Microelectronic Engineering 178 (2017) 108–111

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Research paper

Band offsets and metal contacts in monolayer black phosphorus

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ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form 7 May 2017
Accepted 8 May 2017
Available online 10 May 2017

Keywords:
Band offset
Schottky barrier height
Black phosphorous
DFT
Metal contact
TFET

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 HfO_2 on black phosphorus (b-P) are calculated using density functional theory(DFT). It is confirmed that HfO_2 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 MoS_2, 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 Fig. 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 1.5 eV while the bulk band gap is about 0.3 eV [10,11]. Its band edges are purely p-type so that the carrier mobility is much higher than that of MoS_2 because p states are less sensitive to disorder and localisation than d states [12–13]. Field effect mobilities as high as 1000–2000 $cm^2\ V^{-1}\ s^{-1}$ have been reported by various experimental groups [10–14]. Theoretical predictions of upper limit are up to 10,000 $cm^2\ V^{-1}\ s^{-1}$ [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 hetrostructure 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 Fig. 2(b), consistent

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http://dx.doi.org/10.1016/j.mee.2017.05.010
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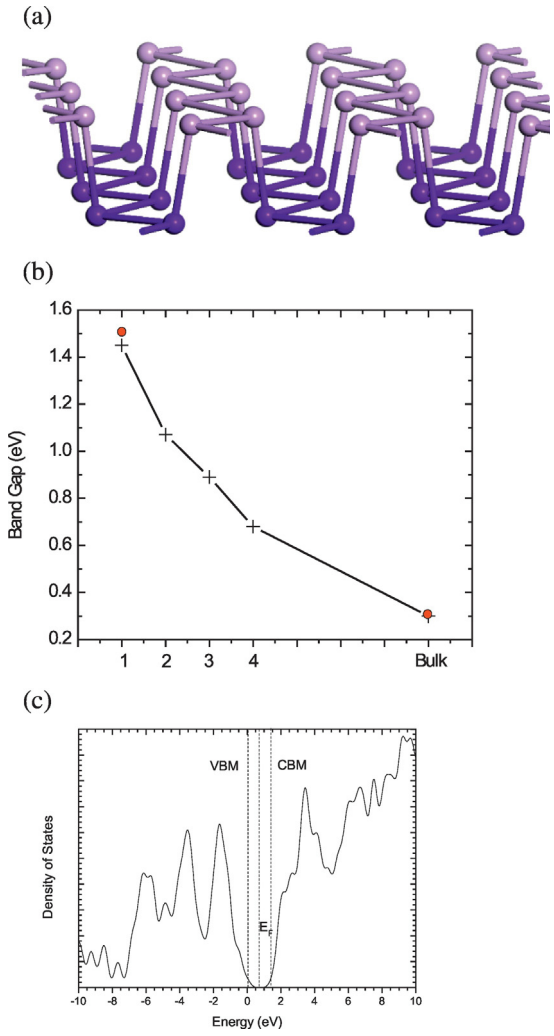

Fig. 1. (a) Atomic structure of monolayer b-P. Light and dark colours are used distinguished between top and bottom layer P atoms. (b) Band gap of few layer b-P as a function of layer number. The experimental data are shown in red circles [11]. (c) The density of states for monolayer b-P. A smearing width of 0.1 eV is used when plotting. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

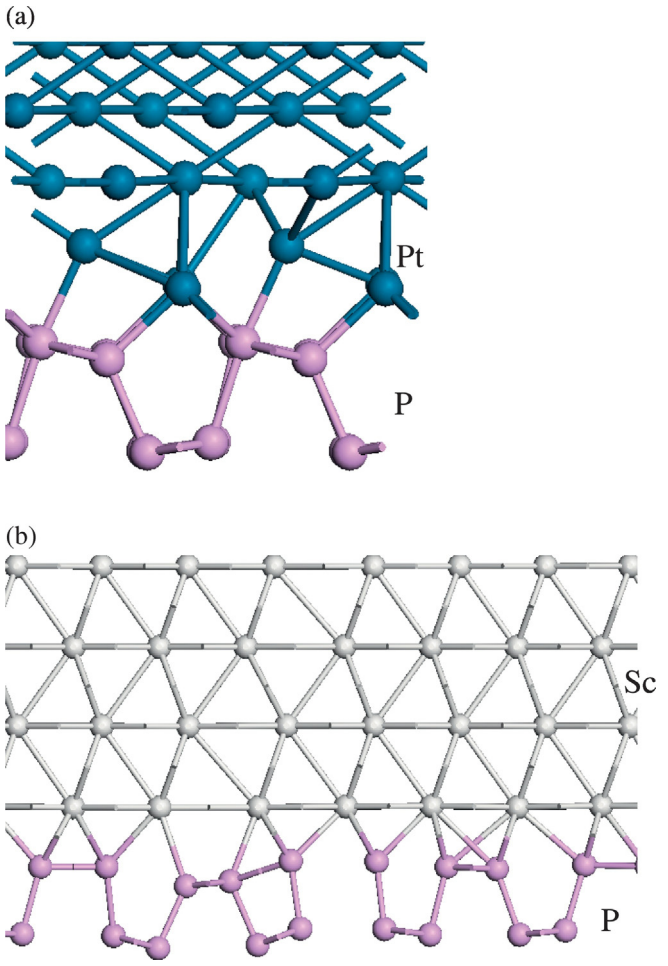

Fig. 2. Atomic structure of Pt (a) and Sc (b) on top b-P. A supercell size of 4×6 and 1×5 is used for Pt and Sc respectively. Pt - dark blue. Sc - silver. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 480 eV 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 Fig. 2 for Sc and Pt respectively. The work functions of the metals range from 3.5 eV (Sc) to 5.65 eV (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.

Table 1
Calculated lattice constants for b-P.

		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