Insights into the Mechanical and Electrical Properties of a Metal–Phosphorene Interface: An Ab Initio Study with a Wide Range of Metals

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ABSTRACT: Finding a metal contact with higher interface adhesion and lower contact resistivity is a major challenge in realizing 2D material-based field-effect transistors. The commonly used metals in the semiconductor industry have different interface chemistry with phosphorene. Although phosphorene FETs have been fabricated with gold, titanium, and palladium contacts, there are other metals with a better interface. In this work, using DFT, a systematic ab initio study of metal–phosphorene interfaces is carried out for a set of 18 potentially suitable metals with different resistivity, electronegativity, and work-function. The interface between these metals and phosphorene is studied to identify factors responsible for mechanical and electrical behavior of the metal contacts. The work of separation is calculated to measure the adhesion strength of the metal contacts, while the density of states, Schottky barrier height, tunnel barrier height, and the mid-interface charge density calculations are performed to analyze the electrical behavior. Both mechanical and electrical performance of the metal contacts are linked to the interface chemistry. Many important observations which deviate from the general trend are reported and explained.

INTRODUCTION

Two-dimensional materials (2DMs) have attracted a significant interest of the scientific community in the last 15 years because of their remarkable electronic, mechanical, and optical properties.1,2 The field effect transistors (FETs) with the 2DMs (such as graphene and transition metal dichalcogenides (TMDCs)) are currently being studied as potential candidates for sub-2 nm CMOS technology nodes.3–5 The graphene has a very low band gap thus restricting its usage for low power circuit applications. On the other hand, the TMDCs (MoS2, WSe2, etc.) have a higher band gap. However, because TMDCs have lower intrinsic mobility, their usability in high-speed circuits is questionable.

Phosphorene, another important 2DM, came into light in early 2014.6–8 Phosphorene has a layer-dependent band gap in the range of 0.3–2.0 eV,9–12 which is ideal for most FET applications. Further, the anisotropic transport properties and high carrier mobility (∼1000 cm²/(V s)) of phosphorene make it a promising candidate for the next-generation FETs.6,13–16

However, one of the major roadblocks in realizing the 2DM-based FETs is high contact resistance (at the interface between bulk metal and 2DMs). The metal contacts enable carrier movement between the circuit back-end and FETs. The poor contact resistance can drastically deteriorate the overall FET performance in spite of excellent material properties of 2DMs. Note that in atomically thin limit of the 2DMs, the contact resistance is mostly governed by properties of the metal–2DM interface. Therefore, it is essential to study this interface and identify factors contributing to the contact resistance in order to achieve technological maturity of 2DM-based FETs.

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Different metal–phosphorene contacts have been studied (both experimentally and theoretically) in the past few years. In experimental studies, the interface properties are often overshadowed by possibilities of imperfect interfaces. The impurities on the interface such as resist residues or some other fabrication anomalies can have a huge impact on the contact resistance. Therefore, it is often not possible to derive a clear relation between the contact resistance and interface properties from the experimental studies.

There are many first-principles-based theoretical studies of the metal–phosphorene contact. However, these studies have used a smaller set of metals. Therefore, cross-referencing to different input conditions used for the simulation of the interface properties of the metal–phosphorene contacts have been studied (both experimentally and theoretically) in the past few years. In experimental studies, the interface properties are often overshadowed by possibilities of imperfect interfaces. The impurities on the interface such as resist residues or some other fabrication anomalies can have a huge impact on the contact resistance. Therefore, it is often not possible to derive a clear relation between the contact resistance and interface properties from the experimental studies.

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Table 1. Size of the Metal Super-Cell (SC) and the Phosphorene SC Used in This Computational Study; Calculated Percentage Lattice Strain along the x and the y Directions (Δx% and Δy%), the Work of Separation (Wsep), the Average Equilibrium Metal–Phosphorene Interfacial Distance (dfe), the Schottky Barrier Height for Injection of Electrons and Holes (ΦBa,n and ΦBp,n), the Tunnel Barrier Height (TBH), and the Mid-Interface Charge Density (p) for Different Metal–Phosphorene Interfaces

| type | s. no. | metal | metal SC | BP SC | Δx% | Δy% | Wsep (J/m²) | dfe (Å) | ΦBa,n (eV) | ΦBp,n (eV) | TBH (eV) | p (e⁻/Å⁻³) |
|------|-------|-------|----------|-------|-----|-----|-------------|---------|------------|------------|---------|-----------|
| 1    | 1.    | Zn(0001) | 5 × 1 4 × 1 | 0.75 0.50 | 0.60 | 2.75 | 0.09 0.83 | 1.74 0.006 |
| 2    | 2.    | Ag(111) | 5 × 2 3 × 3 | 4.10 1.21 | 0.88 | 2.54 | 0.50 0.42 | 1.59 0.126 |
| 3    | 3.    | Al(110) | 4 × 5 5 × 3 | 1.82 3.09 | 1.05 | 2.37 | 0.42 0.50 | 0.74 0.112 |
| 4    | 4.    | Au(110) | 4 × 5 5 × 3 | 1.09 3.85 | 1.15 | 2.32 | 0.97 0.00 | 1.10 0.174 |
| 5    | 5.    | Cu(111) | 4 × 3 3 × 1 | 3.13 4.54 | 1.27 | 2.34 | 0.73 0.19 | 0.83 0.168 |
| 6    | 6.    | Mo(110) | 1 × 1 1 × 1 | 4.54 1.79 | 1.82 | 2.25 | 0.75 0.17 | 0.00 0.285 |
| 7    | 7.    | Pd(111) | 5 × 1 4 × 1 | 4.17 2.81 | 1.86 | 2.13 | 1.16 0.00 | 0.00 0.266 |
| 8    | 8.    | W(110) | 1 × 1 1 × 1 | 4.24 3.46 | 1.91 | 2.11 | 1.02 0.00 | 0.00 0.292 |
| 9    | 9.    | Co(0001) | 9 × 3 5 × 4 | 2.42 1.19 | 2.61 | 1.87 | 0.89 0.03 | 0.00 0.370 |
| 10   | 10.   | Ni(111) | 9 × 3 5 × 4 | 3.23 2.02 | 2.56 | 1.86 | 1.16 0.00 | 0.00 0.374 |
| 11   | 11.   | Pt(111) | 5 × 1 4 × 1 | 5.00 3.67 | 2.45 | 2.12 | 1.36 0.00 | 0.00 0.283 |
| 12   | 12.   | Nb(110) | 1 × 1 1 × 1 | 0.00 0.80 | 2.55 | 1.99 | 0.87 0.05 | 0.00 0.304 |
| 13   | 13.   | Sc(0001) | 1 × 4 1 × 5 | 0.30 0.94 | 2.59 | 2.07 | 0.56 0.36 | 0.00 0.197 |
| 14   | 14.   | Ru(0001) | 5 × 1 4 × 1 | 2.27 1.00 | 2.63 | 2.15 | 1.00 0.00 | 0.00 0.273 |
| 15   | 15.   | Ta(110) | 1 × 1 1 × 1 | 0.30 1.08 | 2.68 | 1.94 | 1.14 0.00 | 0.00 0.288 |
| 16   | 16.   | Ti(0001) | 3 × 2 2 × 3 | 4.43 3.23 | 2.97 | 2.00 | 0.39 0.53 | 0.00 0.233 |
| 17   | 17.   | Cr(110) | 5 × 4 3 × 5 | 3.67 1.26 | 3.18 | 1.93 | 0.72 0.20 | 0.00 0.316 |
| 18   | 18.   | V(110) | 3 × 3 2 × 4 | 2.16 2.95 | 3.25 | 1.93 | 0.72 0.20 | 0.00 0.310 |

This work reports in detail an ab initio study of metal and monolayer phosphorene interfaces. A systematic analysis of mechanical and electrical properties is presented. The interfaces between 18 potentially suitable metals (silver (Ag), aluminum (Al), gold (Au), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), niobium (Nb), nickel (Ni), palladium (Pd), platinum (Pt), ruthenium (Ru), scandium (Sc), tantalum (Ta), titanium (Ti), tungsten (W), vanadium (V), zinc (Zn)) and monolayer phosphorene are studied. The different metal–phosphorene interfaces are analyzed to identify the factors affecting the mechanical and electrical properties of the metal–phosphorene contacts. The work of separation (Wsep) calculation is performed to measure the adhesion strength of the metal contacts. At the same time, the density of states, Schottky barrier height, tunnel barrier height, and the mid-interface charge density calculations are performed to analyze the electrical performance. Both the mechanical and electrical performance of the metal contacts is linked to the interface chemistry, which allows a fair comparison between different metal contacts and also establishes a link between the mechanical and electrical properties.

The paper is organized as follows. In the first two sections, the detailed analysis of mechanical and electrical properties are performed. The simulation methodology along with the input parameters used in the simulation, criteria for metal selection and the interface modeling approach are discussed in sections after Conclusions.

**RESULTS AND DISCUSSION**

**Evaluation of Mechanical Properties.** The mechanical strength of the metal–phosphorene interface is characterized in terms of the work of separation (Wsep). The Wsep represents antipeeling strength or adhesion strength of the surface and is calculated as...
\[ W_{sep} = \frac{(E_M + E_p - E_{MP})}{A} \]

Here, \( E_M \) and \( E_p \) are energies of the metal and phosphorene system, respectively. The \( E_{sep} \) is energy of the combined metal–phosphorene slab system and \( A \) is surface area of the interface.

The calculated values of \( W_{sep} \) for all the metals are summarized in Table 1. The higher value of \( W_{sep} \) indicates higher adhesive strength and vice versa. According to the calculation, \( V \) has the highest adhesive strength, while \( Zn \) has the lowest. This is in agreement with ref 20. A threshold value \( W_{sep} \) of 1.5 J/m² is chosen to categorize the metals into two types, viz., type 1 and type 2. The type 1 metals with \( W_{sep} < 1.5 \) J/m² are classified as the low adhesive metals, and the type 2 metals with \( W_{sep} > 1.5 \) J/m² are classified as the high adhesive metals. Although \( W_{sep} \) of 1.5 J/m² does not divide the calculated range of \( W_{sep} \) equally, this particular value is chosen because it leads to an interesting observation. All the type 1 metals have filled d-orbitals, while the type 2 metals have vacant d-orbitals except \( Pd \). Therefore, it could be inferred that the vacant d-orbitals which lead to the hybridization of the phosphorene’s s- and p-orbitals also result in higher adhesion of the metal with the phosphorene surface. The vacant d-orbital of metals leads to the formation of a stronger bond with phosphorene. It, therefore, serves as an important criterion while selecting the metal to ensure a better mechanical strength. The reason behind \( Pd \) showing higher adhesive strength, in spite of not having a vacant d-orbital, can be attributed to the fact that the 4d- and 5s-orbitals have nearly same energy. The electrons can excite from 4d- to 5s-orbital, creating vacant orbitals for the hybridization and bond formation.

To further confirm the claim, an average interfacial equilibrium distance (\( d_z \)) between the metal and the phosphorene surface is calculated. This is summarized in Table 1. The type 2 metals have lower values of \( d_z \) than the type 1 metals. Also, some of the type 2 metals create a noticeable distortion in the interfacial layer of the phosphorene (see Figure 2). Both of these factors indicate a stronger chemical interaction between the metal–phosphorene and a possible hybridization of the phosphorene surface layers. On the other hand, the type 1 metals show much higher values of \( d_z \), indicating a much weaker or no chemical bonds. Figure 3a plots \( W_{sep} \) as a function of \( d_z \). As shown, the \( W_{sep} \) increases with decreasing \( d_z \), suggesting a stronger correlation between \( W_{sep} \) and the bond strength.

A similar calculation for \( W_{sep} \) is also performed using the PBE+D3 functional. Figure 3b compares the result obtained using the optB86b-vdW and the PBE+D3 functional. An interesting and important observation can be made from Figure 3b. Both the methods individually lead to the conclusion that \( Ta \) forms a better adhesive contact in comparison to \( Nb \) (\( W_{sep} \) of \( Ta \) > \( W_{sep} \) of \( Nb \)). However, if you perform \( W_{sep} \) calculation for \( Nb \) using the PBE+D3 functional and \( W_{sep} \) calculation for \( Ta \) using optB86b-vdW functional, then it can be concluded that \( Nb \) will form a better adhesive contact compared with \( Ta \). This conclusion is misleading. This observation further supports the underlying theme of the paper—that the analysis should be performed using a consistent set of parameters (such as energy threshold, type of smearing used, lattice strain, and the method used for the barrier calculations).

**Evaluation of Electrical Properties.** The ease of carrier flow between 2DM and metal contact is the most important attribute of a good metal contact. However, this depends on a number of parameters. This section investigates different electrical properties of the metal–phosphorene interface, in order to find out the key parameters responsible for charge transfer across the interface and therefore the contact resistance.

**Density of States (DOS) Analysis.** The partial density of states (PDOS) calculation is performed to examine changes in the phosphorene DOS because of the metal contact. It is observed that in the presence of the metal contact, the states are introduced in the band gap of phosphorene because of a change in its atomic structure, which depends on various factors. The increased DOS at/around the Fermi-level (observed for all metal–phosphorene contacts) indicates the metallization of the contacted phosphorene. The chemical interaction of the highly adhesive type 2 metals, which sometimes distorts the phosphorene atomic arrangement, can lead to a significant change in DOS in the band gap. An example of this is shown in Figure 4b. The band gap DOS of the phosphorene is significantly changed compared with the pristine phosphorene, when contacted with type 2 metal Ti.

Further, the lattice parameter of some of the type 2 metals (\( Mo \), \( Nb \), \( W \), and \( Ta \)) is similar to that of phosphorene. This enables an atomic arrangement at the interface as shown in Figure 5. Such an arrangement maximizes the orbital overlap...
and leads to a stronger bond, which further contributes to the formation of energy states within the band gap of phosphorene (see Figure 4d). An increased orbital overlap also facilitates carrier flow across the interface and reduces the contact resistivity. 

For type 1 metals, even though the contacted part of phosphorene is metalized (states in the band gap), the change in the DOS is not significant. It is expected since there is a weak interaction (weaker bonds) between the type-1 metals and phosphorene. For example, consider Figure 4c, where the DOS in the band gap of Au (type 1 metal) contacted phosphorene is not significantly altered with respect to the pristine phosphorene. Apart from this, the vdW force and strain induced on the phosphorene layer could also cause the DOS to change.

Since all the metals lead to metalization of phosphorene, it is hard to segregate metals with respect to their contact resistance solely based on the DOS analysis. Moreover, the observations made in this section are qualitative. A quantitative distinction between metals in terms of their ability to form a low resistive contact could not be established, and further analysis is required.

Figure 6a shows the schematic diagram of a typical 2D-FET. Here, the source and drain contacts form the metal–
The metals leading to a higher conduction band energy ($E_C$) of the pristine phosphorene as mentioned below.

\[ \Phi_{B,p} = I_p - \phi_M \]  

Here, $\phi_M$ is the work-function of the metal. $\chi_p$ and $I_p$ are the electron affinity and the ionization potential of pristine phosphorene, respectively.

To calculate SBH, the vacuum level of the pristine phosphorene is aligned with that of the contacted phosphorene across the interface CD, as shown in Figure 6b. The planar averaged electrostatic potential calculation is performed in order to get the vacuum level. Since the vacuum level is aligned, eqs 2 and 3 can be converted in terms of the work-function of the combined metal–phosphorene system and the conduction band energy ($E_C$)/valence band energy ($E_V$) of the pristine phosphorene as mentioned below.

\[ \Phi_{B,n} = \phi_{MP} - |E_C| \]  

\[ \Phi_{B,p} = |E_V| - \phi_{MP} \]  

Note that the calculation of SBH in eqs 2 and 3 uses the $\phi_M$ which corresponds to the metal work-function without considering any interaction at the surface. Such calculation of SBH follows the traditional Schottky–Mott model. However, the metal interacts with the phosphorene surface and this lead to phenomena such as Fermi-level pinning. To capture this, the work-function of the combined metal–phosphorene system $\phi_{MP}$ is used in eqs 4 and 5. As depicted in Figure 7, the $\phi_{MS}$ differs from the $\phi_M$. Such a method of calculating SBH can be viewed as a modified version of the Schottky–Mott method, which takes care of Fermi-level pinning, something that is neglected in the traditional Schottky–Mott model.

Figure 7 shows the calculated $\phi_M$ for all metal–phosphorene systems considered in this work along with $E_C$, $E_V$ and Fermi-level ($E_F$) of the pristine phosphorene. The calculated SBH for electrons and holes ($\Phi_{B,n}$ and $\Phi_{B,p}$) is shown in Table 1. Note that all negative values of SBH are converted to zero as they represent ohmic contact either for the electron or the hole. The metals leading to a higher $\phi_M$ (Co, Cr, Cu, Nb, Sc, and V) with phosphorene form p-type Schottky contact at the CD interface. Similarly, the metals leading to a lower $\phi_M$ (Al, Ti, and Zn) form n-type Schottky contact at the CD interface. Au, Ni, Pd, Pt, Ru, Ta, and W are found to form ohmic contacts, and none of them show ambipolar characteristics.

The SBH calculated in this work are compared with the other theoretical studies in Table 2. It is interesting to note that the results of this study agree with some of the previous studies and disagree with others. As stated before, this is because the output of the first-principles calculation is highly dependent on the method used for the barrier calculations. For instance, Chanana et al.\textsuperscript{19} considered formation of barrier only for the vertical conduction (interface across AB as shown in Figure 6a) for the carrier injection. On the other hand, Pan et al.\textsuperscript{17} calculated the Schottky barrier for the lateral conduction (interface across CD as shown in Figure 6a) using the Schottky–Mott model. The output also depends on simulation parameters such as exchange correlation functional, k-points mesh size, and threshold energy for the structural-optimization. Therefore, it is beneficial to study different metal–phosphor

\[ \Delta V = (E_F - E_C) - (E_F - E_V) \]

\[ d = \frac{\Delta V}{\sigma} \]

| s. no. | metal | SBH\textsuperscript{17} | SBH\textsuperscript{19} | SBH\textsuperscript{18} | SBH (this work) |
|-------|-------|-----------------|-----------------|-----------------|-----------------|
| 1.    | Al(110)| 0.23/0.68 | NA              | NA              | 0.42/0.50       |
| 2.    | Au(110)| 0.71/0.20 | NA              | 0.89/0.01       | 0.97/0.00       |
| 3.    | Cr(110)| 0.58/0.33 | NA              | NA              | 0.70/0.22       |
| 4.    | Cu(111)| 0.76/0.15 | NA              | NA              | 0.72/0.20       |
| 5.    | Ni(111)| 0.89/0.02 | NA              | 0.18/0.72       | 1.16/0.00       |
| 6.    | Pd(111)| 0.00/0.00 | ohmic           | 0.93/0.00       | 1.16/0.00       |
| 7.    | Ti(0001)| 0.40/0.51 | intermediate    | 0.41/0.49       | 0.39/0.53       |

As discussed, the possibility of a tunnel barrier between metal and phosphorene across the interface AB can affect the charge transfer and eventually the contact resistance. The probability of carrier tunneling across the interface AB depends on height ($\Delta V$) and width ($d$) of the tunnel barrier. $\Delta V$ can be characterized from height of the midgap (region between metal and phosphorene across AB) peak in the planar averaged electrostatic potential plot above
Notably, all type 2 metals have 100% phosphorene contact. However, as explained earlier, the metals Mo, Nb, Ta, and W show a higher adhesive strength, lower SBH at interface CD, and no tunnel barrier at interface AB. Therefore, a combined SBH and TB analysis with a consistent interface AB, they could have a higher contact resistance. The work of separation calculation, which is a measure of the chemical bonding at the interface is basis for the adhesion, the bonding electrons are expected to be found at mid of the interface or slightly shifted toward the more electronegative atom. Note that the bonding strength has a strong correlation with the amount of charge participation in bonding. Therefore, the $\rho$ is expected to be an increasing function of $W_{sep}$. Figure 9a plots $\rho$ as a function of $W_{sep}$. As expected, the $\rho$ increases with $W_{sep}$. Figure 9b provides visualization of $\rho$ for 2 metals, that is, (a) Co (highest value of $\rho$) and (b) Zn (lowest value of $\rho$).

Note that a planar-averaged ($x$–$y$ plane) charge density calculation along the z-direction (perpendicular to the interface) is performed, and $\rho$ is calculated as depicted in Figure 10. The values of $\rho$ for all the 18 metals considered in this work is summarized in Table 1. The metals Sc and Ti show a deviation form the general trend of $\rho$ vs $W_{sep}$. Although there is no clear answer, an interesting observation that can lead to the possible link is shown in Figure 11. Figure 11 plots the value of intrinsic resistivity of the metals.29 Sc and Ti that deviate form the $\rho$-$W_{sep}$ trend are also the metals with highest value of metallic resistivity. Although with this exception as a general trend, the $\rho$ can serve as an indicator of a higher chemical bonding or mechanical strength. Also, the metals with higher $\rho$ is expected to show higher conductivity across the interface AB. However, since the overall conductivities and thus the electrical behaviors depend on both the interfaces (AB and CD), both Schottky and tunneling barrier heights serve as excellent indicator for exploring the "good" metal contacts.

**CONCLUSIONS**

A systematic analysis of the mechanical and electrical properties of the metal–phosphorene contacts was presented. The work of separation calculation, which is a measure of the adhesion strength of the metal contacts, was used to classify the metals into two types: type 1/2 metals have lower/higher adhesion implying a weaker/higher bond with the phosphorene. Using the DOS analysis, it was found that all the metals led to the metallization of the contacted phosphorene. However, the carrier flow from contacts to phosphorene encounter two interfaces and hence both the tunnel barrier height and the Schottky barrier height across these interfaces govern the overall contact resistance. Both these barrier heights...
were calculated, and the results showed that a combined analysis of both is necessary to analyze the electrical behavior of the contacts. Further, the mid-interface charge density calculations were found to be a useful tool to predict the mechanical and electrical properties of the contacts. On the basis of these calculations, it was established that type 1 metals not only have lower adhesion but also have poor electrical performance. The type 2 metals showed a stronger bond and excellent electrical properties. An exception to this observation was also found, where type 2 metals Mo, Nb, Ta, and W showed poor electrical performance because of broken interlayer p–p bonds.

Figure 9. (a) Mid-interface charge density ($\rho$) as a function of work of separation ($W_{sep}$) for different metal–phosphorene interfaces. A positive correlation between $\rho$ and $W_{sep}$ can be clearly seen. (b) Visualization of $\rho$ for Zn-phosphorene and Co-phosphorene interfaces. The Zn-phosphorene interface has the lowest value of $\rho$ and the Co-phosphorene interface has the highest value of $\rho$.

Figure 10. Planar-average charge density along z-direction for (a) Ti-phosphorene, (b) Au-phosphorene, and (c) Nb-phosphorene interfaces. The value of the calculated mid-interface charge density is also mentioned.

Figure 11. Intrinsic resistivity of various metals used in this study. Sc, Ti, and V have higher resistivity compared with others.

## METHODOLOGY

### Computational Methodology.

The Vienna Ab Initio Simulation Package (VASP)\textsuperscript{26,27} is used to perform density functional theory (DFT) calculations under the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) exchange-correlational functional.\textsuperscript{28} The projector-augmented wave (PAW) pseudopotential\textsuperscript{29} and a plane wave basis set with a cut off energy of 400 eV are used for both geometry optimization and electronic structure calculations. Besides, the spin polarized calculation in ferromagnetic configuration is performed for the metals showing ferromagnetic properties (Co and Ni). The threshold force and threshold energy required for the structural optimization are fixed to be less than 0.01 eV/Å and $1 \times 10^{-5}$ eV respectively. The Methfessel–Paxton smearing scheme with sigma value of 0.01 is employed for the energy calculations, since it yields very accurate results for the total energy.\textsuperscript{30} However, for electronic structure calculations such as Fermi-energy, density of states (DOS), and vacuum-level, the tetrahedron smearing with Blochl-correction is used, as it is known to give a good account of the electronic density of states.\textsuperscript{31} The optB86b-vdW\textsuperscript{32} is included for the dispersion correction, crucial for calculation of the geometrical and electrical properties for noncovalent interactions. A vacuum buffer level of at least 12 Å in the direction perpendicular to the metal–BP interface (z-axis) is used to avoid repeated cell interactions of slabs. Note that for some of the metals, more...
than 12 Å vacuum-level is used, which is required to converge the vacuum potential. In contrast, the periodicity along the x- and y-axis is kept unaltered (see Figure 1). A dipole correction along the z-axis is also employed to account for the unsymmetrical slab system. Since, a large number of metal species with varying lattice parameters are used in the current study, utmost care is taken to reduce the interface strain to a minimum.

■ METAL SELECTION AND INTERFACE MODELING
A set of 18 potentially suitable metals is selected for this study. This set has metals with a wide range of resistivity, electronegativity, work function, and lattice mismatch (with respect to phosphorene). To commensurate with the metal supercell, the supercell of phosphorene is constructed by expanding its unit cell in the x and the y directions (see Figure 1). An orthogonal cell of 5 layers of each metal with surface oriented along the z-direction is considered to emulate bulk crystalline properties of the metal. The heterostructure of the metal and phosphorene constructed in this manner is periodic in the x–y plane. A vacuum thickness is provided along the z-direction. The surface of the metal at the interface is chosen such that the lattice strain is minimum. The percentage lattice strain (Δx and Δy in the x and the y-direction respectively) is calculated as Δx(y) = lx(y) − lx(y)/lx(y). Here, lx(y) are the lattice parameters of phosphorene and metals in the x(y) directions, respectively. The lattice strain is maintained to be within 5%. The lattice strain can further be reduced, however, this will require building a larger supercell, which is not computationally feasible for the DFT calculations. Note that the metallic surfaces having the highest atomic densities are preferred over other surfaces. However, for some metals, those surfaces would require a very large supercell for lower values of lattice strain. In those cases, other surfaces are selected which reduce the lattice strain. The information related to metal selection and interface modeling is provided in Table 1.

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**Notes**

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