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Graphene Oxide as a Promising Hole Injection Layer for MoS₂-Based Electronic Devices

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ABSTRACT The excellent physical and semiconducting properties of transition metal dichalcogenide (TMDC) monolayers make them promising materials for many applications. The TMDC monolayer MoS₂ has gained significant attention as a channel material for next-generation transistors. However, while n-type single-layer MoS₂ devices can be made with relative ease, fabrication of p-type transistors remains a challenge as the Fermi-level of elemental metals used as contacts are pinned close to the conduction band leading to large p-type Schottky barrier heights (SBH). Here, we propose the utilization of graphene oxide (GO) as an efficient hole injection layer for single-layer MoS₂-based electronic and optoelectronic devices. Using first-principles computations, we demonstrate that GO forms a p-type contact with monolayer MoS₂, and that the p-type SBH can be made smaller by increasing the oxygen concentration and the fraction of epoxy functional groups in GO. Our analysis shows that this is possible due to the high work function of GO and the relatively weak Fermi-level pinning at the MoS₂/GO interfaces compared to traditional MoS₂/metal systems (common metals are Ag, Al, Au, Ir, Pd, Pt). The combination of easy-to-fabricate and inexpensive GO with MoS₂ could be promising for the development of hybrid all-2D p-type electronic and optoelectronic devices on flexible substrates.

KEYWORDS: MoS₂ . graphene oxide . DFT . Schottky barrier . hole injection layer . p-type FET
with low SBH relative to the valence band. Recent density functional theory calculations for numerous metal electrodes in contact with monolayer MoS2 show a p-type Schottky contact only in the case of platinum, while all other metal contacts lead to n-type behavior due to a Fermi level pinning mechanism at the MoS2/metal interface.21 As a consequence, even if high work function metals are used, the SBH to the valence band is large, producing, de facto, n-type devices.

In an effort to overcome this issue, Fontana et al. demonstrated the operation of p-type multilayer MoS2 FETs through hole injection using palladium (Pd) contacts in the limit of large gate fields.22 Recently, Chuang et al. proposed the use of substoichiometric molybdenum trioxide (MoO\(_x\), x < 3), a high work function metal, as an efficient hole injection layer sandwiched between Pd and TMDC monolayers.20 However, such inorganic hole injection layers require complex high temperature evaporation and deposition techniques in high vacuum chambers. Here, as an alternative process, we demonstrate the utilization of solution-processable graphene oxide (GO) films as promising hole injection layers for TMDC-based electronic and optoelectronic devices.

GO can be defined as a sheet of graphene with oxygen functional groups, predominantly in the form of epoxies and hydroxyls, randomly attached to its basal plane. The presence of oxygen groups disrupts the sp\(^2\) network in graphene, thereby making it an insulator.23 The utilization of GO in next-generation TMDC devices has many advantages. Production of GO using the widely available Hummers’ method is simple and inexpensive.23 Further, GO can be processed in solution, allowing precise control over the number of deposited GO layers, down to a monolayer.23 Using first-principles computations, we show that GO forms a p-type contact with monolayer MoS2, and that it is possible to tune and obtain smaller p-type SBHs by increasing the oxygen concentration and the fraction of epoxy functional groups in GO.

We present several possible device architectures (Figure 1) for fabricating FETs with GO as a hole injection layer between MoS2 and metal contacts. One architecture is proposed in Figure 1a, where MoS2 is used as the active channel material, and hafnia, a high-k oxide, is employed as the top-gate dielectric.8,11 In Figure 1b, we show another possible device configuration, which is essentially “inverted”, but functions similar to the one proposed in Figure 1a. Such architectures have been used recently to fabricate MoS2 FETs with graphene contacts.24 We point out that, experimentally, it could be easier to fabricate a device based on an “inverted” architecture, by depositing GO layers on metal contacts using lithography and etching techniques, as recently demonstrated by Roy et al.24 We highlight that the role of GO in MoS2 FETs is not limited to that of obtaining p-FETs. As depicted in Figure 1c, GO can be used as a substrate to control p-type doping in MoS2 as evidenced from our calculations. The oxygen concentration and the functional group fraction can be used as handles to tune the doping level. As an alternative, GO could be directly used as a monolayer gate insulator instead of bulk hafnia, as proposed in Figure 1d.

In integrated circuits to date8,25 silicon (Si) is typically used as a back-gate to tune the carrier density. It is well-known that Si, in normal stable conditions, becomes oxidized, creating a superficial layer of SiO2. This means that, effectively, the MoS2 monolayer is always in contact with SiO2. The conducting properties of MoS2 are therefore strongly influenced by the SiO2 layer and the current polarity in an ultrathin MoS2 monolayer deposited on SiO2 remains unclear.26,27 In fact, both n-type11,13,28,29 and p-type30 conductivities have been reported, depending on the experimental conditions. This behavior is due to the unintentional
doping of SiO$_2$\textsuperscript{26} that could occur during the synthesis and sample preparation. A more reliable way to control the conductivity of the MoS$_2$ monolayer is to directly dope it,\textsuperscript{27} for example, with electron irradiation\textsuperscript{31} or sputtering techniques.\textsuperscript{32} Other methods proposed to control the electrical and optical properties of MoS$_2$ rely on surface-chemistry-based approaches.\textsuperscript{33} The use of GO as a substrate to modulate the properties of monolayer MoS$_2$ may be advantageous compared to the use of these more complex and expensive techniques.

In order to construct an appropriate supercell for studying MoS$_2$/GO interfaces, we consider an interface between a (5/C$_{25}$5) layer of graphene (50 C atoms) and a (4/C$_{24}$4) layer of MoS$_2$ (16 Mo and 32 S atoms), a combination used in previous works.\textsuperscript{34,35} In this arrangement, the graphene lattice parameter is expanded by 3.29\% to match that of MoS$_2$. Upon computing the electronic structure (see Supporting Information Figure S1a), we find that the band structure of strained graphene does not vary significantly from the unstrained case and retains a band gap of zero, consistent with the work of Bernardi et al.\textsuperscript{36} Another possibility would be to strain MoS$_2$ while keeping graphene unstrained; this case was not considered since it led to a considerable reduction (by $\sim$1 eV) in the band gap of MoS$_2$ (see Supporting Information Figure S1b). Hence, we have adopted the former configuration for all our simulations.

Regarding the stacking between the two monolayers, different combinations have been generally adopted.\textsuperscript{34,35,37} We have chosen the so-called TM configuration,\textsuperscript{35} where one C atom sits exactly above a Mo atom, as illustrated in Figure 2a. Another arrangement, where a C atom sits above a S atom, has been shown to be energetically and electronically equivalent to that of the TM configuration.\textsuperscript{34,35}

Once the graphene/MoS$_2$ supercell is constructed, oxygen functional groups are randomly attached above and below the graphene plane.\textsuperscript{38,39} GO structures are obtained by relaxing the supercell without the MoS$_2$ monolayer first, and then the MoS$_2$ monolayer is introduced with an initial distance between the C plane of GO and the Mo plane of MoS$_2$ of 4.85 Å, which is the van der Waals distance obtained for the MoS$_2$/graphene case. We found that deviations from this value did not significantly change the total energy of the system for different GO structures (see Supporting Information Figure S2). This is attributed to the homogeneously distributed effects of reconstruction of the oxygen atoms bound to GO facing the interface. Our analysis of the interface energy also predicts that all the MoS$_2$/GO interfaces considered in this work are energetically favorable (see Supporting Information Figure S3).

GO is nonstoichiometric and has a predominance of epoxy and hydroxyl functional groups randomly attached to the graphene basal plane because of harsh conditions employed during its synthesis.\textsuperscript{40,41} In order to account for the heterogeneity, we have constructed different interfaces, varying the epoxy to hydroxyl ratio (1:1, 2:3, 3:2, only epoxy and only hydroxyl) and the oxygen concentration (4–24\%, in atom percent).\textsuperscript{42} We further considered a statistical set of at least 10
structures for a given oxygen concentration and functional group ratio to obtain meaningful averages of the computed properties. This sampling is necessary, since the oxygen atoms in our calculations are randomly attached to the graphene plane following a uniform random distribution, thus giving GO a multitude of possible configurations.

Examples of relaxed GO/MoS$_2$ structures are shown in Figure 2. Upon comparing the side views in the case of GO with low (Figure 2c) and high (Figure 2d) oxygen concentrations, we note the higher graphene plane buckling in the latter case. The corrugation is more emphasized when GO has a greater content of epoxy groups.

RESULTS AND DISCUSSION

We obtain a direct band gap value of 1.65 eV for monolayer MoS$_2$, consistent with previous DFT calculations employing the PBE functional.$^{21,43,44}$ By way of example, Figure 3 shows the density of states (DOS) and band structure plots from a single interface calculation. Note that the electronic structure of MoS$_2$ is minimally perturbed by the presence of GO sheets, which do not introduce defect states within the band gap of MoS$_2$. As expected, the electronic structure of GO presents numerous defect states within the conduction and valence band edges due to the random rearrangement of oxygen atoms on the graphene basal plane and a heterogeneous sp$^2$–sp$^3$ mixed phase.

For each hybrid structure, the DOS and the band structure have been computed to obtain a value for the MoS$_2$ p-type SBH. We define the energy difference between the Fermi level and the minimum of the conduction band as the n-type SBH, and similarly the p-type SBH is given by the energy difference between the valence band maximum and the Fermi energy (see Figure 3), consistent with previous DFT simulations of MoS$_2$/graphene contacts$^{26}$ and MoS$_2$/metal contacts.$^{21,45}$

Figure 3. Example DOS plot showing the definition of n-type and p-type SBH, with the corresponding band structure.

Figure 4 shows the correlation between the MoS$_2$ p-type SBH and the oxygen concentration in the GO monolayer, functionalized with different ratios of epoxy to hydroxyl groups. Each data point is obtained by averaging over at least 10 structures, and the error bars represent the standard error of the mean. The general trend is clear: p-type SBHs consistently decrease with increasing oxygen concentration for all functional group composition values considered. Furthermore, the p-type SBH can be decreased by increasing the proportion of epoxy functional groups with respect to the hydroxyl groups, an effect that grows with oxygen content. In particular, we obtained a significantly low p-type SBH value of 0.02 eV in the case of a GO sheet with $\approx 25\%$ oxygen concentration, functionalized with epoxy groups alone. In addition to obtaining low SBH values, our calculations also show the possibility to tune the SBH (up to nearly 1 eV) at the MoS$_2$/GO interface by controlling the oxygen concentration and the relative fraction of functional groups in GO.

We next proceed to investigate the reason for the decreasing p-SBH with increasing concentration of
oxygen and fraction of epoxy functional groups. It is known that the position of the Fermi-level of the adsorbate/metal system (and thus the p- and n-type SBH) can, in principle, be controlled by the work function of the metal. However, in the case of the MoS2/metal interface, it has been demonstrated that such control is difficult to realize owing to the mechanism of Fermi-level pinning. A strong d-orbital rehybridization of Mo atoms has been observed upon the formation of the interface, and the dominant contribution of these d-orbitals pins the Fermi-level close to the conduction band, leading to n-type SBH even in the case of metals with high work function (for example, Ir with a work function of 5.89 eV).\(^{21}\)

In order to understand how the Fermi-level of the MoS2/GO interfaces changes depending on the structural characteristics of GO, we have first computed the work function of hydroxyl- and epoxy-only GO (Figure 5a). As expected, the work function increases with higher oxygen concentration, although while hydroxyl functionalized GO varies by only a small amount (0.2 eV), the epoxy case changes by more than 1.2 eV, attributed to the higher electron-withdrawing ability of the epoxy groups.\(^{46}\) Figure 5b shows a plot of the Fermi-level shift of GO relative to the valence band maximum of MoS2, upon formation of the interface, as a function of the corresponding work function of GO. Linear fits give the slopes 0.36 (epoxy case) and 0.47 (hydroxyl case), values much lower than the 0.71 fitted for monolayer MoS2 in contact with six different metals,\(^{21}\) indicating that Fermi level pinning in the case of monolayer MoS2/GO is, in comparison, weaker. We recall here that such a weak pinning of the Fermi level is necessary to achieve p-type FETs, which to date have been challenging to fabricate.

In order to shed light on the charge transfer process at the interface, we have investigated the plane-averaged electron density difference $\Delta n(z) = n_{\text{GO}|\text{MoS}_2} - n_{\text{GO}} - n_{\text{MoS}_2}$, where $n_{\text{GO}|\text{MoS}_2}$ is the total electron density of the MoS2/GO interface system and $n_{\text{GO}}$ and $n_{\text{MoS}_2}$ are those of individual GO and MoS2 structures, respectively. Figure 6 shows the charge density difference for GO with two different oxygen concentrations for the epoxy (Figure 6a,b) and hydroxyl (Figure 6c,d) functionalizations. While in GO with low oxygen concentration there is only charge depletion between MoS2 and GO, in the high oxygen concentration case we observed charge accumulation as well. This qualitative analysis suggests that the electrons are effectively being transferred from MoS2 toward the GO plane at higher oxygen contents (see also Supporting Information Figure S4). It should be noted that the equilibrium distance between the two monolayers depends on the oxygen content of GO. Increasing oxygen concentration progressively weakens the interlayer van der Waals bonding between MoS2 and GO, leading to increasing interlayer separation (see Supporting Information Figure S5 for details). Moreover, our results reveal a decreased charge redistribution at the interface as well as within MoS2, compared to that observed in MoS2/metal systems (see Gong et al.\(^{21}\)), consistent with the weaker Fermi level pinning observed here.

In addition, our PDOS plots revealed no significant gap states in contrast to some MoS2/metal systems.\(^{21}\) Such a decreased charge distribution and absence of gap states imply weaker hybridization and dipole formation at the interface. Consequently, greater variations of the p-SBH can be obtained by tuning the work function of GO (see Figure 5c).

CONCLUSION

We have used \textit{ab initio} simulations to investigate the role of solution-processable GO as a hole injection layer for MoS2-based devices. We demonstrate that, by increasing the oxygen concentration as well as the fraction of epoxy functional groups in GO, the p-type SBH can be decreased significantly. Our analyses show...
that the reason behind low p-type SBHs is a weak Fermi level pinning effect at the interface between GO and MoS2, that could allow efficient p-FET device fabrication. Overall, we highlight the remarkable potential held by GO for next-generation MoS2-based electronic and optoelectronic devices.

COMPUTATIONAL DETAILS

All calculations are performed using plane-wave density functional theory (DFT), as implemented in the VASP package.\textsuperscript{47} We used the projector-augmented-wave method to describe the core electrons,\textsuperscript{48,49} and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.\textsuperscript{50} Van der Waals (vdW) corrections are included through Grimme’s DFT-D2 method as implemented in VASP.\textsuperscript{51,52} While the spin–orbit interactions are not accounted for here consistent with previous studies,\textsuperscript{21,53} given that their computational cost is high (for >100 atoms in the unit cell), and their main effect being splitting of the valence band, which does not affect the computed SBH trends. A kinetic energy cutoff of 500 eV is used, and the atomic positions have been relaxed using the conjugate gradient method, until the residual atomic force on each atom is less than 0.03 eV/Å. A vacuum region of 17 Å normal to the surface is employed to avoid interaction between the slab images. A (5 × 5 × 1) Γ-centered k-point grid is used for structural relaxations, while the k-point grid is increased to (9 × 9 × 1) to obtain the DOS and the interface band structure. The electronic properties for several cases have been computed with the hybrid HSE06 functional,\textsuperscript{54} and good agreement with the PBE trends was observed (see Figures S6 and S7 in the Supporting Information for details). The charge-density analysis has been carried out with the grid-based Bader method.\textsuperscript{55,56}

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Figure S1: Strain effects on the DOS of graphene and MoS2, upon building of the supercell. Figure S2: Effect of varying the distance between GO and MoS2 monolayers. Figure S3: Interface energy as a function of the oxygen concentration in the GO layer, for only-epoxy and only-hydroxyl functionalization. Figure S4: Charge transfer at the GO/MoS2 interface, as a function of oxygen concentration in the GO layer, for only-epoxy and only-hydroxyl functionalization. This material is available free of charge via the Internet at http://pubs.acs.org/.

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REFERENCES AND NOTES


Figure 6. Plots of the plane-averaged electron density difference (Δn(z)) along the direction perpendicular to the interface of GO. (a,b) Epoxy-functionalized GO with low and high oxygen concentrations, respectively. (c,d) Corresponding plots for hydroxyl-functionalized GO. The light and dark colors indicate electron accumulation and depletion, respectively. The atomic plane positions are given at the top of each figure for reference. For the atoms legend, see Figure 2.