provide an atomically sharp interface if no defect or doping presented in the monolayer. Many important applications require specific band alignment between the monolayers. In figure 2 we also show the band alignment of b-P with other 2D materials including TMD and III-IV monolayers. TFET requires a type III hetrostructure. It is obvious that bulk b-P provide the highest VBM and lowest CBM in all the materials. Thus, it is a good candidate for both valence band and conduction band part in a TFET. Therefore, $\text{WSe}_2/\text{b-P}$ or $\text{b-P}/\text{HfS}_2$ are two potential pairs for TFET. The different symmetry of b-P and other 2D materials could effectively minimize the interaction between the two parts, which could further lower the sub-threshold leakage.

Contact resistance limits device performance for many semiconductors [35]. Hence, we have calculated the band alignments of metals on b-P for the top contact geometry, for the case of ideal contacts (no defects such as phosphorus vacancy or interstitial). The calculated p-type barrier heights are shown in Fig 4 for a wide range of metals plotted against the metal work function. The pinning factor S (slope of this plot) is found to be 0.1 for the bulk and $S=0.11$ for the monolayer. This is strong pinning. The pinning factor for TMDs is usually from 0.2-0.3 [28]. The pinned Fermi level is close to valence band due to the charge neutrality level (also plotted in the figure) being close to valence band. The pinning factor is calculated based on a perfect interface model. Any defects, including vacancy, interstitial, or stacking fault as discussed in previous work [25,37], will further lower the pinning factor.

The strong pinning occurs because the metal atoms become quite close to the P atoms, as shown in Fig 5, and thus form chemical bonds. The distance is smaller than that of MoS₂ interface. It is not van der Waals bonding as it is between metal atoms and carbon as at graphene contacts. This is due to the lone pair of P atom forming bonds to the metal interface. The exposed lone pair can interact with metal actively. The strong pinning is in the absence of defects. If intrinsic defect is presented such as P vacancy, the pinning factor should be even smaller due to the limit of doping [36]. A similar strong bonding occurs for metals on MoS₂ [28]. Thus, we cannot change barrier heights much by varying the metal. Nevertheless, barrier heights are small or zero for p-type doping.

4. Conclusions

In summary, we calculate the band offsets and metal contact for monolayer and bulk b-P. HfO₂ is identified as a good high-k gate oxide for b-P. The band offsets between HfS₂ and WSe₂ with b-P allow possible high speed TFET based on these 2D materials. The metal contact shows a strong p-type Fermi level pinning with a pinning factor about 0.1, even smaller than that of TMDs. However, the p-type Schottky barrier heights are small or zero.

References

1. A K Geim, K S Novoselov, *Nat. Mats.* 6 183 (2007)
2. B Radisavljevic, A Radenovic, J Brivio, V Giacometti, A Kis, *Nature Nano.* 6 147 (2011)
3. G Fiori, F Bonaccorso, G Iannaccone, T Palacios, D Neumaier, A Seabaugh, S K Banerjee, L Colombo, *Nat Nano* 9 768 (2014)
4. M. S. Fuhrer, J. Hone, *Nature Nano* 8, 146 (2013)
5. R Fivaz, E Mooser, *Phys Rev* 163 743 (1967).
6. S. Das, H. Y. Chen, A. V. Penumatcha, J. Appenzeller, *NanoLett* 13 100 (2013)
7. S McDonnell, R Addou, C Buie, R M. Wallace, C L. Hinkle, *ACS Nano* 8, 2880 (2014)
8. S Chuang, C Battaglia, A Azcatl, S McDonnell, J S Kang, X Yin, M Tosun, R Kapadia, H Fang, R M Wallace, A Javey, *Nanoletts* 14 1337 (2014)
9. Y Guo, D Liu, J Robertson, submitted (2014)
10. L Li, Y Yu, Q Ge, X Ou, H Wu, D Feng, X H Chen, Y Zhang, *Nature Nanotech.* 9, 372 (2014)
11. H Liu, A T Neal, Z Zhu, X Xu, D Tomanek, P D Ye, *ACS Nano* 8 4033 (2014);
12. S. Koenig, R. Doganov, H. Schmidt, A. H Castro Neto, B. Ozyilmaz, *Appl. Phys. Lett.* 104, 103106 (2014)
13. J. Qiao, X. Kong, Z.-X. Hu, F. Yang, W. Ji, *Nature Commun*, 5, 4475 (2014)
14. A Morita, *Appl Phys A* 39227 (1986)
15. F. Xia, H. Wang, Y. Jia. *Nature Commun*, 5 4458 (2014)
16. Z. Zhu, D. Tomanek, *Phys. Rev. Lett.*, 112, 176802 (2014)
17. A S. Rodin, A. Carvalho, A.H. Castro Neto, *Phys. Rev. Lett.* 112, 176801 (2014)
18. V. Tran, R. Soklaski, Y. Liang, L. Yang, *Phys. Rev. B.* 89 235319 (2014)
19. R Fei, L Yang, *Nano Lett.* 14, 2884 (2014)
20. P Li, I Appelbaum, *Phys Rev B* 90 115439 (2014)
21. A N Rudenko, M I Katsnelson, *Phys Rev B* 89 201408 (2014)
22. Y.Cai, G. Zhang, Y.W. Zhang, *Sci. Report* 4,6677 (2014)
23. Y Liu, F Xu, Z Zhang, E S Penev, B I Yakobson, *Nanolets* 14 6782 (2014)
24. T Takahashi, H Tokailin, S Suzuki, T Sagawa, I Shirotani, *Phys Rev B* 29 1105 (1984); C Q Han et al, *Phys Rev B* 90 05101 (2014)
25. Y. Guo and J. Robertson, *Sci Rep.* 5 14165 (2015)
26. S. J. Clark and J. Robertson, *Phys Rev B* 82 085208 (2010).
27. D. Liu, Y. Guo, L. Fang, J. Robertson, *Appl. Phys. Lett.* 103 183113 (2013)
28. Y. Guo and J. Robertson *ACS Applied Material & Interface*, 7, 25709 (2015)
29. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, and M. C. Payne, *Kristallogr.* 220, 567 (2005)
30. H. B. Michaelson, *J App Phys* 48 4729 (1977)
31. S. Grimme. *J. Comp. Chem.* 27, 1787 (2006); E R. McNellis, J Meyer, K Reuter *Phys. Rev. B* 80, 205414 (2009)
32. E A Kraut, R W Grant, J R Waldrop, S P Kowalczyk, *Phys Rev Lett* 44 1620 (1980)
33. J. Robertson, *J. Appl. Phys.* 104 124111 (2008)

34. J. Robertson, *J. Vac. Sci. & Technol.* 18 1785 (2000)
35. J. Robertson, O. Sharia, A. Demkov, *Appl. Phys. Lett.*, 91 132912 (2007)
36. J. Robertson, S.J. Clark, *Phys. Rev. B* 83 075205 (2011)
37. S. Lei, H. Wang, L. Huang, Y.-Y. Sun, S. Zhang, *Nano Lett.* 16 1317-1322 (2016)

ACCEPTED MANUSCRIPT

		a	b	c
Bulk	Experiment [30]	10.47	3.31	4.37
	This work	10.794	3.291	4.379
Monolayer	Other work		3.32	4.58
	This work		3.279	4.521

Table 1 Calculated lattice constants for b-P.

	Super cell	strain
Sc	1×5	2%
Al	4×8	5%
Mo	3×1	4%
Cu	4×3	3%
Rh	6×4	4%
Co	3×4	3%
Ni	6×4	4%
Pd	4×6	3%
Ir	5×4	3%
Pt	4×6	2%

Table 2 Lattice mismatch between different metals and b-P.

Figure Captions:

Fig. 1 (a) Atomic structure of monolayer b-P. Light and dark colours are used distinguished between top and bottom layer P atoms. (b) Band gap of few layer b-P as a function of layer number. The experimental data are shown in red circles [11]. (c) The density of states for monolayer b-P. A smearing width of 0.1eV is used when plotting.

Fig. 2 Atomic structure of Pt (a) and Sc (b) on top b-P. A supercell size of 4×6 and 1×5 is used for Pt and Sc respectively. Pt – dark blue. Sc – silver.

Fig. 3 Band alignment of various 2D materials and HfO₂.

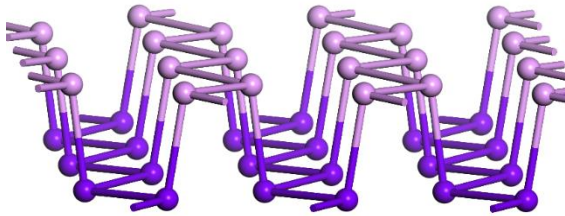
Fig. 4 Fermi level pinning of metal contact on monolayer and bulk b-P. The VBM is set to be 0. CBM is labelled on top of the figure. The slope of the fitted line is extracted as pinning factor. CNL is also labelled for comparison.

Fig. 5 The bond length of P-metal bond formed in the interface.

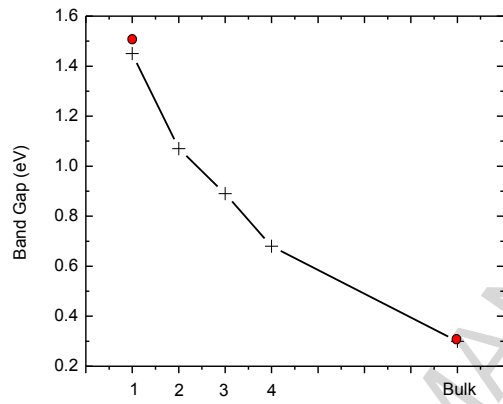
ACCEPTED MANUSCRIPT

Fig. 1

(a)



(b)



(c)

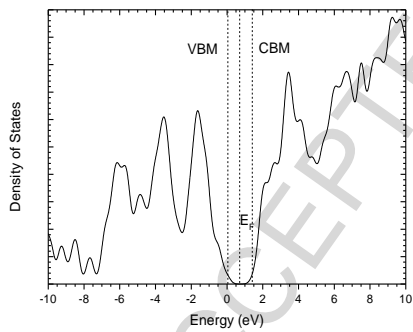
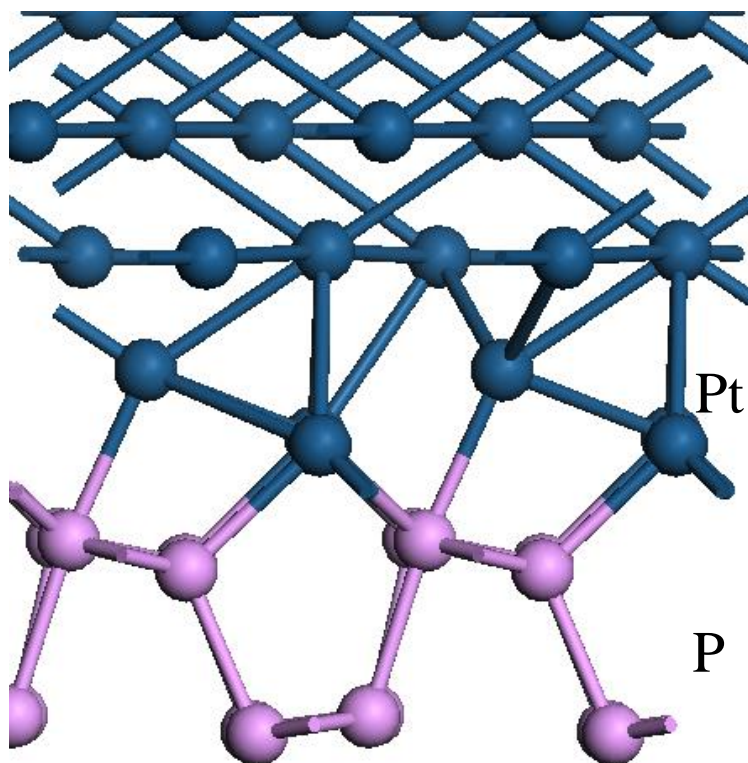


Fig. 2

(a)



(b)

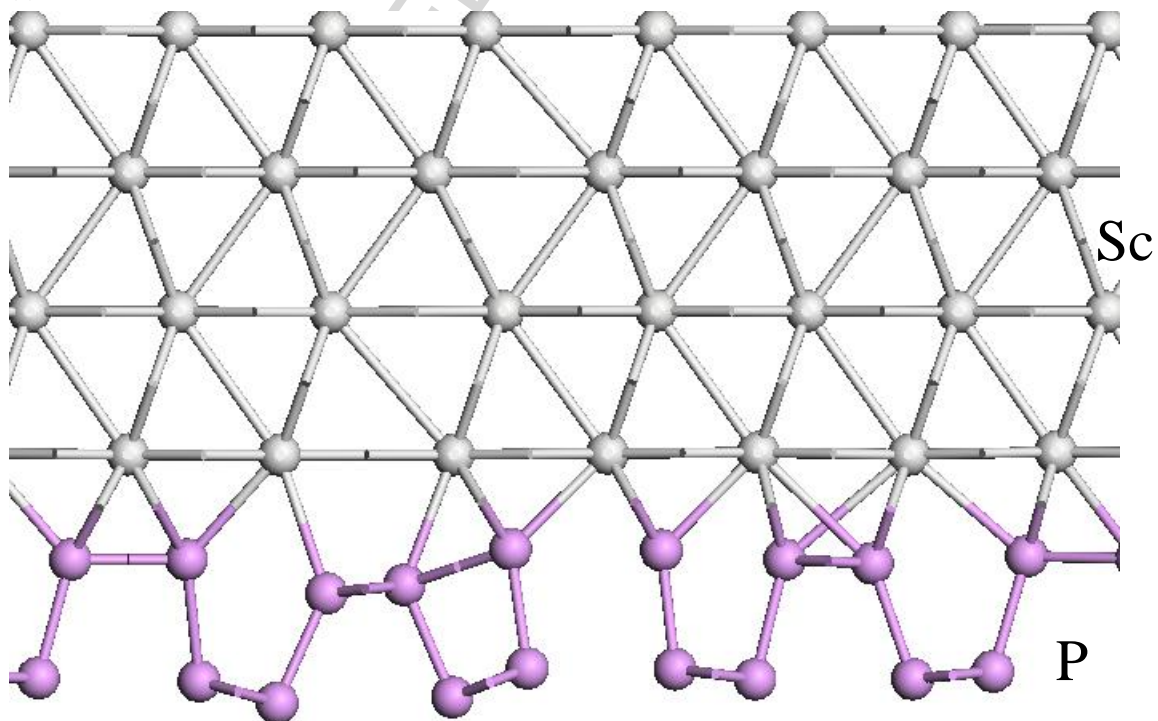


Fig. 3

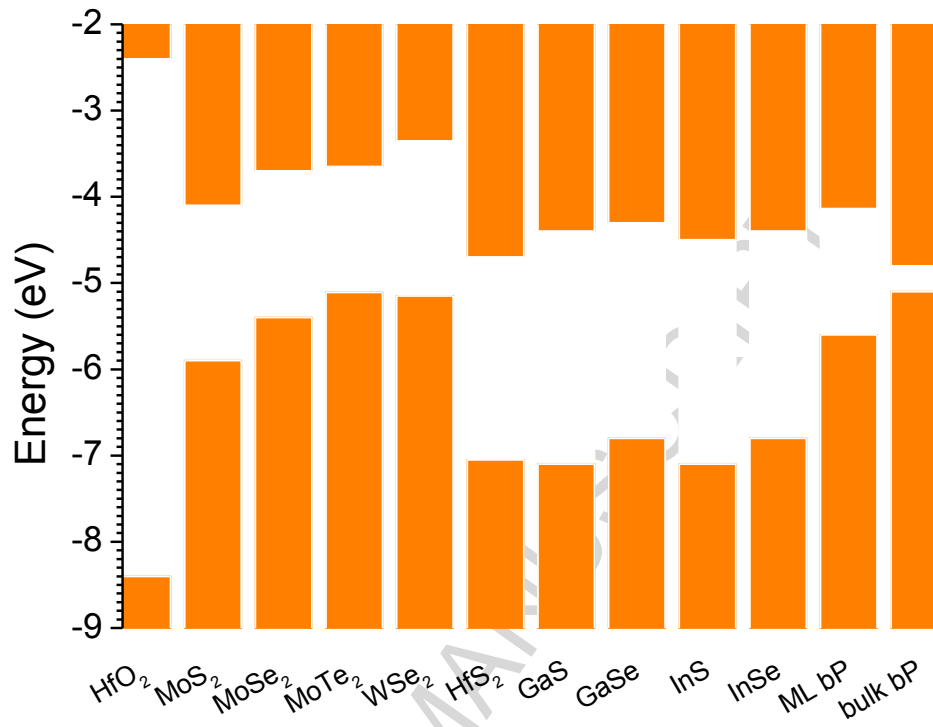


Fig. 4

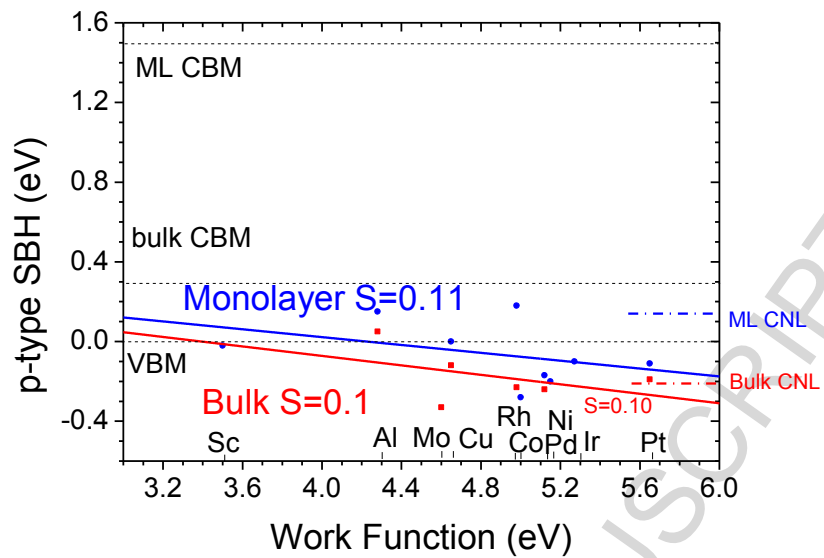
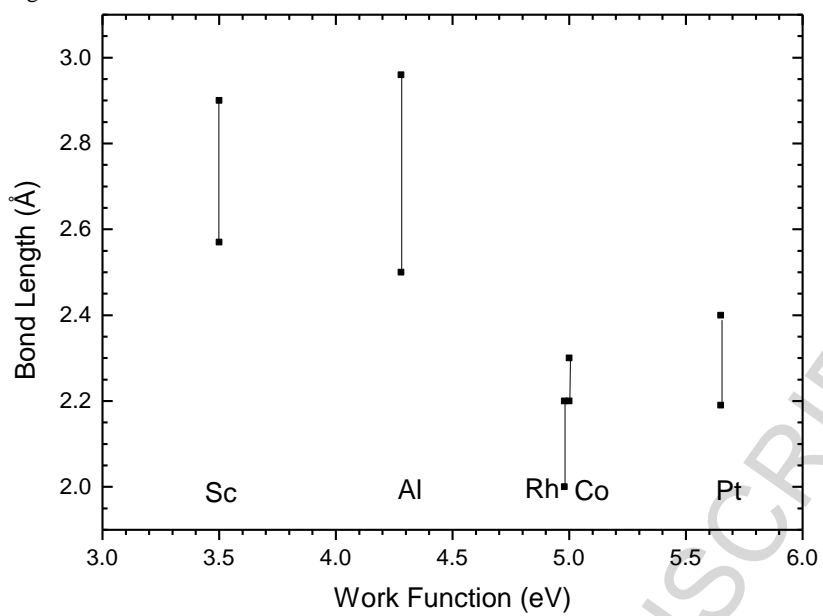
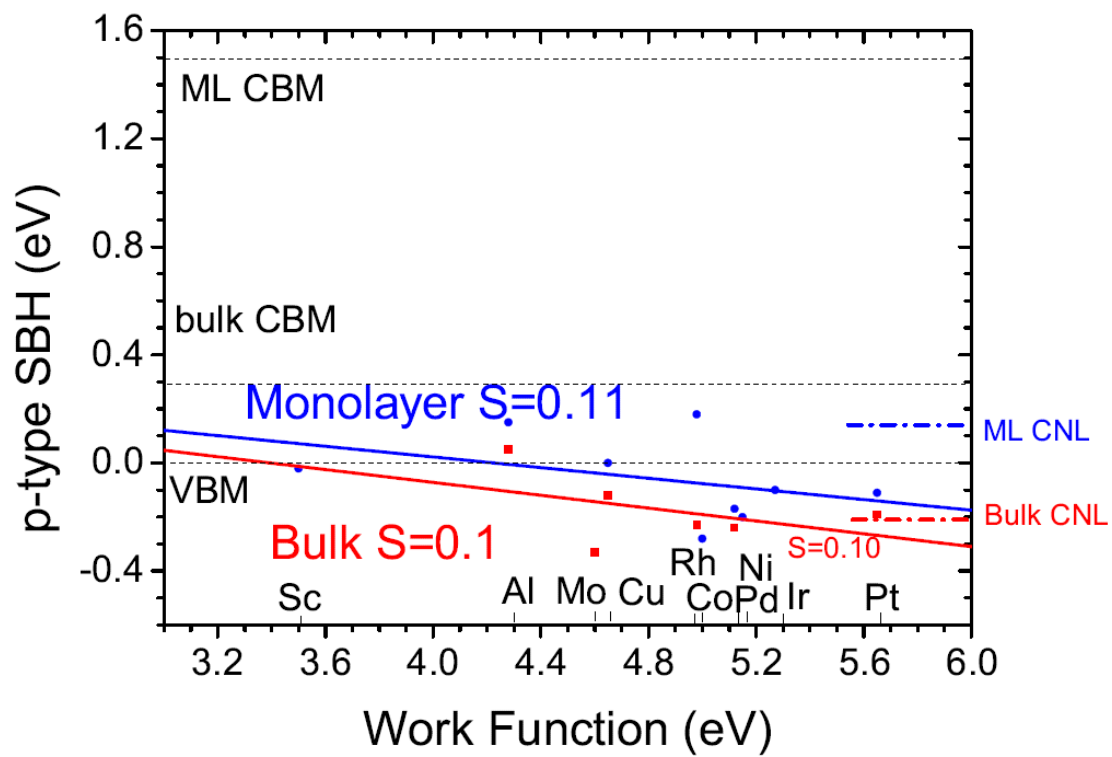


Fig. 5



ACCEPTED MANUSCRIPT



Highlights

- It is confirmed that HfO_2 can provide good band alignment for both conduction and valence band.
- $\text{WSe}_2/\text{b-P}$ could be a good candidate for Tunnel FET application.
- A strong p-type Fermi level pinning has been observed due to stronger metal-P bonding.

ACCEPTED MANUSCRIPT