Electrical Contact between an Ultrathin Topological Dirac Semimetal and a Two-Dimensional Material

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Ultrathin films of the topological Dirac semimetal Na3Bi have recently been revealed as unusual electronic materials with field-tunable topological phases. Here we investigate the electronic and transport properties of ultrathin Na3Bi as an electrical contact to a two-dimensional (2D) metal (i.e., graphene) and 2D semiconductors (i.e., MoS2 and WS2 monolayers). Using combined first-principles density-functional theory and nonequilibrium Green’s function simulation, we show that the electrical coupling between bilayer-Na3Bi thin film and graphene results in a notable interlayer charge transfer, thus inducing sizable n-type doping in the Na3Bi/graphene heterostructures. In the case of MoS2 and WS2 monolayers, the lateral Schottky transport barrier is significantly lower than for many commonly studied bulk metals, thus revealing bilayer Na3Bi to be a high-efficiency electrical contact material for 2D semiconductors. These findings open up an avenue for utilizing topological semimetal thin film as an electrical contact to 2D materials, and further expand the family of 2D heterostructure devices into the realm of topological materials.

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I. INTRODUCTION

Two-dimensional (2D) layered materials and topological semimetals are two of the most-active research fields of current condensed-matter physics, materials science, and applied device engineering. The ever-expanding family of 2D materials, such as graphene [1], transition metal-dichalcogenides (TMDCs) [2], black phosphorus [3], group-VI Xenes [4], MXenes [5], and ferromagnetic Cr2Ge2Te6 and Fe3GeTe2 [6,7], is widely regarded as a material class of key importance in electronic [8], photonic [9], optoelectronic [10], energetic [11], spintronic [12], and valleytronic [13,14] devices with strong potential in revolutionizing the next-generation solid-state technology. Electrically contacting 2D materials with a metal, however, remains one of the major bottlenecks for the realization of high-performance industrial-grade electronic devices. Although having Ohmic contact is more desirable in reducing power dissipation [15–17], most 2D semiconductors are inevitably plagued by the formation of Schottky contacts with inherently large contact resistance when contacted by a bulk metal [18–21]. Achieving high-quality electrical contact to 2D materials remains an ongoing quest that is critically important for the development of industrial-grade 2D-material-based devices [22,23].

On the other hand, three-dimensional (3D) topological semimetals [24–26] that host exotic topologically protected band crossing in the bulk and topological surface states are another emerging condensed-matter system. For example, 3D topological Dirac semimetals, such as Cd3As2 and Na3Bi [27,28], which host a pair of 3D massless Dirac quasiparticles, have attracted considerable interest in the experimental and theoretical communities [29–31]. The unusual physical properties of topological semimetals has led to myriad unusual physical properties, such as chiral anomaly [30], linear quantum magnetoresistance [32,33], oscillating quantum spin Hall effect [34], charge-carrier mobility exceeding 6000 cm2 V−1 s−1 [35], logarithmically diverging giant diamagnetism at the Dirac nodal point [36,37], gate-tunable surface states [38],
and strong optical nonlinearity [39]. Intriguingly, Na₃Bi becomes a topological insulator with a band gap of approximately 300 meV in the ultrathin limit of a few atomic layers [40], in which the band structure can be tuned between a topological insulator and a band insulator via an external electric field [41]. The experimental demonstration of a field-effect-tunable topological phase transition in bilayer Na₃Bi [40] thus opens up the possibility of topological nanodevices in which the charge conduction is controlled by the field-effect modulation of the transport channel.

Although both 2D materials and 3D topological semimetals have been extensively studied, the union of topological Dirac semimetals and 2D material in terms of contact engineering remains largely unknown thus far. In this work, we explore the integration of topological semimetal ultrathin film into the design of 2D-material-based electronic devices. We propose a concept of utilizing ultrathin films of topological semimetals as an electrical contact to 2D materials. Using a field-effect-transistor setup, we show that the Schottky-barrier height formed at the bilayer Na₃Bi/2D semiconductor is markedly lower than that formed by many bulk metals (see Fig. 6), thus unrevealing the potential of Na₃Bi ultrathin film as an efficient electrode contact to 2D semiconductors. Furthermore, unlike many bulk metals that metalize the 2D semiconductor during contact formation, the electronic band structures of MoS₂ and WS₂ remain intact when contacted by Na₃Bi, thus offering a useful platform for studies of optical, valley, and excitonic physics in 2D TMDCs [42,43]. Importantly, ultrathin Na₃Bi undergoes a metal-to-insulator transition and a topological phase transition from a trivial band insulator to a topological insulator with conducting edge states when it is subjected to an external gate voltage [40,41]. Such gate-tunable electronic properties may be further harnessed as a control for the design of electronic devices. Our findings will open up an avenue toward sub-10-nm-device technology via the union of 2D materials and ultrathin films of 3D topological materials, and further expands the family of 2D-material-based heterostructure devices into the realm of quantum materials with nontrivial topological phases.

II. COMPUTATIONAL METHODS

We perform a first-principles density-functional-theory (DFT) simulation as implemented in the VASP code [44,45] to study the contact between ultrathin bilayer Na₃Bi and (i) semimetallic graphene and (ii) semiconducting MoS₂ and WS₂ monolayers. The geometric optimization and electronic properties of the heterostructures are calculated via DFT simulation as implemented in the VASP code [44,45]. The calculation uses the projector-augmented-wave pseudopotential [46]. During the structure relaxations, spin-orbit coupling (SOC) is not included. SOC is included in the electronic structure calculations. The cut-off energy is set to 500 eV. A vacuum layer of 30 Å in the vertical direction is chosen to avoid interaction between the top and bottom surfaces. Monkhorst-Pack k-point sampling is set to be 11 × 11 × 1. The method of Grimme (DFT-D3) for the van der Waals (vdW) interaction functional is used in the calculations [47], and the dipole correction is also added. The residual force is converged to less than 0.01 eV/Å, and the convergence criterion for the total energy is set to be 10⁻⁶ eV. In addition, the transport properties for the two-probe systems are calculated with use of the Atomistix ToolKit 2018 package based on DFT combined with the nonequilibrium Green’s functions [48–51]. SOC is also included in the transport simulation.

III. RESULTS AND DISCUSSION

A. Bilayer-Na₃Bi/graphene heterostructure

Figures 1(a) and 1(b) illustrate the bilayer-Na₃Bi/graphene heterostructure in top and side views, respectively. The optimized lattice parameters of bilayer Na₃Bi are a =

![FIG. 1. (a) Top view and (b) side view of the bilayer-Na₃Bi/graphene heterostructure. (c),(d) Projected band structures with SOC and without SOC, respectively. The blue (red) dot projection originates from bilayer Na₃Bi (graphene). (e) Band alignments of the Na₃Bi/graphene heterostructure. ΔV represents the potential change generated by the interaction between graphene and bilayer Na₃Bi. The work functions of Na₃Bi and graphene are denoted as W_Na₃Bi and W_gr, respectively.](image-url)
structures of both Na$_3$Bi and graphene are well preserved [52], thus suggesting the cell of bilayer Na$_3$Bi. The lattice mismatches are 0.77\% and 0.73\%, respectively. In Figs. 2(b)–2(d), we show the transfer of electrons from Na$_3$Bi to graphene. Such transfer of bilayer Na$_3$Bi changes from 300 to 121 meV when forming the heterostructure, while the band gap of graphene contacted by bulk metals [54–56].

B. Bilayer-Na$_3$Bi/MoS$_2$ and bilayer-Na$_3$Bi/WS$_2$ heterostructures

We next study the contact between bilayer Na$_3$Bi and monolayers of MoS$_2$ and WS$_2$ (see Fig. 2). The Na$_3$Bi/MoS$_2$ and Na$_3$Bi/WS$_2$ heterostructures are constructed via stacking along the $z$ direction. For MoS$_2$ and WS$_2$, the lattice parameters are $a = b = 3.182$ Å and $a = b = 3.180$ Å, respectively. The $\sqrt{3} \times \sqrt{3}$ unit cells of MoS$_2$ and WS$_2$ are adjusted to match the $1 \times 1$ unit cell of bilayer Na$_3$Bi. The lattice mismatches are 0.77\% and 0.73\%, respectively. In Figs. 2(b)–2(d), we show the three possible stacking modes—namely, the AA, BB, and AB stacking configurations of Na$_3$Bi/MoS$_2$—as a representative example as the WS$_2$-based contact exhibits the same stacking structures. Here all S (yellow) [Mo (dark cyan)] atoms are above the Na (purple) and Bi (blue) atoms in the AA (BB) case and all atoms of Na$_3$Bi lie directly over the center of a hexagon in the upper MoS$_2$ (or WS$_2$) sheet in the AB case. The total energy of the Na$_3$Bi/MoS$_2$ and Na$_3$Bi/WS$_2$ heterostructures for different interlayer distances is shown in Fig. S2 in Supplemental Material [52]. After structural relaxation, we find that the different stacking modes exhibit various interlayer distances (see Table I). As the interlayer distances are close to the sum of the covalent radii of Na and S atoms, covalent bonds are expected to form between the two layers. To examine the energetic stability of Na$_3$Bi/MoS$_2$ and Na$_3$Bi/WS$_2$ electrical contacts, the binding energy $E_b$ is calculated as $E_b = E_{\text{Na}_3\text{Bi/MoS}_2 (\text{WS}_2)} - E_{\text{Na}_3\text{Bi}} - E_{\text{MoS}_2 (\text{WS}_2)}$, where $E_{\text{Na}_3\text{Bi/MoS}_2 (\text{WS}_2)}$ represents the total energy of the heterostructure and $E_{\text{Na}_3\text{Bi}}$ and $E_{\text{MoS}_2 (\text{WS}_2)}$ represent the energy of the isolated Na$_3$Bi and MoS$_2$ (WS$_2$), respectively. The calculated binding energies have negative values, thus indicating that the structures considered in our simulations are energetically stable. The calculated heterostructure parameters are summarized in Table I.

The band structures of an isolated Na$_3$Bi bilayer and a $\sqrt{3} \times \sqrt{3}$ MoS$_2$ (WS$_2$) monolayer are shown in Figs. 3(a)–3(c). Bilayer Na$_3$Bi exhibits a direct band gap of 0.1 eV at the $\Gamma$ point, which is consistent with previous results [40]. The band gap is 1.73 eV for MoS$_2$ and 1.6 eV for WS$_2$, which are slightly less than the values reported in previous studies due to the presence of strain in the heterostructures considered here [57]. The projected band structures of the electrical contacts are shown in Figs. 3(d)–3(i) (see Fig. S3 in Supplemental Material [52] for the projected band structures without SOC). Here red, blue, and violet symbols denote the contributions from Na$_3$Bi, MoS$_2$, and WS$_2$, respectively. Compared with the band structures of isolated bilayer Na$_3$Bi, $\sqrt{3} \times \sqrt{3}$ MoS$_2$,
TABLE I. Calculated parameters of the Na$_3$Bi/2D-semiconductor heterostructures. $d$ is the interlayer distance, $d_a$ is the minimum distance between Na and S atoms, $E_b$ is the binding energy, $E_{g(N)}$ and $E_{g(S)}$ are the band gap for Na$_3$Bi and MoS$_2$ or WS$_2$ after contact, respectively, $D$ is the dipole moment, and $W$ is the work function of the system.

<table>
<thead>
<tr>
<th>Stacking</th>
<th>Na$_3$Bi/MoS$_2$</th>
<th>Na$_3$Bi/WS$_2$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$AA$</td>
<td>$BB$</td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>2.665</td>
<td>2.186</td>
</tr>
<tr>
<td>$d_a$ (Å)</td>
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<td>2.84</td>
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<tr>
<td>$E_b$ (eV)</td>
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<td>$-3.831$</td>
</tr>
<tr>
<td>$E_{g(N)}$ (eV)</td>
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<td>0.274</td>
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<tr>
<td>$E_{g(S)}$ (eV)</td>
<td>1.701</td>
<td>1.653</td>
</tr>
<tr>
<td>$D$ (D)</td>
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<td>1.091</td>
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<tr>
<td>$W$ (eV)</td>
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<td></td>
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<td>$BB$</td>
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<tr>
<td>$d$ (Å)</td>
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<td>$-3.673$</td>
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<tr>
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<tr>
<td>$E_{g(S)}$ (eV)</td>
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</tr>
<tr>
<td>$D$ (D)</td>
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</tr>
<tr>
<td>$W$ (eV)</td>
<td>3.975</td>
<td>4.005</td>
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</table>

and WS$_2$ [Figs. 3(a)–3(c)], the band structures of Na$_3$Bi are not only up-shifted and show metallic behavior but also exhibit obvious band splitting. Strong splitting of the valence band around $-0.5$ eV at the $\Gamma$ point is observed, which originates from the interactions between bilayer Na$_3$Bi and 2D TMDCs when they are forming the heterostructure. The valence bands of both MoS$_2$ and WS$_2$ are energetically down-shifted. The conduction-band minimum is shifted from the $\Gamma$ point to the $M$ point, and crosses the Fermi level, thus indicating the formation of an Ohmic contact across the vdW gap [see Figs. 3(g)–3(i)]. The Ohmic contact persists even in the case of ten-layer-Na$_3$Bi (approximately-5-nm) contacts to MoS$_2$ and WS$_2$ (see Fig. S4 in Supplemental Material in [52]). Such an Ohmic vertical interface is in stark contrast to the case of 2D TMDCs contacted by Au and Ag, where a Schottky barrier is formed across the vertical vdW gap [58–60], which impedes the efficiency of charge injection. For other bulk metal electrodes such as Sc, Ti, and Pt electrodes, the band structures of 2D TMDCs are metalized in the contact region [58–60]. This is again in contrast to the case of Na$_3$Bi contacts to 2D TMDCs, where the hybridization between the two materials is weak. The band structures of 2D TMDCs are retained without the formation of a Schottky barrier across the vertical contact interface. Such Ohmic nature of the Na$_3$Bi-contacted MoS$_2$ and WS$_2$ suggests that electrons can be more efficiently injected through the vertical interfaces—a favorable characteristic for electronics and optoelectronics applications.

To further understand the detailed nature of the charge transfer at the Na$_3$Bi and MoS$_2$ and WS$_2$ interfaces, we calculate the charge difference between the combined heterostructure system and the sum of the isolated Na$_3$Bi and MoS$_2$ or WS$_2$ [see Figs. 4(a) and 4(c)]. The charge-density difference is calculated as $\Delta \rho = \rho_H - \rho_{Na3Bi} - \rho_{MoS2 (WS2)}$, where $\rho_H$, $\rho_{Na3Bi}$, and $\rho_{MoS2 (WS2)}$ are the charge density of the heterostructure, freestanding bilayer Na$_3$Bi, and isolated MoS$_2$ (WS$_2$), respectively. The blue regions represent electron depletion, while the red regions represent the accumulation of electrons in the heterostructures relative to their two isolated components. In the interfacial region, several charge-transfer oscillations are observed. The main charge depletion is contributed by the first layer of Na$_3$Bi closest to MoS$_2$.
FIG. 4. Plane-averaged differential charge density \( \Delta \rho \) and electrostatic potentials of Na\(_3\)Bi with (a),(b) MoS\(_2\) and (c),(d) WS\(_2\) heterostructure at equilibrium along the \( z \) direction. The insets show side views of the isosurfaces of the differential charge density of the heterostructure. \( \Delta V \) reflects the difference between the work function on the Na\(_3\)Bi side and on the 2D-semiconductor side.

or WS\(_2\). Moreover, some extra charge is found to accumulate around the Mo and W atoms. Compared with metal/MoS\(_2\) and metal/WS\(_2\) contacts, the major difference is the charge accumulation located in the MoS\(_2\) or WS\(_2\) interface \([57,58]\). In general, both the charge depletion and the charge accumulation constitute the interfacial charge-redistribution behavior, leading to electron-wave-function polarization and, hence, the formation of an interfacial electric dipole. The presence of such an interfacial dipole directly modifies the interfacial band alignment \([61]\), thus leading to the band-structure modification shown in Figs. 3(d)–3(i).

To illustrate the key strengths of ultrathin Na\(_3\)Bi as an electrical contact to 2D TMDCs over other bulk metals, we simulate a field-effect-transistor device with 5-nm channel length [see Fig. 5(a)]. We use a nonequilibrium Green’s function approach \([52]\) to extract the height of the Schottky barrier laterally extending into the 2D channel by calculating the local device density of states, which reflects the energy-band distribution in real space along the simulated device \([62,63]\). The lateral electron Schottky-barrier height(\( \Phi_{L,T}^e \)) of the MoS\(_2\) and WS\(_2\) transistors is estimated as the energy difference between the Fermi level, \( E_F \), and the conduction-band minimum of the 2D channel [labeled in Figs. 5(b) and 5(c)]. \( \Phi_{L,T}^e \) is calculated to be 0.32 and 0.18 eV, respectively, for MoS\(_2\) and WS\(_2\) [Figs. 5(b) and 5(c)], values which are appreciably lower than those of many other commonly studied bulk metals \([59,60]\) because of the low work function of bilayer Na\(_3\)Bi (2.44 eV). In Fig. 6, \( \Phi_{L,T}^e \) is plotted versus the isolated-metal work function (\( \Phi_M^e \)) with use of the data for WS\(_2\) and MoS\(_2\) 5-nm field-effect transistors extracted from Refs. \([59,60]\]. Here \( \Phi_{L,T}^e \) of bilayer Na\(_3\)Bi is substantially lower than that of other bulk metals. Particularly for WS\(_2\) contacted by bilayer Na\(_3\)Bi , \( \Phi_{L,T}^e \) is the lower than for other common bulk metal electrodes (i.e., Sc, Ti, Ag, Cu, Pd, and Pt electrodes) \([60]\). The relatively low \( \Phi_{L,T}^e \) thus reveals the potential of bilayer Na\(_3\)Bi as another candidate electrode material to achieve high-efficiency charge injection into 2D TMDCs. We further remark that the pronounced Stark effect in Na\(_3\)Bi ultrathin film allows the band gap to be tuned and closed and the electronic band structure to be switched between a trivial band insulator and a topological insulator by an external gate voltage \([40,41]\). Such a gate-tunable metallic-insulator transition and topological phase transitions may offer a physical mechanism for the design of functional devices that is not found in conventional metal-semiconductor contacts and that is worthy of further exploration.

Finally, we remark that Na\(_3\)Bi is prone to degradation under ambient air conditions. Nonetheless, recent experiments \([40]\) have successfully used angle-resolved photoemission spectroscopy and scanning tunneling microscopy to study the field-effect-tunable band structure in Na\(_3\)Bi, revealing a major step toward the fabrication of a Na\(_3\)Bi device. More recently, Na\(_3\)Bi ultrathin film passivated by...
MgF₂ or Si capping layers was demonstrated to be stable in air and the transport properties remained intact after such passivations [64]. Encapsulated Na₃Bi devices thus provide a potential route toward air-stable hybrid Na₃Bi/2D-semiconductor devices.

IV. CONCLUSION

In summary, we investigate the electronic and transport properties of the ultrathin topological Dirac semimetal Na₃Bi as an electrical contact to graphene, MoS₂, and WS₂ via first-principles calculations. We show that the Na₃Bi/graphene contact leads to n-type doping in graphene, which can be useful for electronics and optoelectronics applications, such as a p-n junction and a photodetector. For Na₃Bi/MoS₂ and Na₃Bi/WS₂, the prevalence of an Ohmic vertical interface and a low lateral Schottky-barrier height indicates the potential of Na₃Bi as an energy-efficient electrical contact. The findings reported here could ve a harbinger for the exploration of an emerging class of heterostructure electronic devices [65] that synergize 2D materials and the ever-expanding family of topological semimetals where nodal point, line, link, chain, double-helix, hourglass, surface, and many other exotic topological phases are continually being unearthed.

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[52] See Supplemental Material http://link.aps.org/supplemental/10.1103/PhysRevApplied.13.054030 for the total energies of bilayer Na3Bi/graphene (Fig. S1), bilayer Na3Bi/MoS2, and bilayer Na3Bi/MoS2 (Fig. S2), the projected band structures of bilayer Na3Bi/MoS2 and bilayer Na3Bi/MoS2 without SOC (Fig. S3), and the projected band structures of ten-layer Na3Bi/MoS2 and ten-layer Na3Bi/MoS2 with SOC (Fig. S4).


