RESEARCH ARTICLE | JULY 19 2023

First-principles based study of 8-Pmmn borophene and metal interface 📀

Vaishnavi Vishnubhotla 🔟 ; Sanchali Mitra 🔟 ; Santanu Mahapatra 💌 💿

(Check for updates

Journal of Applied Physics 134, 034301 (2023) https://doi.org/10.1063/5.0144328





AIP Advances

Why Publish With Us?



740+ DOWNLOADS average per article







First-principles based study of 8-*Pmmn* borophene and metal interface

Cite as: J. Appl. Phys. **134**, 034301 (2023); doi: 10.1063/5.0144328 Submitted: 29 January 2023 · Accepted: 30 June 2023 · Published Online: 19 July 2023



Vaishnavi Vishnubhotla, 匝 Sanchali Mitra, 匝 and Santanu Mahapatraª) 匝

AFFILIATIONS

Nano-Scale Device Research Laboratory, Department of Electronic Systems Engineering, Indian Institute of Science (IISc) Bangalore, Bangalore 560012, India

^{a)}Author to whom correspondence should be addressed: santanu@iisc.ac.in

ABSTRACT

Borophene, the lightest member of mono-elemental 2D materials family, has attracted much attention due to its intriguing polymorphism. Among many polymorphs, digitally discovered 8-*Pmmn* stands out owing to its unique tilted-Dirac fermions. However, the property of interfaces between 8-*Pmmn* and metal substrates has so far remained unexplored, which has critical importance of its application in any electronic devices. Here, with the help of density functional theory, we show that the unique tilted-Dirac property is completely lost when 8-*Pmmn* borophene is interfaced with common electrode materials such as Au, Ag, and Ti. This is attributed to the high chemical reactivity of borophene as observed from crystal orbital Hamilton population and electron localization function analysis. In an effort to restore the Dirac property, we insert a graphene/hexagonal-boron-nitride (hBN) layer between 8-*Pmmn* and metal, a technique used in recent experiments for other 2D materials. We show that while the insertion of graphene successfully restores the Dirac nature for all three metals, hBN fails to do so while interfacing with Ti. The quantum chemical insights presented in this work may aid in to access the Dirac properties of 8-*Pmmn* in experiments.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0144328

I. INTRODUCTION

Two-dimensional boron, commonly known as borophene, has attracted tremendous attention since its first synthesis in 2015.¹ Borophene is then widely studied for its promising properties such as anisotropic electron structure, high thermal conductance, mechanical compliance, and optical transparency.²⁻⁵ Unlike graphene, in these experimental efforts, 2D networks of boron atoms are found in various polymorphs, which are metallic in nature. Parallel to these experimental investigations, a number of stable phases of boron have been computationally predicted over the years. These phases contain various arrangements of twodimensional layers made of boron as well as clusters and symmetries. In order to increase the stability of these predicted phases, various deformations and vacancies have been proposed, and an inert surface is generally used as a substrate for stability and extended layer growth.⁶ The experimental growth of borophene is initially guided by the investigation of stable 2D boron sheets.⁷ The monolayer of 2D boron was proposed by Wang's group^{10,11} after the discovery of the planar hexagonal B₃₆ cluster. Subsequently, other phases of borophene such as α , β_{12} , δ_6 , and χ_3 have been

studied with a combination of hollow hexagons and triangular lattice of borophene.^{12,13} Borophene sheets with different phases have been grown on Cu,¹⁴ Au,¹⁵ Ag,¹⁶ and Al¹⁷ substrates.

It is important to note that while bulk boron is naturally semiconducting, the computationally predicted borophene phases appear in different varieties, including metallic, semiconducting, and even magnetic.¹⁸⁻²⁰ Among these, the most unique polymorph is the 8-Pmmn Borophene structure, which exhibits tilted Dirac fermions.²¹ The unit cell of 8-*Pmmn* borophene contains eight atoms belonging to the space group *Pmmn*, which is highly anisotropic with two sub-lattices exhibiting ionic features. The orthorhombic 8-Pmmn borophene is one of the energetically stable structures, having ground state energy lower than that of the α -sheet structures and its analogs.²² The ionic nature of this phase of borophene has a significant impact on electronic bandgap, infrared adsorption, and dielectric constants. The possibility of Dirac cones in borophene opens door to novel opportunities in atomic scale engineering and leads to interesting electronic and transport properties such as anisotropic Friedel oscillation, Weiss oscillation in magnetoconductivity, undamped plasmon mode at high energies, oblique Klein

tunneling, and direction-dependent optical conductivity.²²⁻²⁴ By varying the intensity of circularly polarized light, the semi-metallic 8-*Pmmn* borophene phase can be transformed into an insulator and the topology of the band structure deviates from the usual π berry phase opening up possibilities to realize photoinduced hall effect,²⁵ making 8-*Pmmn* borophene a promising candidate for applications in optoelectronic devices. The structure also exhibits a large pseudo-magnetic field and scalar potential under strain, which can be detected through Landau quantization, Faraday effect, and quantum valley hall effect and can be applied to valley-tronics device development.²⁶

Dirac cones are singularities in the spectrum of Hamiltonians with linear dispersion around discrete points.²⁷ In order to make the existence of Dirac cones possible, the Hamiltonian should meet a set of conditions (referred to as von-Neumann Wigner theorem²⁸) for energy degeneracy. Time-space inversion symmetry provides an effective constraint on Hamiltonian to match the number of independent variables to the number of equations. Due to constraints on symmetry and Hamiltonian parameters, Dirac materials are rare in nature. Originally, Dirac cones were first observed and synthesized in graphene's two-dimensional honeycomb lattice.^{29–31} Symmetry properties of this structure lead to gapless points in the band structure where conduction and valence bands meet in a cone shape, which induces electronic excitations called massless Dirac fermions. This leads to fractal quantum hall effects,^{32–34} ballistic charge transport,³⁵ ultrahigh carrier mobility,³ and other interesting properties.^{37,38} Subsequently, Dirac natur Subsequently, Dirac nature was identified in several materials such as silicene, germanene, some kinds of graphyne,^{40,41} and other composite systems.^{21,4}

However, interfacing borophene with metals is a prerequisite for practical device applications. Due to the atomic scale thickness of 2D materials, the metal–2D interface may significantly influence the device's performance. Therefore, understanding borophene–metal interactions are essential for fabricating borophene-based devices. Since the experimental realization of single-layer graphene, several works have been reported on the study of interactions between graphene and different metal surfaces.^{44–50} It was shown that graphene forms physisorption interfaces with some metals (Au, Cu, and Ir) in which the Dirac properties of graphene remains preserved.⁵¹ In contrast, graphene is chemisorbed on some metals (Ni, Co, Ru, Pd, or Ti), resulting in the loss of its Dirac nature.⁵¹ Such studies on graphene–metal interfaces helped facilitate possible ways to control the interface interactions in graphene-based devices. However, the interfacial properties of metal–borophene still remain elusive.

In this work, we use first principles-based simulations to understand the geometrical and electronic properties of 8-*Pmmn* borophene contacted with some metals (Au, Ag, and Ti) and 2D materials (graphene, hBN, and MoS₂). We found that borophene is physisorbed on the 2D materials; hence, its Dirac nature remains preserved. However, unlike graphene, borophene forms chemisorbed interfaces with all three metals, disrupting Dirac nature. From crystal orbital Hamilton population (COHP) and electron localization function (ELF) studies, we found that 8-*Pmmn* borophene is more reactive than graphene, resulting in strong chemical reactions with the metal surfaces. Such chemical interactions between metal and borophene layers can be shielded by inserting single-layer graphene or hBN, leading to the restoration of Dirac nature.

II. COMPUTATIONAL METHODS

The initial guess geometries of the interfaces were created using the interface builder module of QuantumATK.^{52,53} To build the metal-borophene heterostructures, six layers of <111> cleaved surfaces of Au, Ag, and <0001> cleaved surface of Ti were used. To create an interface of borophene with metals and other 2D materials, the nonstrained supercells of the two surfaces were first created. Then, the borophene supercell was rotated to align the Bravais lattice vectors of the two surfaces and, finally, strain was applied on borophene to match the aligned supercells. The supercell size should be increased to reduce the strain. In experiments, when one material is deposited onto a substrate, by default, it aligns in the direction containing least strain with the substrate. As the experimental structures consist of thousands of atoms, the strain between the interfaces is usually below 0.5%. However, due to the huge computational cost, it is difficult to achieve the experimental strain. In this work, the applied strain was maintained near 2% so that there is no significant alternation of electronic properties and also the number of atoms remains below 200, which is feasible for further computations. To build buffer-inserted heterostructures, the interfaces between metal and buffer layers were first created and the borophene structure was then interfaced with the formed buffer (graphene/hBN)-metal surfaces. All the details regarding the interface building, including the supercell size, surface rotation angle, applied strain, and total number of atoms are given in Table S1 in the supplementary material. A vacuum layer of 20 Å was added to eliminate interaction between two periodic replicas. Ground state geometries of the formed heterostructures were then obtained by minimizing their energies using density functional theory (DFT). DFT calculations were performed using the projected augmented wave method⁵⁴ implemented in Vienna *Ab initio* Simulation Package (VASP).^{55,56} Generalized gradient approximation with Perdew-Burke-Ernzerhof⁵⁷ functional and van der Waals correction proposed by the Grimme DFT-D3 method with Becke-Johnson damping⁵⁸ have been used. Geometric relaxations were performed at the gamma point, and for electronic density of states calculations, $\frac{60}{a} \times \frac{60}{b} \times 1$ k-mesh is used, where a, b, and c are lattice dimensions. A cut-off energy of 520 eV was used. The Gaussian smearing method with a smearing width of 0.05 eV was used. As self-convergence criteria, the energy difference in successive iterations was set to 10^{-6} eV. The geometry was optimized until the force on every atom fell below 0.05 eV/Å. Dipole correction was applied to eliminate the pseudo-interaction of dipole moments due to the periodicity in the z-direction. During geometry relaxations, the atoms in the three layers of metal toward the borophene or buffer layer were allowed to change positions, whereas the three metal layers toward the vacuum side were fixed. For the structural visualization and charge isosurface plot, VESTA is used.⁶

III. RESULTS AND DISCUSSIONS

A. 8-Pmmn borophene vs graphene

The crystal structure of 8-*Pmmn* borophene contains two sublattices with four boron atoms each. These sublattices comprise two types of non-equivalent boron atoms within the orthorhombic unit

cell referred to as ridge and inner atoms.⁶ The two sublattices could contain different physical and chemical properties as indicated by their local environment. The top view and side view images of the structure are shown in Fig. 1(a) with different coloration for two sublattices. The lattice parameters are mentioned in the figure caption. From previous studies,⁶ we know that there is a charge transfer from inner to ridge atoms making 8-Pmmn borophene a single-element-based 2D material that, being covalent, exhibits ionic nature. The inner atoms of 8-Pmmn borophene form an underlying hexagonal structure, which is topologically equivalent to uniaxially strained graphene, characterized by the π berry phase. It has been further reported that these inner atoms in the buckled geometry, which form the hexagonal network, directly contribute to the Dirac cones in the band structure. The orbital contributions to the band structure of 8-Pmmn pristine borophene are shown in Fig. S1 in the supplementary material, and it can be seen that s and p orbitals are completely hybridized. The ionic bonding between inner and ridge atoms forms anisotropic triangular lattice and induces out-of-plane buckling.^{25,61} The coupling and buckling between two sublattices and the vacancy give rise to the energetic and structural stability as well as tilted anisotropic Dirac cones.

As graphene is a well-known and originally identified Dirac material with several potential applications, we compare the properties of 8-*Pmmn* borophene with graphene in terms of COHP⁶² and ELF.⁶³ COHP analysis partitions the band structure energy in terms of orbital-pair contributions based on the tight binding approach into bonding, non-bonding, and anti-bonding contributions. The interaction between two orbitals is described by the corresponding



FIG. 1. (a) Top and side views of $3 \times 3 \times 1$ supercell of 8-*Pmmn* borophene. The lattice parameters are a = 3.26 Å, b = 4.52 Å, and h = 2.19 Å. The inner and ridge atoms are denoted by blue and green atoms, respectively. (b) Crystal orbital Hamilton population (COHP) analysis and (c) electron localization function (ELF) plot for graphene and 8-*Pmmn* borophene.

Hamiltonian matrix element. The product of this term with the density of states gives bonding strength as the product lowers, indicating bonding, or raises, indicating anti-bonding energy. Bonding and anti-bonding interactions are represented by negative and positive values of the COHP, while the non-bonding interactions are indicated by zero values of the COHP. In order to perform the chemical bonding analysis, the Hamilton and overlap matrix elements have to be reconstructed using auxiliary atomic orbitals. This information is projected from plane waves using projected COHP analysis.⁶⁴ This pCOHP technique is implemented in the Local Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) program.⁶⁵ The projected COHP analysis shown in Fig. 1(b) is plotted with Fermi level as the reference $(E_F = 0 \text{ eV})$. It can be seen that there are more anti-bonding states near the Fermi level for borophene compared to graphene, which indicates weaker bonds in borophene. This makes borophene more reactive than graphene considering the COHP as a metric for comparison.

ELF plots for graphene and borophene are shown in Fig. 1(c). ELF is an intuitive tool that allows for visualization of lone pairs and bonding pairs that are usually localized in certain regions of the molecule. It gives an insight into chemical bonding based on the topological analysis of local quantum mechanical functions related to the Pauli exclusion principle.⁶⁶ ELF can have several maxima. The positions of these maxima are called acceptors. These acceptor positions indicate where the electrons are localized. The value of ELF lies between 0 and 1. ELF = 1 indicates perfect localization, and ELF = 0.5 indicates homogeneous free electron gas. It can be observed from Fig. 1(c) that graphene has two peaks at 0.724; however, borophene has a peak at 0.68. The lower value of the electron localization peak indicates that borophene is more reactive compared to graphene, corroborating with the results of the COHP.

B. Metal-borophene interface

To evaluate the electronic properties of 8-*Pmmn* borophenemetal systems, borophene is interfaced with three metals Au, Ag, and Ti that are most commonly used as electrode materials. Due to



FIG. 2. Top and side view images of crystal structures of interfaces of 8-Pmmn borophene with metals (Au, Ag, and Ti), graphene, hexagonal boron nitride (hBN), and MoS₂.

TABLE I. Interlayer properties of 8-*Pmmn* borophene–metal (Au, Ag, and Ti); borophene–2D materials (graphene/hBN/MoS₂); borophene–graphene–metal (Au/Ag/Ti) and borophene–hBN–metal heterostructures. d_1 , d_2 , and d_3 are the average vertical distances between metal (/2D materials)–borophene (Fig. 2), metal–graphene(/hBN) (Fig. 4), and graphene(/hBN)–borophene (Fig. 4), respectively. E_b is the average binding energy calculated using Eqs. (1)–(3).

| | B interface | | C-B interface | | | hBN-B interface | | |
|------------------|------------------------------|------------|------------------------------|-----------|------------|------------------------------|-----------|------------|
| | <i>d</i> ₁ (Å) | E_b (eV) | <i>d</i> ₂ (Å) | d3 (Å) | E_b (eV) | <i>d</i> ₂ (Å) | d3 (Å) | E_b (eV) |
| Au | 2.29 | -0.76 | 3.23 | 3.18 | -0.34 | 3.12 | 3.06 | -0.34 |
| Ag | 2.2 | -0.63 | 3.18 | 3.29 | -0.34 | 3.16 | 3.18 | -0.35 |
| Ti | 2.11 | -2.8 | 2.07 | 3.19 | -1.34 | 2.11 | 2.68 | -1.57 |
| С | 3.29 | -0.114 | | | | | | |
| hBN | 3.28 | -0.105 | | | | | | |
| MoS ₂ | 3.08 | -0.14 | | | | | | |

partially filled d-orbitals, Ti is more reactive compared to Au and Ag. Most of the 2D materials are usually physiosorbed on Au and Ag, while chemisorbed on Ti. The relaxed geometries of the metalborophene interfaces are shown in Fig. 2. The structure of

borophene slightly distorts while interfacing with Au and Ag. However, for Ti, there is a strong distortion in the borophene structure. The average vertical distance (d_1) between the top layers of borophene and the bottom layers of metals and binding energies are listed in Table I. The average interlayer distances are comparable with the sum of covalent radii of the metal and borophene atoms, implying the formation of chemical bonds between them. The average binding energy is defined as follows:

$$E_b^{B-M} = [E_{B-M} - E_B - E_M]/N,$$
 (1)

where E_{B-M} , E_B , and E_M denote the total energies of borophenemetal systems, pure boron, and pure metal surfaces, respectively. N is the number of atoms in the top layer of borophene in direct contact with metal atoms. Table I shows that among the metal-borophene interfaces, the binding energy for Ti is the most negative and the interlayer distance is the shortest for Ti, making it the most reactive to borophene. The projected band structures of borophene on the three metal interfaces are depicted in Fig. 3. The corresponding Brillouin zones and projected density of states for borophene are shown in Fig. S2 in the supplementary material. The Dirac nature of borophene is entirely destroyed on all



FIG. 3. Projected band structure of borophene interfaced with metal (Au, Ag, and Ti), graphene, hBN, and MoS₂. The Fermi level is at 0 eV. Energy is plotted with respect to k_A . k_B and k_C values are 0 for interfaces with Au, Ag, Ti, and graphene. k_B = 0.375, k_C = 0 for borophene–hBN interface and k_B = 0.292, k_C = 0 for borophene–MoS₂ interface.

ARTICLE

| 000000 | 000000 | 000000 |
|---------------------|----------------------|---|
| 000000 | 000000 | 000000 |
| 000000 | 000000 | 000000 |
| 000000 Au | 000000 ^{Ay} | 000000 Ti |
| 000000 | 000000 | 000000 |
| 000000 | 000000 | 000000 |
| ၜၹၹၹၴႍၹႍႍႍႍ | o co co co co co | 000000 C |
| SEC SER B | ,5-2,5-2 B | , 5 2, 5 2 B |
| 0000 | 000000 | 0000 |
| 0 0 0 0 | 000000 | $\circ \circ \circ \circ$ |
| 0000 | oooooo Ag | о о о _{ті} |
| o o o Au | 000000 | o o o o '' |
| 0 0 0 0 | 000000 | \bigcirc \bigcirc \bigcirc \bigcirc |
| 0000 | 000000 | 9090 |
| 00000000 hBN | ംംംംംം hBN | 00000000000 hBN |
| | - | 8-0-0-8 0-0 8 P |

FIG. 4. Top and side view images of crystal structures of 8-Pmmn borophenegraphene-metal (Au/Ag/Ti) and 8-Pmmn borophene-hBN-metal (Au/Ag/Ti) interfaces. three metals implying the chemisorption of borophene on all the metal surfaces. However, it was reported that graphene's Dirac nature is preserved on Au and Ag due to physisorption. This difference can be explained by the higher chemical reactivity of borophene obtained from COHP and ELF analysis.

C. Interface with 2D materials

We further extended the study to evaluate borophene's geometrical and electronic properties with commonly used 2D materials such as graphene, hBN, and MoS₂. The relaxed geometries of these interfaces are shown in Fig. 2. Unlike metal–borophene interfaces, no such structural deformations are observed in the borophene layer in 2D heterostructures. The interlayer distances (d_1) between borophene and other 2D materials are 3.0–3.5 Å (Table I), which are much higher than borophene–metal distances. The binding energies are also significantly lower compared to metal– borophene interfaces. These large interlayer distances, structural uniformity, and lower binding energies indicate the van der Waals interaction between borophene and graphene (/hBN/MoS₂), resulting in physisorption.

Projected band analysis shows that borophene's Dirac nature is preserved on the surfaces of all three 2D materials (Fig. 3). While calculating the band structures, we found that in some cases, the



FIG. 5. Projected band structure of borophene for 8-*Pmmn* borophene–graphene–metal (Au/Ag/Ti) and 8-*Pmmn* borophene–hBN–metal (Au/Ag/Ti) structures. The Fermi level is at 0 eV. Energy is plotted with respect to k_A . k_B = 0.125, k_C = 0 for Au–hBN–borophene structure and k_B =0, k_C = 0 for all other structures.

Dirac points of borophene did not appear along the k-paths containing high symmetry points. Therefore, first, we have calculated the projected density of states to check the presence of the Dirac point in borophene and find out the k-paths containing Dirac points. The projected energy bands are then evaluated along the k-path. For hBN and MoS₂-based heterostructures, the Dirac points appear along the path joining the k-points having fractional coordinates $(-0.2,0.375,0) \rightarrow (0.5,0.375,0)$ and $(0,0.292,0) \rightarrow (0.25,0.292,0)$. Along these paths, the coordinates of k-points along k_B and k_C directions remain the same. Therefore, the band structures are plotted with respect to one direction of the Brillouin zone (k_A), whereas the other two directions (k_B and k_C) have constant coordinates in each case. The corresponding Brillouin zones and projected density of states for borophene are shown in Fig. S3 in the supplementary material.

D. Buffer layer insertion

Due to the physisorption of borophene on the graphene and hBN surfaces, sandwiching a graphene or hBN layer between the metal and borophene may screen the strong chemical interactions and restore the semi-metallic nature of borophene. Graphene and hBN have already been used as buffer layers in metal-2D semiconductor interfaces due to their atomic thickness, easy deposition, and van der Waals interactions with most 2D materials.⁶ Several theoretical and experimental studies demonstrated the reduction in the Schottky barrier heights and Fermi-level depinning in graphene-inserted MoS2-metal interfaces.⁷⁰⁻⁷² Recently, graphene and hBN insertion in the metal interfaces of emerging semiconducting 2D materials other than MoS_2 have also been explored.^{73,74} It was reported that graphene and hBN could prevent the metallization of the metal-contacted 2D semiconductors and create vertical Schottky barriers whose heights can be varied by changing the metal electrodes. Inspired by these studies, we have attempted to determine the consequence of graphene and hBN insertion between borophene and the three metal (Au, Ag, and Ti) surfaces.

The relaxed geometries of these interfaces are shown in Fig. 4. No structural deformation is observed in the borophene layer for all the three-graphene inserted heterostructures. The interlayer distances between the graphene and borophene layers for these heterostructures are comparable to van der Waals distances implying weak chemical interactions between these two layers. In the case of the Ti-graphene-borophene structure, the interlayer distance between Ti and graphene is much lower and the binding energy is more negative compared to the corresponding graphene-inserted Au and Ag based heterostructures (Table I). The binding energies are evaluated as follows:

$$E_b^{B-C-M} = [E_{B-C-M} - E_B - E_C - E_M]/N,$$
(2)

$$E_{b}^{B-hBN-M} = [E_{B-hBN-M} - E_{B} - E_{hBN} - E_{M}]/N,$$
(3)

where E_{B-C-M} , $E_{B-hBN-M}$, E_B , E_C , and E_M denote the total energies of borophene–graphene–metal systems, borophene–hBN–metal systems, pure boron, pure graphene, and pure metal surfaces, respectively. N is the number of atoms in the top layer of borophene in direct contact with graphene or hBN atoms. Due to the high chemical reactivity of Ti, graphene is chemisorbed on Ti while physisorbed on Au and Ag. However, the chemisorption of graphene does not significantly impact the geometry and electronic properties of borophene. Projected bands (Fig. 5) show that for all three graphene inserted heterostructures, the Dirac nature of the 8-*Pmmn* borophene is preserved, indicating that graphene can successfully shield the chemical reaction between the metal and borophene. Due to the loss of symmetry, while making the interface, we observed multiple Dirac-like points along the BZ (Fig. 5). However, it is difficult to identify the exact Dirac point



FIG. 6. Top and side views of structures showing charge density difference for metal (Au/Ag/Ti)–borophene, metal (Au/Ag/Ti)–graphene–borophene, and metal (Au/Ag/Ti)–hBN–borophene structures. The blue regions represent the electron depletion, and yellow regions represent the electron accumulation. The isosurface values for Au, Ag, and Ti structures are 0.09, 0.065, and 0.05, respectively.

corresponding to the pristine 8-*Pmmn* phase borophene. The Dirac points, however, are shifted with respect to the Fermi level. Even if the strong chemical reactions of borophene and metal are screened by graphene, some charge transfers are between borophene and graphene layers, resulting in the shifting of Dirac points. As graphene is chemisorbed on Ti, the Dirac property of graphene is lost, and

graphene is completely metalized. The projected band structures of graphene for these three metals (Au/Ag/Ti)–graphene–borophene structures are given in Fig. S4 in the supplementary material.

Now, we use hexagonal boron nitride (hBN) as a buffer layer between the metal-borophene interface to analyze how borophene's Dirac behavior is affected. These crystal structures are shown in



FIG. 7. Average effective potential vs z-axis position for (a) borophene–Ag interface and (b) borophene–graphene–Ag interface. Effective tunnel barrier height is calculated as $\varphi_{TB} = V_{gap} - E_{Fermi}$. (c) Tunnel barrier heights for different interfaces. The black squares represent φ_{TB} in borophene–metal (Au/Ag/Ti) structures. The blue circles, red triangles, and green rhombuses represent φ_{TB} in borophene–graphene–metal, borophene–hBN–metal, and borophene–2D material (graphene/hBN/MoS₂) structures, respectively.

19 July 2023 12:41:40

Fig. 4. Table I shows that the interlayer distances between metalhBN and hBN-borophene layers are between 3.0 and 3.5 Å in the case of Au and Ag. The large interlayer distances and structural uniformity (Fig. 4) indicate van der Waals interactions between Au/Ag-hBN and hBN-borophene. Interlayer distances and binding energies suggest that, like graphene, hBN is chemisorbed on Ti. However, unlike graphene, the chemisorption of hBN results in a strong chemical interaction with borophene. Figure 4 shows that the borophene structure is distorted in the Ti-hBN-borophene heterostructure. The interlayer distance between hBN and the borophene layer is also reduced to 2.68 Å, much lower than the van der Waals distance. Interestingly, the Ti-hBN and borophene interface results in boron (hBN)-boron (borophene) bonding. The projected band structures (Fig. 5) show that the Dirac nature of borophene is preserved in the case of Au-hBN-borophene and Ag-hBN-borophene heterostructures. However, multiple Dirac-like points are observed for these structures similar to the graphene-inserted heterostructures explained earlier (Fig. 5). For Ti-hBN-borophene, the Dirac point is lost and borophene becomes completely metalized. The density of states plots projected on borophene and the corresponding Brillouin zones for metal (Au/Ag/Ti)-grapheneborophene and metal (Au/Ag/Ti)-hBN-borophene structures are shown in Figs. S5 and S6 in the supplementary material.

E. Charge transfer analysis

The chemical reactions across the interfaces are further evaluated by the charge transfer analysis. The isosurface plots of the charge density in metal-borophene, metal-graphene-borophene, and metal-hBN-borophene heterostructures are shown in Fig. 6. Isosurface values are kept constant for each metal, which are mentioned in the figure caption. When borophene is directly contacted with metals, significant charge transfer takes place between the two layers, resulting in the loss of the Dirac nature of borophene. However, when the buffer layer is inserted, the charge transfers across the interfaces reduce significantly. In Au- and Ag-based heterostructures, only minor charge transfer takes place between the layers. As a result, borophene Dirac is preserved. However, due to minor charge transfer between borophene and the buffer material, borophene is lightly doped, resulting in the shifting of Dirac with respect to the Fermi level. In Ti-based heterostructures, significant charge transfer occurs between Ti and buffer layers (graphene/hBN). However, the charge transfer between hBN and borophene is more substantial compared to that of graphene and borophene, corroborating the loss of Dirac in the Ti-hBN-borophene structure.

F. Tunnel barrier analysis

We further investigated the electrostatic potentials at metalborophene and metal-graphene(/hBN)-borophene interfaces to evaluate the tunneling barrier [Figs. 7(a) and 7(b)]. The tunnel barrier is described by its height and width. Barrier height (ΔV) is calculated as the difference between the average gap potential (V_{gap}) and Fermi level (E_{Fermi}) as shown in Figs. 7(a) and 7(b). The width of the barrier (w_B) is defined as the full width at half maximum of ΔV . The calculated tunnel barrier heights of the structures are shown in Fig. 7(c). The strong chemical reaction results in very low barrier heights and widths for

| table II. | Carrier | tunneling | probabilities | from | metal, | metal-graphene | (/hBN), | and |
|------------|---------|-------------------------|---------------|------|--------|----------------|---------|-----|
| graphene (| /hBN/Mo | S ₂) to bor | ophene. | | | | | |

| Interface | $\Delta V (\text{eV})$ | w_B (Å) | T_B (%) |
|-----------------------------|------------------------|-----------|-----------|
| Au-borophene | 1.144 | 0.781 | 42.51 |
| Ag-borophene | 0.708 | 0.664 | 56.43 |
| Ti–borophene | 0.000 | 0.000 | 100.00 |
| Au-graphene-borophene | 4.084 | 1.640 | 3.36 |
| Ag–graphene–borophene | 3.930 | 1.720 | 3.05 |
| Ti-graphene-borophene | 3.812 | 1.374 | 6.41 |
| Au-hBN-borophene | 3.895 | 1.608 | 3.88 |
| Ag-hBN-borophene | 3.763 | 1.685 | 3.52 |
| Ti-hBN-borophene | 2.645 | 0.789 | 26.88 |
| Graphene-borophene | 4.373 | 1.480 | 4.20 |
| hBN–borophene | 4.580 | 1.440 | 4.26 |
| MoS ₂ -borophene | 4.400 | 1.398 | 4.96 |

metal-borophene interfaces. The insertion of the buffer layer between metal and borophene increases the barrier height, indicating reduced chemical bonding strength. Among the metals, Ti has less barrier height and width than Au and Ag for both direct and buffer-layer inserted interfaces with borophene, making it the most reactive among the metals chosen. The barrier heights for borophene-hBN-metal interfaces are slightly lower than those for borophene-graphene-metal interfaces [Fig. 7(c)], indicating that the hBN buffer layer is more reactive to borophene than graphene. The carrier tunneling probabilities $(T_B)^{75,76}$ from metal $\frac{10}{5}$ and metal-graphene (/hBN) to borophene are estimated using a square potential barrier model as

where m is the free electron mass and \hbar is the reduced Planck constant. The values of T_B for different interfaces are listed in Table II. The tunneling probability is directly related to the contact resistance.^{77,78} A higher efficiency carrier injection leads to lower contact resistance. The strong chemical bonding between Ti and borophene leads to inject electrons from metal to borophene freely, resulting in 100% tunneling efficiency and, hence, ultra-low contact resistance. As the chemical bonding becomes weak, the tunneling probability reduces. For metal-graphene (/hBN)-borophene and 2D (graphene/hBN/MoS₂)-borophene interfaces, the tunneling efficiencies are significantly low compared to pure metal-borophene interfaces. We started this study by inserting a buffer layer between the metal and borophene to preserve the Dirac nature of borophene. However, this comes at the cost of increasing the tunneling barrier, reducing the carrier injection efficiency and, subsequently, contact resistivity of the interface.

IV. CONCLUSIONS

In this work, we have used DFT calculations to evaluate the geometric and electronic properties of the 8-*Pmmn* borophene

interfaced with metals (Au, Ag, and Ti) and some 2D materials (graphene, hBN, and MoS₂). The Dirac nature of borophene is preserved on these 2D materials as they are physisorbed on 8-Pmmn borophene. However, borophene is chemisorbed on all three metals, resulting in the loss of semi-metallic behavior. Inserting 2D buffer layers (graphene/hBN) shields chemical interactions between borophene-metal and restores the Dirac nature 8-Pmmn borophene in the case of Au and Ag. In the case of Ti-graphene-borophene, titanium is chemisorbed on graphene, destroying its Dirac nature. However, graphene successfully shields the chemical interaction between Ti and borophene, restoring borophene's Dirac nature. When hBN is used as a buffer layer between Ti and 8-Pmmn borophene, hBN reacts with borophene, resulting in boron-boron bonds, and the Dirac nature of borophene is completely lost. This work can form a basis for further research into the combination of metals and buffer layers that affect the Dirac nature of 8-Pmmn borophene, inspiring investigation into other innovative properties of 2D monolayer boron, which can be used in the design of systems in fields varying from optics, electromagnetics, and valleytronics, among others.

SUPPLEMENTARY MATERIAL

See the supplementary material for interface formation details, projected density of states, projected band structures of 8-*Pmmn* borophene, and corresponding Brillouin zones for metal–borophene, metal–graphene–borophene, and metal–hBN–borophene heterostructures. Band structures projected on graphene for metal– graphene–borophene heterostructures.

ACKNOWLEDGMENTS

The authors acknowledge the Supercomputer Education and Research Center (SERC), Indian Institute of Science (IISc), Bangalore, for CPU- and GPU-based computations. The computational charges were aided by the Mathematical Research Impact Centric Support (MATRICS) scheme of Science and Engineering Research Board (SERB), Government of India, under Grant No. MTR/2019/000047.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Vaishnavi Vishnubhotla: Data curation (lead); Formal analysis (equal); Investigation (lead); Methodology (lead); Validation (equal); Visualization (equal); Writing – original draft (equal). Sanchali Mitra: Formal analysis (equal); Validation (equal); Visualization (equal); Writing – original draft (equal). Santanu Mahapatra: Conceptualization (lead); Funding acquisition (lead); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material and available from the corresponding author upon reasonable request.

REFERENCES

¹A. J. Mannix, X. F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, N. P. Guisinger, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, and M. C. Hersam, "Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs," *Science* **350**(6267), 1513–1516 (2015).

²A. J. Mannix, Z. Zhang, N. P. Guisinger, B. I. Yakobson, and M. C. Hersam, "Borophene as a prototype for synthetic 2D materials development," Nat. Nanotechnol. 13(6), 444–450 (2018).

³Z. Zhang, E. S. Penev, and B. I. Yakobson, "Two-dimensional boron: Structures, properties and applications," Chem. Soc. Rev. **46**(22), 6746–6763 (2017).

⁴Y. Huang, S. N. Shirodkar, and B. I. Yakobson, "Two-dimensional boron polymorphs for visible range plasmonics: A first-principles exploration," J. Am. Chem. Soc. **139**(47), 17181–17185 (2017).

⁵S. Gupta, S. N. Shirodkar, A. Kutana, and B. I. Yakobson, "In pursuit of 2D materials for maximum optical response," ACS Nano 12(11), 10880–10889 (2018).

⁶A. Lopez-Bezanilla and P. B. Littlewood, "Electronic properties of 8–Pmmn borophene," Phys. Rev. B **93**(24), 241405 (2016).

⁷I. Boustani, "Systematic *ab initio* investigation of bare boron clusters: Determination of the geometry and electronic structures of B n (n = 2-14)," Phys. Rev. B **55**(24), 16426 (1997).

⁸H. Tang and S. Ismail-Beigi, "Novel precursors for boron nanotubes: The competition of two-center and three-center bonding in boron sheets," Phys. Rev. Lett. **99**(11), 115501 (2007).

9Y. Liu, E. S. Penev, and B. I. Yakobson, "Probing the synthesis of twodimensional boron by first-principles computations," Angew. Chem. Int. Ed. 52(11), 3156-3159 (2013).

¹⁰Z. A. Piazza, H. S. Hu, W. L. Li, Y. F. Zhao, J. Li, and L. S. Wang, "Planar hexagonal B36 as a potential basis for extended single-atom layer boron sheets," Nat. Commun. 5(1), 1–6 (2014).

¹¹W. L. Li, X. Chen, T. Jian, T. T. Chen, J. Li, and L. S. Wang, "From planar boron clusters to borophenes and metalloborophenes," Nat. Rev. Chem. 1, 0071 (2017).

¹²E. S. Penev, S. Bhowmick, A. Sadrzadeh, and B. I. Yakobson, "Polymorphism of two-dimensional boron," Nano Lett. **12**(5), 2441–2445 (2012).

¹³X. Wu, J. Dai, Y. Zhao, Z. Zhuo, J. Yang, and X. C. Zeng, "Two-dimensional boron monolayer sheets," ACS Nano 6(8), 7443–7453 (2012).

¹⁴R. Wu, I. K. Drozdov, S. Eltinge, P. Zahl, S. Ismail-Beigi, I. Božović, and A. Gozar, "Large-area single-crystal sheets of borophene on Cu (111) surfaces," Nat. Nanotechnol. 14(1), 44–49 (2019).

¹⁵B. Kiraly, X. Liu, L. Wang, Z. Zhang, A. J. Mannix, B. L. Fisher, B. I. Yakobson, M. C. Hersam, and N. P. Guisinger, "Borophene synthesis on Au (111)," ACS Nano 13(4), 3816–3822 (2019).

¹⁶A. J. Mannix, X. F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, and N. P. Guisinger, "Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs," Science **350**(6267), 1513–1516 (2015).

¹⁷W. Li, L. Kong, C. Chen, J. Gou, S. Sheng, W. Zhang, H. Li, L. Chen, P. Cheng, and K. Wu, Sci. Bull. 63, 282–286 (2018).

¹⁸M. H. Zhu, X. J. Weng, G. Gao, S. Dong, L. F. Lin, W. H. Wang, Q. Zhu, A. R. Oganov, X. Dong, Y. Tian, X.-F. Zhou, and H. T. Wang, "Magnetic borophenes from an evolutionary search," Phys. Rev. B **99**(20), 205412 (2019).

¹⁹Y. L. Zhang, J. H. Yang, H. Xiang, and X. G. Gong, "Fully boron-sheet-based field effect transistors from first-principles: Inverse design of semiconducting boron sheets," J. Phys. Chem. Lett. **12**(1), 576–584 (2021).

ARTICLE

²⁰S. Guha, A. Kabiraj, and S. Mahapatra, "Discovery of clustered-P1 borophene" and its application as the lightest high-performance transistor," ACS Appl. Mater. Interfaces 15(2), 3182-3191 (2023).

²¹X. F. Zhou, X. Dong, A. R. Oganov, Q. Zhu, Y. Tian, and H. T. Wang, "Semi metallic two-dimensional boron allotrope with massless Dirac fermions," Phys. Rev. Lett. 112(8), 085502 (2014).

22S. Verma, A. Mawrie, and T. K. Ghosh, "Effect of electron-hole asymmetry on optical conductivity in 8-pmmn borophene," Phys. Rev. B 96(15), 155418 (2017).

23S. F. Islam and A. M. Jayannavar, "Signature of tilted Dirac cones in Weiss oscillations of 8-pmmn borophene," Phys. Rev. B 96(23), 235405 (2017).

²⁴S. H. Zhang and W. Yang, "Oblique Klein tunneling in 8–P m m n borophene p-n junctions," Phys. Rev. B **97**(23), 235440 (2018). ²⁵B. D. Napitu, "Photoinduced Hall effect and transport properties of irradiated

8-pmmn borophene monolayer," J. Appl. Phys. 127(3), 034303 (2020).

A. D. Zabolotskiy and Y. E. Lozovik, "Strain-induced pseudomagnetic field in the Dirac semimetal borophene," Phys. Rev. B 94(16), 165403 (2016).

27 R. M. Kaufmann, S. Khlebnikov, and B. Wehefritz-Kaufmann, "Singularities, swallowtails and Dirac points. An analysis for families of Hamiltonians and applications to wire networks, especially the gyroid," Ann. Phys. 327(11), 2865-2884 (2012).

28K. Asano and C. Hotta, "Designing Dirac points in two-dimensional lattices," Phys. Rev. B 83(24), 245125 (2011).

29K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. Firsov, "Two-dimensional gas of massless Dirac fermions in graphene," Nature 438(7065), 197-200 (2005).

30Y. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim, "Experimental observation of the quantum Hall effect and Berry's phase in graphene," Nature 438(7065), 201-204 (2005).

³¹P. R. Wallace, "The band theory of graphite," Phys. Rev. 71(9), 622 (1947).

32C. R. Dean, L. Wang, P. Maher, C. Forsythe, F. Ghahari, Y. Gao, J. Katoch, M. Ishigami, P. Moon, M. Koshino, T. Taniguchi, K. Watanabe, K. L. Shepard, J. Hone, and P. Kim, "Hofstadter's butterfly and the fractal quantum Hall effect in Moiré superlattices," Nature 497(7451), 598-602 (2013).

33L. A. Ponomarenko, R. V. Gorbachev, G. L. Yu, D. C. Elias, R. Jalil, A. A. Patel, A. Mishchenko, A. S. Mayorov, C. R. Woods, J. R. Wallbank, M. Mucha-Kruczynski, B. A. Piot, M. Potemski, I. V. Grigorieva, K. S. Novoselov, F. Guinea, V. I. Fal'ko, and A. K. Geim, "Cloning of Dirac fermions in graphene superlattices," Nature 497(7451), 594-597 (2013).

34B. Hunt, J. D. Sanchez-Yamagishi, A. F. Young, M. Yankowitz, B. J. LeRoy, K. Watanabe, T. Taniguchi, P. Moon, M. Koshino, P. Jarillo-Herrero, and R. C. Ashoori, "Massive Dirac fermions and Hofstadter butterfly in a van der Waals heterostructure," Science 340(6139), 1427-1430 (2013).

35Y. P. Bliokh, V. Freilikher, and F. Nori, "Ballistic charge transport in graphene and light propagation in periodic dielectric structures with metamaterials: A comparative study," Phys. Rev. B 87(24), 245134 (2013).

³⁶K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer, "Ultrahigh electron mobility in suspended graphene," Solid State Commun. 146(9-10), 351-355 (2008).

37A. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene," Rev. Mod. Phys. 81(1), 109 (2009).

38N. O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, and X. Duan, "Graphene: An emerging electronic material," Adv. Mater. 24(43), 5776 (2012).

39S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, and S. Ciraci, "Two-and onedimensional honeycomb structures of silicon and germanium," Phys. Rev. Lett. 102(23), 236804 (2009).

40 D. Malko, C. Neiss, F. Viñes, and A. Görling, "Competition for graphene: Graphynes with direction-dependent Dirac cones," Phys. Rev. Lett. 108(8), 086804 (2012).

⁴¹H. Huang, W. Duan, and Z. Liu, "The existence/absence of Dirac cones in graphynes," New J. Phys. 15(2), 023004 (2013).

⁴²W. Li, M. Guo, G. Zhang, and Y. W. Zhang, "Gapless MoS₂ allotrope possessing both massless Dirac and heavy fermions," Phys. Rev. B 89(20), 205402 (2014).

43V. Pardo and W. E. Pickett, "Half-metallic semi-Dirac-point generated by quantum confinement in TiO2/VO2 nanostructures," Phys. Rev. Lett. 102(16), 166803 (2009).

⁴⁴G. Bertoni, L. Calmels, A. Altibelli, and V. Serin, "First-principles calculation of the electronic structure and EELS spectra at the graphene/Ni (111) interface," Phys. Rev. B 71(7), 075402 (2005).

⁴⁵P. W. Sutter, J. I. Flege, and E. A. Sutter, "Epitaxial graphene on ruthenium," Nat. Mater. 7(5), 406-411 (2008).

⁴⁶S. Marchini, S. Günther, and J. Wintterlin, "Scanning tunneling microscopy of graphene on Ru (0001)," Phys. Rev. B 76(7), 075429 (2007). ⁴⁷G. A. K. P. A. Giovannetti, P. A. Khomyakov, G. Brocks, V. M. Karpan, J. van

den Brink, and P. J. Kelly, "Doping graphene with metal contacts," Phys. Rev. Lett. 101(2), 026803 (2008).

48K. T. Chan, J. B. Neaton, and M. L. Cohen, "First-principles study of metal adatom adsorption on graphene," Phys. Rev. B 77(23), 235430 (2008).

49 I. Pletikosić, M. Kralj, P. Pervan, R. Brako, J. Coraux, A. T. N'diaye, C. Busse, and T. Michely, "Dirac cones and minigaps for graphene on Ir (111)," Phys. Rev. Lett. 102(5), 056808 (2009).

50S. Barraza-Lopez, M. Vanević, M. Kindermann, and M. Y. Chou, "Effects of metallic contacts on electron transport through graphene," Phys. Rev. Lett. **104**(7), 076807 (2010).

⁵¹C. Gong, G. Lee, B. Shan, E. M. Vogel, R. M. Wallace, and K. Cho, "First-principles study of metal-graphene interfaces," J. Appl. Phys. 108(12), 123711 (2010).

52S. Smidstrup, T. Markussen, P. Vancraeyveld, J. Wellendorff, J. Schneider, T. Gunst, B. Verstichel, D. Stradi, P. A. Khomyakov, U. G. Vej-Hansen, M.-E. Lee, S. T. Chill, F. Rasmussen, G. Penazzi, F. Corsetti, A. Ojanperä, K. Jensen,

M. L. N. Palsgaard, U. Martinez, A. Blom, M. Brandbyge, and K. Stokbro, "QuantumATK: An integrated platform of electronic and atomic-scale modelling tools," J. Phys.: Condens. Matter 32(1), 015901 (2020).

53D. Stradi, L. Jelver, S. Smidstrup, and K. Stokbro, "Method for determining optimal supercell representation of interfaces," J. Phys.: Condens. Matter 29(18), 8 185901 (2017).

54P. E. Blöchl, "Projector augmented-wave method," Phys. Rev. B 50(24), 17953 (1994). 40

⁵⁵G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," Phys. Rev. B 59(3), 1758 (1999).

⁵⁶G. Kresse and J. Furthmüller, "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set," Comput. Mater. Sci. 6(1), 15-50 (1996).

⁵⁷J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett. 77(18), 3865 (1996).

⁵⁸J. Moellmann and S. Grimme, "DFT-D3 study of some molecular crystals," Phys. Chem. C 118(14), 7615-7621 (2014).

⁵⁹S. Grimme, S. Ehrlich, and L. Goerigk, "Effect of the damping function in dispersion corrected density functional theory," J. Comput. Chem. 32(7), 1456-1465 (2011).

60K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," J. Appl. Crystallogr. 44(6), 1272-1276 (2011).

⁶¹F. Ma, Y. Jiao, G. Gao, Y. Gu, A. Bilic, Z. Chen, and A. Du, "Graphene-like two-dimensional ionic boron with double Dirac cones at ambient condition," Jano Lett. 16(5), 3022-3028 (2016).

62 V. L. Deringer, A. L. Tchougréeff, and R. Dronskowski, "Crystal orbital Hamilton population (COHP) analysis as projected from plane-wave basis sets," J. Phys. Chem. A 115(21), 5461-5466 (2011).

63 A. Savin, R. Nesper, S. Wengert, and T. F. Fässler, "ELF: The electron localization function," Angew. Chem. Int. Ed. Engl. 36(17), 1808-1832 (1997).

⁶⁴S. Steinberg and R. Dronskowski, "The crystal orbital Hamilton population (COHP) method as a tool to visualize and analyze chemical bonding in intermetallic compounds," Crystals 8(5), 225 (2018).

ARTICLE

⁶⁵S. Maintz, V. L. Deringer, A. L. Tchougréeff, and R. Dronskowski, "LOBSTER: A tool to extract chemical bonding from plane-wave based DFT," J. Comput. Chem. 37(11), 1030–1035 (2016).

⁶⁶D. B. Chesnut, "An electron localization function study of the lone pair," J. Phys. Chem. A **104**(49), 11644–11650 (2000).

⁶⁷R. S. Chen, G. Ding, Y. Zhou, and S. T. Han, "Fermi-level depinning of 2D transition metal dichalcogenide transistors," J. Mater. Chem. C 9(35), 11407–11427 (2021).

⁶⁸J. Wang, Q. Yao, C. W. Huang, X. Zou, L. Liao, S. Chen, Z. Fan, K. Zhang, W. Wu, X. Xiao, C. Jiang, and W. W. Wu, "High mobility MoS2 transistor with low Schottky barrier contact by using atomic thick h-BN as a tunneling layer," Adv. Mater. 28(37), 8302–8308 (2016).

⁶⁹J. Su, L. Feng, W. Zeng, and Z. Liu, "Controlling the electronic and geometric structures of 2D insertions to realize high performance metal/insertion–MoS₂ sandwich interfaces," Nanoscale **9**(22), 7429–7441 (2017).

⁷⁰A. Chanana and S. Mahapatra, "Prospects of zero Schottky barrier height in a graphene-inserted MoS₂-metal interface," J. Appl. Phys. **119**(1), 014303 (2016).
 ⁷¹Y. Du, L. Yang, J. Zhang, H. Liu, K. Majumdar, P. D. Kirsch, and D. Y. Peide,

¹¹Y. Du, L. Yang, J. Zhang, H. Liu, K. Majumdar, P. D. Kirsch, and D. Y. Peide, "MoS₂ field-effect transistors with graphene/metal heterocontacts," IEEE Electron Device Lett. **35**(5), 599–601 (2014). 7^{2} S. S. Chee, D. Seo, H. Kim, H. Jang, S. Lee, S. P. Moon, K. H. Lee, S. W. Kim, H. Choi, and M. H. Ham, "Lowering the Schottky barrier height by graphene/Ag electrodes for high-mobility MoS₂ field-effect transistors," Adv. Mater. **31**(2), 1804422 (2019).

⁷³S. Mitra, O. Kesharwani, and S. Mahapatra, "Ohmic-to-Schottky conversion in monolayer tellurene-metal interface via graphene insertion," J. Phys. Chem. C 125(23), 12975–12982 (2021).

⁷⁴S. Mitra and S. Mahapatra, "Schottky–Mott limit in graphene inserted 2D semiconductor–metal interfaces," J. Appl. Phys. **132**(14), 145301 (2022).

⁷⁵H. Zhong, R. Quhe, Y. Wang, Z. Ni, M. Ye, Z. Song, and J. Lu, "Interfacial properties of monolayer and bilayer MoS₂ contacts with metals: Beyond the energy band calculations," Sci. Rep. 6(1), 1–16 (2016).
⁷⁶Y. Pan, Y. Wang, M. Ye, R. Quhe, H. Zhong, Z. Song, X. Peng, D. Yu, J. Yang,

⁷⁶Y. Pan, Y. Wang, M. Ye, R. Quhe, H. Zhong, Z. Song, X. Peng, D. Yu, J. Yang, J. Shi, and J. Lu, "Monolayer phosphorene–metal contacts," Chem. Mater. 28(7), 2100–2109 (2016).

77 F. Xia, V. Perebeinos, Y. M. Lin, Y. Wu, and P. Avouris, "The origins and limits of metal-graphene junction resistance," Nat. Nanotechnol. 6(3), 179-184 (2011).

⁷⁸X. Ji, J. Zhang, Y. Wang, H. Qian, and Z. Yu, "A theoretical model for metalgraphene contact resistance using a DFT-NEGF method," Phys. Chem. Chem. Phys. 15(41), 17883–17886 (2013).