Electronic Supplementary Information for Reduction of Fermi Level Pinning at Cu-BP Interfaces by Atomic Passivation

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S1. Selecting of Passivating Atoms

The candidates of passivating atoms in the present study were carefully chosen as H, N, F, S, and Cl atoms after we have thoroughly investigated the references. The candidates of passivating atoms in the present study were carefully chosen as H, N, F, S, and Cl atoms after we have thoroughly investigated the references. Below we detailed the rationale for selecting those atoms.

a) **H**: the interaction between hydrogen and transition metal is a crucial part of many chemical processes, e.g., hydrogenation, dehydrogenation, and hydrogenolysis, being significant for many chemical industries;

b) **N**: Copper-based catalysts are used in methanol synthesis, the reduction and decomposition of nitrogen oxides, and the oxy-dehydrogenation (i.e., oxidation) of ammonia;[1]

c) **S**: The adsorption of sulfur on metal electrodes is of great interest because of its application in the electrodeposition of well-defined semiconductor thin films, which are promising candidates for optoelectronic devices in nano-scale.[2] Furthermore, the study of chemisorbed sulfur is critical to understanding the self-assembled monolayers with thiol groups, which has been applied in the construction of bio-sensor and electronic devices;[3-6]

d) **Halogens (F, Cl, and Br)**: work-function changes induced by the adsorbates play an important role in many applications, such as a mean to improve the performance of fluorescent lamp cathode surfaces, and in electrochemistry where specifically adsorbed ions directly influence the electrode potential through the induced work-function change. Even though Br is not considered in the present study, it will also be a potential candidate to effective tune the work-function of Cu and weaken to FLP at the interface.

Among the list of passivating atoms, we note that the atomic radius plays a critical role in affecting the interface separation and bond weakening, the synergetic effect of which prescribes the Fermi level unpinning and thus SBH reduction. However, the atomic radius is not necessarily the only factor. Generally speaking, for good candidates of passivating atoms, two results need to be achieved for increase the Fermi-level unpinning effect: (1) weakening the metal substrate interaction with BP and (2) increasing the separation. A large atomic radius will definitely increase the separation. In addition, the passivating atoms ought to be easily adsorbed on the metal surface, thus facilitating the passivation process, and they should not actively interact with BP.

For instance, the O atom would have a larger radius than H and F, and thus if we use the atomic radius as the indicator, it would be more effective in passivation than H and F. However, BP is susceptible to oxidation under ambient environment. According to previous studies, O_2 will firstly metastably physisorb on the BP surface, followed by dissociative adsorption to form two dissociated O atoms.[7] This process is highly exothermic with an energy release of 4 eV per O_2 molecule. The dissociated O atoms will break the P−P bond and become an interstitial atom between two phosphorus atoms, eventually leading to the formation of the phosphorus oxide. Such phenomenon has also been confirmed by our benchmark results, which show that O atoms will actively interact with BP and form phosphorus oxides if the O atoms are passivated on the Cu(111) surface (as shown in Figure S1). The dissociative adsorption of O_2 on the BP surface was confirmed to play a dominant role in modifying the electronic properties of BP when exposure to air. The oxidization of the BP surface causes the wave functions of valence and conduction bands to become spatially discontinuous around the P atoms in the vicinity of the O-P bonds. Consequently it is apparent that O would not be a suitable candidate for passivation.[7]

S2. Mechanism of Fermi Level Unpinning due to Atom Passivation

As mentioned in the main text, the Fermi level unpinning achieved by atom passivation is essentially attributed to the passivation effectively creating an air or van der Waals (vdW) gap between the semiconductor and metal. Such gap acts as a buffer layer to block the penetration of electron waves from metal electrodes, thus supressing MIGS and weakening FLP. From previous studies, introducing a vdW gap between the metal-semiconductor interface (MSI) to tune the Schottky barrier of MSI can also be achieved by other methods.[8-15] For instance, Liu et al. proposed that the Schottky barrier at MSI can be overcome by replacing the traditional 3D metals with 2D metals, which are bounded with 2D semiconductors through vdW interactions.[10] Quhe et al. demonstrated that the 2D metal and 2D metal/bulk metal hybrid contacts can improve the monolayer BP FETs device performance by ab-initio energy band calculations and quantum transport calculations.[15] Besides, the interface properties can also be tuned by air passivation of chalcogen vacancies in 2D semiconductors.[11] Overall, it is advisable that any method that leads to a different structure for the interface could potentially unpinning the Fermi level and change the SBH between the same MSI.[16] However, the atomic passivation directly adjusts the interface structure, and thus would possibly be much more preferred than other techniques for device applications, as the interface would still assures to be “intimate” and benefits from high junction capacitance and efficient, uniform carrier transport.

S3. Case Study of Ni as the Metal Electrode

Based on our results, the interaction between Ni and monolayer BP is much stronger than that for the case of Cu, with the chemical bonding of Ni–P bond observed after the formation of the contact. From the PDOS (see Figure S2 below), a large amount of states occupies the band gap of monolayer BP in contact with bulk Ni, a typical feature of the metallization of BP, which means the SBHs for electron and hole are 0 eV. Since the semiconducting nature of BP is eliminated by contacting with Ni electrode, it will thus impede the applications of BP-based FETs. However, upon atomic passivation, the SBHs for S- and Cl-passivated Ni-BP junctions exhibit smaller p-type SBHs (0.29 eV and 0.15 eV respectively, see Figure S2(b)(c) below), indicative of possible ohmic contact formation and low finite barriers for electron injection.

Those additional results show that atom passivation may serve as a generic method to reduce the FLP for metal electrodes. Nonetheless, it is important to recognize that the effectiveness of a passivating species in Fermi level unpinning may vary as the metal electrode changes. Therefore, it is of importance to establish criteria/guidelines in the identification and selection of candidate passivating atoms, which is certainly worthy of further studies.

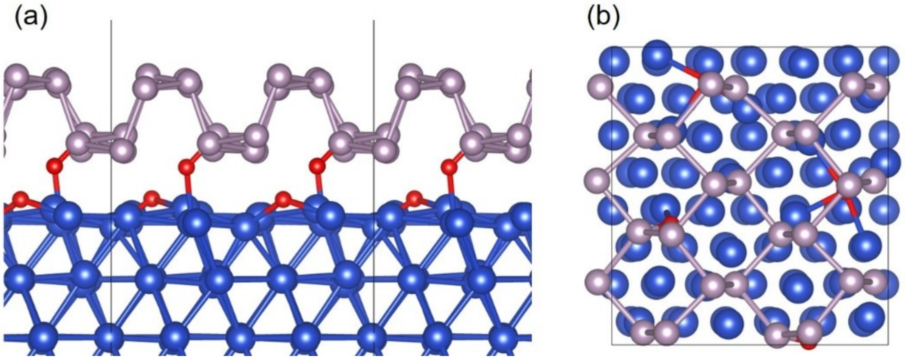

Figure S1. (a) Side and (b) top views of the atomic structure of BP adsorbed on O-passivated Cu(111) surface. Unit cells are indicated by black dashed lines both in (a) and (b). Purple and blue spheres represent P and Cu atoms respectively, while red spheres indicate the passivating O atoms on Cu(111).

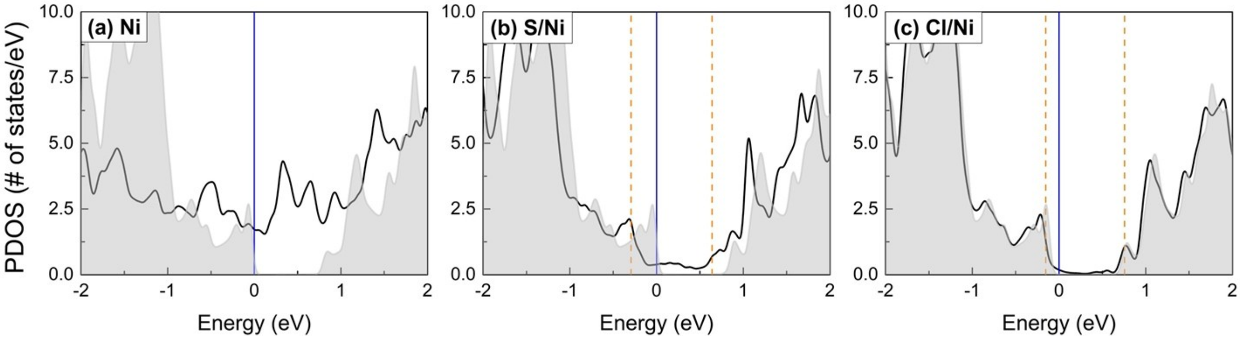

Figure S2. Partial density of states (PDOS) for adsorbed BP on (a) pristine, (b) S-, and (c) Cl-passivated Ni(111) surfaces, with black solid lines representing PDOS and orange dashed lines indicating VBM and CBM of BP at d_{eq} from pristine or atom-passivated Ni(111). The gray shaded regions denote corresponding PDOS plots of BP at about 6Å separation from pristine or atom-passivated Ni(111). Blue solid line indicates the Fermi level (E_F) at d_{eq} and is set to 0 eV.

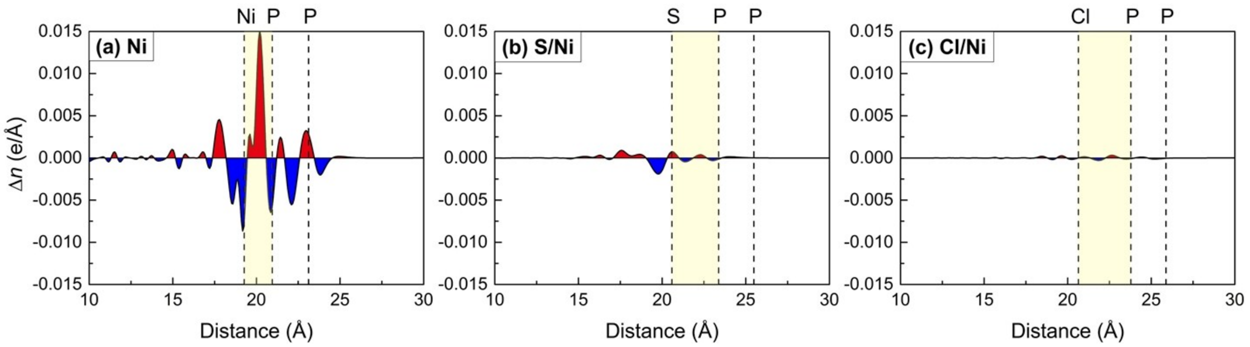

Figure S3. Plane-average charge density difference (Δn) of BP on (a) pristine, (b) S-, and (c) Cl-passivated Ni(111). Red/blue regions indicate the charge accumulation/depletion, respectively. The regions of pristine or atom-passivated Ni-BP interfaces are shaded in yellow.

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