Tuning Magnetic States of Planar Graphene/h-BN Monolayer Heterostructures via Interface Transition Metal-Vacancy Complexes

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Supporting Information

ABSTRACT: Planar graphene/h-BN (GPBN) heterostructures promise low-dimensional magnetic semiconductor materials of tunable bandgap. In the present study, interplay between 3d transition metal (TM) atoms and single vacancies (SVs) at the armchair interface in a planar GPBN monolayer was investigated through first principle density functional theory calculations. The TM-SV complexes were found to give rise to a rich set of magnetic states, originated from the interactions between valence electrons of the TM atom with dangling orbitals at the SV. The magnetic state at a TM-SV complex was further shown to be tunable upon the application of strain and electric field. The present study suggests a route to enrich and engineer the magnetic states of planar GPBN heterostructures, providing new insights for the design of tunable low-dimensional spintronic devices.



1. INTRODUCTION

The two-dimensional (2D) nature and unique electronic properties of graphene and its derivatives bring various new possibilities in the design of nanoelectronic devices.^{1–17} Recently there is a great movement to explore the potential of graphene^{1,2,10,18-27} and its isomorph h-BN^{23,28-34} as building blocks for novel spintronics. However, neither graphene nor h-BN possesses perfect properties for spintronics, as the semimetal nature of graphene^{15,35,36} will inhibit the on/ off switch while on the other hand the wider band gap of h-BN renders very low carrier concentration and electron mobility.³⁷ One viable solution to overcome the above limitations to build planar graphene/h-BN (GPBN) heterostructures.^{6,38,39} With the phase separation and absence of mixing states in graphene boron nitride alloy,³⁹ the GPBN heterostructure will consist of individual graphene or h-BN domains, separated by phase interfaces. Recent studies^{6,16,38-40} demonstrated that the interface type and domain size can be precisely controlled. This promises an effective means to tailor the electron properties of planar GPBN heterostructures. For instance, Bernardi et al.³⁹ showed that the armchair interface in the GPBN heterostructure contributes to a finite band gap opening up to ~1.5 eV which is further tunable by the graphene/h-BN domain size.

The interfaces in planar GPBN heterostructures provide preferential locations for segregation of lattice defects, $^{41-43}$ one predominant category of which being vacancies.⁴¹ Vacancies provide a means to introduce magnetic moments^{33,42,44} and to manipulate the magnetic state.^{27,33,34,44} However, the associated magnetic moments, induced by 2p-like dangling orbitals, are weakly coupled with electrons or hole carriers.^{27,34,45} Meanwhile, vacancies generally have low migration barriers, thus they are susceptible to thermally activated motions and configuration changes^{34,41-44} that induce fluctuation in the

magnetism. The aforementioned weak coupling and thermal instability of vacancies post serious limitations to spintronic related applications. Recently transition metals (TM) with dorbitals have been studied as another group of agents to introduce magnetism in graphene and h-BN.^{27,34,46} The electronic states from d-orbitals give rise to strong spin-orbital coupling. In addition, with the outer shell electron configurations range from 4s²3d¹ (Sc) to 4s²3d¹⁰ (Zn), TM metals constitute a rich set of choices toward controlling magnetic states.

When introduced into GPBN heterostructures, TM atoms, as impurity atoms, may also have the tendency to segregate at graphene/h-BN interfaces, therefore necessarily interacting with vacancies. In this regard, we studied the interplay between TM atoms and single vacancies (SVs) at an armchair (AC) interface in the monolayer GPBN heterostructure. The energetics and magnetic states of the TM-SV complexes, formed by TM atoms adsorbed at different interface SVs, were examined. Detailed analyses of band structures and local charge transfer behaviors at the TM-SV complexes were then performed to elucidate the origin underlying the magnetism at those defect complexes. Furthermore, the application of strain and electric field as means to further engineer the magnetic states were explored. Finally the implications of our results to the design of tunable low-dimensional spintronic devices was discussed.

2. COMPUTATIONAL METHODOLOGY

Spin-polarized DFT calculations employing the Perdew-Burke-Ernzerhof (PBE) functional^{47,48} and projector aug-

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mented-wave $(PAW)^{49}$ method were performed using the Vienna ab initio simulation package (VASP).⁵⁰ Test case calculations using other functionals, i.e., PBE+U and B3LYP, have been performed, which yield essentially the same results as the ones obtained using PBE (see the Supporting Information). In all calculations, a 12 × 6 supercell, consisting of 144 atoms with equal partition of the graphene and *h*-BN domains was used, as illustrated in Figure 1a. The graphene and *h*-BN



Figure 1. (a) Supercell (prior to vacancy creation and transition metal doping) used in the DFT calculations, where *C*, *B*, and *N* atoms are colored brown, green, and silver respectively; the subfigure on the right illustrates the local configuration of a vacancy, where d_1 , d_2 , and d_3 are the pairwise distances between the three atoms immediately neighboring the vacancy with $d_1 < d_2 < d_3$. The band structures along with partial charges of occupied (cyan contours) and unoccupied (yellow contours) impurity states are shown for GPBN systems with a (b) B_{SV} (c) N_{SV} (d) C_{SV}^B , and (e) C_{SV}^N at the graphene/*h*-BN interface. The bands consist of vacancy impurity states are colored, with the sizes of circle symbols in those bands indicating the respective partitions of impurity states. $E_{\rm F}$ denotes the Fermi energy.

domains are connected through armchair interfaces as semiconducting GPBN heterostructures³⁹ are of interests in this study. A cutoff energy, 500 eV of the plane wave basis set and a $1 \times 3 \times 1$ k-point grid are used in all structural optimization calculations, while $7 \times 9 \times 1$ k-point grid are used in all static calculations. Benchmark calculations with larger cutoff energies up to 800 eV and denser k-point grids been performed (see Supporting Information), showing an energy difference less than 0.02 eV. The vacuum spacing between two neighboring GPBN monolayers is set as 15 Å to avoid image interactions.

Starting from the lattice configuration constructed above, SVs were created by removing designated atoms at the graphene/*h*-BN interface. There are four possible SVs at the interface, namely C vacancy neighboring a B atom, C vacancy neighboring an N atom, N vacancy and B vacancy, denoted in the following as C_{SV}^{B} , C_{SV}^{N} , N_{SV} , and B_{SV} , respectively. The rightmost subfigure in Figure 1a illustrates the local configuration at C_{SV}^{B} as a representative, where three

parameters, i.e., d_1 , d_2 and d_3 , are introduced to describe the local geometry at a SV, being the pairwise distances between the three atoms immediately neighboring the vacancy and satisfying $d_1 < d_2 < d_3$. In view of the possible effects due to defect—defect interactions across the periodic boundaries, benchmark calculations using larger supercells were performed to confirm no size dependence of our results (see the Supporting Information). The influence of van der Waals interactions has been evaluated (with the vdW-DF2 functional^{51–54} and was found to ignorable on the adsorption energetics, and magnetic and electronic properties (see the Supporting Information). As a result, van der Waals correction is not invoked in our calculations.

3. RESULTS AND DISCUSSION

3.1. Ground States of Interface SVs in GPBN Monolayer. The ground states of the four SVs, i.e., C_{SV}^B , C_{SV}^N , N_{SV} , and B_{SV} , at graphene/*h*-BN were obtained, with corresponding geometry parameters, i.e., d_i (i = 1, 2, 3), listed in Table 1. Clear differences among the d_i values of different

Table 1. Magnetism and Local Geometry Parameters (i.e., d_1 , d_2 , and d_3) of Four Single Vacancies at the Graphene/*h*-BN Interface

system	C_{SV}^B	C_{SV}^N	N_{SV}	B_{SV}
magnetic moment $(\mu_{\rm B})$	2 (2 ⁴²)	1.68 (2 ⁴²)	1 (1 ³³)	1 (3 ³³)
d_1 (Å)	1.90 (C-	1.80 (C–	2.06 (B-	2.23 (C–
	B)	C)	B)	N)
d_2 (Å)	2.52 (C-	2.53 (C-	2.52 (C-	2.47 (C–
	B)	N)	B)	N)
<i>d</i> ₃ (Å)	2.58 (C–	2.59 (C–	2.61 (C–	2.63 (N–
	C)	N)	B)	N)

^{*a*}The numbers in parentheses are magnetic moments of corresponding single vacancies in graphene (i.e., C single vacancies) or h-BN (i.e., B and N single vacancies).

SVs are observed, indicating different local bond reconstructions. To understand the bonding situations at those SVs, we examined the corresponding impurity partial charge contours in Figure 1. We note σ bond reforming within the pentagon at C_{SV}^B , C_{SV}^N and N_{SV} as indicated by the overlapping of dangling σ electrons (cf. Figure 1b–d), while no overlapping is observed at B_{SV} (cf. Figure 1e). The above observations well echo with the fact that B_{SV} exhibits the largest d_1 (cf. Table 1).

The corresponding band structures of those vacancydecorated GPBN systems were then calculated, also shown in Figure 1. The contributions from dangling orbitals are illustrated by circle symbols, colored differently for different bands. A few observations can be drawn from the band structure plots. First we see that the impurity states are hybridized with bulk states of GPBN. Second we note that the impurity states from different bands coincide into the same energy level, indicating that those states remain localized. Additionally, for the cases of C_{SV}^N and N_{SV} , dispersive distributions of impurities states (represented by small symbols in Figure 1c,d), though insignificant, also exist and are hybridized with bulk GBN states.

The magnetic moments associated with the four interface SVs are also listed in Table 1, where we see that B_{SV} and N_{SV} both exhibit a magnetic moment of 1 μ_B while C_{SV}^B and C_{SV}^N show magnetic moments of 2 and 1.68 μ_B respectively. The origin of such magnetic moments can be traced to the bonding

configuration and band structures in Figure 1, elaborated as follows.

For C_{SV}^{B} because of the C–B bond reconstruction in the 5ring, there is one dangling σ bond left from the other C atom. Meanwhile, dangling π orbitals are also present in the C–C–B trio at C_{SV}^{B} . The two types of dangling bonds are well indicated in the band diagram shown in Figure 1b, where two groups of impurity states, sitting at ~1.3 and ~0.1 eV below $E_{\rm F}$ (at Γ point) respectively. These thus lead to an overall magnetic moment of 2 $\mu_{\rm B}$. Similarly to $C_{SV}^{\rm B}$, at $C_{SV}^{\rm N}$ there are also a bond reconstruction in the 5-ring and dangling π orbitals in the C-C-N trio surrounding the SV. Yet the bond reconstruction results in the formation of a C-C bond, and consequently all dangling σ bonds on C atoms are saturated. Accordingly only one group of impurity states, at ~1.2 eV below $E_{\rm F}$ (at Γ point), is observed (see Figure 1c). The lack of dangling σ bonds also renders less significant polarization at C_{SV}^N than C_{SV}^B and thus a smaller magnetic moment of 1.68 $\mu_{\rm B}$ (than 2 $\mu_{\rm B}$, the one for C_{SV}^{B}). For N_{SV} , with the σ bond reforming, the dangling bond of the C atom is not saturated and local atoms are thus polarized, in accordance to which, a localized energy level appears at ~ 0.2 eV below the Fermi level $E_{\rm F}$ (at Γ point) in the band diagram shown in Figure 1d. Consequently a total magnetic moment of 1 $\mu_{\rm B}$ is resulted. For B_{SV} , the reforming of σ bond does not occur, and no localized band is observed. There exist conjugated π orbitals among the C–N–N trio encircling B_{SV} and one dangling σ bond from the C atom, which are reflected in the band diagram in Figure 1e that shows two group of impurity states, one sitting just below $E_{\rm F}$ (at Γ point) while the other is at ~0.3 eV below $E_{\rm F}$ (at Γ point). Though these bonding features closely resemble the ones of C_{SV}^{B} , B_{SV} only exhibits a much smaller magnetic moment of 1 $\mu_{\rm B}$. This discrepancy is likely attributed to the large electronegativity of N atoms which leads to relative localization of electrons in the C–N–N trio and thus a much weaker π bond than the one at C_{SV}^B .

3.2. Interplay between TM Atoms and Interface SVs in GPBN Monolayer. In the situation when TM atoms and SVs coexist at the graphene/h-BN interface, the adsorption energy of a TM atom at a SV, denoted as E_a can be analyzed as

$$E_{a} = E(\text{GPBN}_{SV}^{TM}) - E(\text{GPBN}_{SV}) - E(\text{TM})$$
(1)

where $E(\text{GPBN}_{SV})$, $E(\text{GPBN}_{SV}^{TM})$ and E(TM) denote calculated total energies of an GPBN sheet containing one SV, corresponding GPBN sheet with a TM atom at the SV, and the TM in vacuum. It should be noted that in the above definition we assume the adsorption procedure occurs as isolated TM atoms in gas phase depositing into GPBN. We also considered another definition where a stable TM crystal is used as the reference state for the TM atom (see Supporting Information). The values of E_a for various TM atoms at the four interface SVs are shown in Figure 2a. We see that in general the TM atoms form strong binding with SVs as evidenced by the appreciably negative values of E_a . The strong binding is also reflected by the appreciable distortion induced by the adsorption of a TM atom at a SV, as illustrated in the inserted figure in Figure 2d (showing a Cr atom at N_{SV} as an example). It is also worth noting that the TM adsorption generally induces noticeable out-of-plane displacement (see the Supporting Information). The corresponding values of electronegativity and elevation (defined as the vertical distance between the TM atom and GPBN sheet) of TM atoms at different SVs are presented in Figure 2b,d. We see that in



Figure 2. (a) Adsorption energies, (b) magnitudes of elevation, and (c) magnetic moments, of TM atoms at an AC interface of the GPBN heterostructure. (d) The values of electronegativity of TM atoms, where the inset figure shows the relaxed configuration of a Cr atom adsorbed at N_{SV} .

general higher electronegativity and lower elevation lead to a lower E_{av} i.e., stronger binding between the adsorbed TM atom and the host SV.

Meanwhile, the resultant magnetic moments of the TM-SV complexes are shown in Figure 2c, varying from 0 to 4 $\mu_{\rm B}$. As elaborated below, these magnetic states can be understood from the interplay between valence electrons of the TM atom with dangling orbitals at the SV. We follow a procedure similar to the one outlined by Santos et al.⁵⁵ and divide the TM atoms into three groups: (i) Sc^R and Ti; (ii) V, Cr, and Mn^R; (iii) Fe, Co, Ni^R, Cu, and Zn, for ease and clarity of the explanation. For each group, we select one TM atom as a representative (as indicated by the superscript "R") and consider the four corresponding TM-SV complexes.

3.2.1. Sc^R and Ti. In this group Sc and Ti have 3 and 4 valence electrons in the outer electron shell, respectively. From the spin polarized band structures (SPBSs) and local spin density plots shown in Figure 3, direct charge transfer is observed for the case of $Sc-B_{SV}$ where the three valence electrons of Sc saturate three dangling bonds at B_{SV} , resulting in zero magnetism. While for the case of Sc- N_{SV} , instead of charge transfer, the sp orbitals of N_{SV} hybridize with the sd orbitals of Sc to produce a state of $spd^{4\uparrow}$ $spd^{2\downarrow}$ and thus a magnetic moment of 2 $\mu_{\rm B}$. The above scenarios also apply to Ti atom, i.e., there is one valence electron left after saturating the three dangling bonds at B_{SV} resulting in a magnetic moment of 1 $\mu_{\rm B}$ for Ti- B_{SV} , while the hybridization at Ti- N_{SV} leads to a state of spd^{4†} spd^{3↓} and thus a magnetic moment of 1 μ_B . For the unreconstructed C_{SV}^{B} or C_{SV}^{N} four dangling bonds exist. These dangling bonds are fully saturated upon adsorption of Ti, thus resulting in zero magnetism. On the other hand, Sc is one valence electron short for saturating those dangling bonds, and consequently both $Sc-C_{SV}^{B}$ and $Sc-C_{SV}^{N}$ exhibit a magnetic moment of 1 μ_B . In the particular case of Sc- C_{SV}^B there is direct charge transfer from Sc to C, and meanwhile the remaining valence electrons of Sc hybridize with the dangling p orbital of B. This is indicated in Figure 3c where one band is seen to be at around -0.5 eV in the spin-up band diagram, while sit above $E_{\rm F}$ in the spin-down band diagram. For the case of $Sc-C_{SV}^N$ charge transfer occurs between Sc and C and N atoms. Accordingly in Figure 3d a global shift of energy levels is observed. We can also



Figure 3. Spin-polarized band structures of (a) $\text{Sc-}B_{SV}$ (b) $\text{Sc-}N_{SV}$ (c) $\text{Sc-}C_{SV}^{B}$ and (d) $\text{Sc-}C_{SV}^{N}$. The projected eigenvalues contributed from sp orbitals of dangling C, B, and N atoms are indicated by open circles, whereas the projected eigenvalues contributed from sd orbitals of TM atoms are shown by solid circles. (e) Using Sc as the representative of group (i) TMs, the contributions of surrounding atoms to the magnetism at various Sc–SV couples are illustrated.

see from Figure 3e that the magnetism of $\text{Sc-}C_{SV}^{B}$ mainly originates from the interaction between Sc and B atoms, while the one of $\text{Sc-}C_{SV}^{N}$ mainly comes from the dangling π bond.

3.2.2. V, Cr, and Mn^R. As the number of valence electrons increases, the nonbonding 3d levels become populated. The TM atoms in this group have more than 4 valence electrons but less than 5 electrons in the 3d shell, which gives a strong localized d character.⁵⁵ The TM-SV complex exhibits a high-spin state and the magnetic moment is mainly localized at the TM atom (see the example case of Mn–SV illustrated in Figure 4e). Consequently monotonically increasing magnetic moments (with respect to the number of valence electrons) are expected for TM-SV complexes. The trend is well observed in



Figure 4. Spin polarized band structure of (a) $\text{Mn-}B_{SV}$, (b) $\text{Mn-}N_{SV}$, (c) $\text{Mn-}C_{SV}^{B}$, (d) $\text{Mn-}C_{SV}^{N}$. The projected eigenvalues contributed from sp orbitals of dangling C, B, and N atoms are indicated by open circles, whereas the projected eigenvalues contributed from sd orbitals of TM atoms are shown by solid circles. (e) Using Mn as the representative of group (ii) TMs, the contributions of surrounding atoms to the magnetism at various Mn–SV couples are illustrated.

Figure 2c except for $Mn-N_{SV}$. This exception can be attributed to the particular hybridization between sd orbitals of Mn with sp orbitals of dangling *B* and *C* atoms. This hybridization is reflected in Figure 4b where the impurity states of Mn are observed in the valence bands of both spin-up and spin-down band diagrams.

3.2.3. Fe, Co, Ni^R, Cu, and Zn. In this group, with the number of outer shell electrons continuing to increase, the 3d orbitals shift to low energy levels. In the particular cases of Cu and Zn, the 3d orbitals are fully occupied. In a previous study by Santos et al., ⁵⁵ the bonding between these TM atoms and a carbon SV (denoted as C_{SV}) in monolayer graphene was thoroughly investigated. They showed that for the TM- C_{SV} complex the impurity states close to E_F are predominately contributed by the C atoms neighboring C_{SV} and the nonbonding 3d levels of TM atoms are occupied, resulting in the oscillation of magnetic moment between 0 and 1 μ_B .⁵⁵ Similar bonding characteristics are observed for those interface TM-SV complexes we considered, as illustrated by the band diagrams shown Figure 5 where we see those impurity states



Figure 5. Spin polarized band structure of (a) Ni- B_{SV} , (b) Ni- N_{SV} , (c) Ni- C_{SV}^{B} , (d) Ni- C_{SV}^{N} . The projected eigenvalues contributed from sp orbitals of dangling C, B, and N atoms are indicated by open circles, whereas the projected eigenvalues contributed from sd orbitals of TM atoms are shown by solid circles. (e) Using Ni as the representative of group (iii) TMs, the contributions of surrounding atoms to the magnetism at various Ni–SV couples are illustrated.

largely come from dangling *C* and *B* or *N* atoms. Not surprisingly the magnetic moment of such TM-SV complex in GPBN also oscillates between 0 and 1 $\mu_{\rm B}$ (see Figure 2c). Also we can see from Figure 2c that the magnetic moment of TM- B_{SV} (or TM- N_{SV}) is always offset from the one of TM- C_{SV}^B (or TM- C_{SV}^N) by 1 $\mu_{\rm B}$. This offset is directly attributed to the difference in the number of dangling bonds of the unconstructed SVs, i.e., 3 for B_{SV} (or N_{SV}) and 4 for C_{SV}^B (or C_{SV}^N).

3.3. Further Engineering of Magnetic States of Interface TM-SV Complexes. In addition to the pristine magnetic moment obtained in TM-GPBN, the magnetic states can be further engineered via strain and electric field, discussed below.

3.3.1. Strain Engineering. As discussed above, the adsorption of a TM atom on SV is accompanied by significant lattice distortion. This hints the importance of deformation in

TM-SV interactions. In this regard, we explore the possibility of manipulating the magnetic states of TM-SV couples through strain engineering. Here we consider a strain range from -5% to 5%. This strain range is expected to be feasible for the GPBN given that monolayer graphene and *h*-BN can withstand strains up to 10%.^{56–59} For simplicity, below we focus our investigation on biaxial strain $\varepsilon_{\rm b}$, and select two TM-SV systems, namely, Cr- N_{SV} and Zn- $C_{SV}^{\rm E}$ as representatives.

The magnetic moments of the two systems as functions of strain are shown in Figure 6a, where a transition from low-spin



Figure 6. (a) Magnetic moments of $Cr-N_{SV}$ and $Zn-C_{SV}^B$ as functions of the bixial strain $\boldsymbol{\varepsilon}_b$. The density of states (DOS) plots of (b) Cr- N_{SV} and (c) $Zn-C_{SV}^B$ under different strain states. The local atomic configurations and deformation charge density contour plots at (d) $Cr-N_{SV}$ and (e) at $Zn-C_{SV}^B$ under different strain states. In (d) and (e), Cr and Zn atoms are indicated by large red and silver spheres respectively, while C, B, and N are indicated by small brown, green, and white spheres.

state to high-spin state is induced by compressive strain ($\varepsilon_{\rm b} \leq -5\%$) for Cr- N_{SV} and by tensile strain ($\varepsilon_{\rm b} \geq 5\%$) for Zn- C_{SV}^{B} . These transitions can also be inferred from the DOS plots, shown in Figure 6b,c. For the Cr- N_{SV} system, there is an apparent drop in the Fermi level when it is subjected to sizable compressive strain (e.g., $\varepsilon_{\rm b} = -5\%$). For the Zn- C_{SV}^{B} system, the DOS stays nonpolarized under compression or small tension conditions, but becomes polarized and shows splitting of energy levels at a large tensile strain of $\varepsilon_{\rm b} = 5\%$.

The magnetism evolution observed above can be understood from strain induced bonding reconstructions, elaborated as follows. As seen in Figure 6d, the two otherwise dangling B atoms are brought together by the large compressive strain (e.g., $\varepsilon_{\rm b} = -5\%$) to form a bond, as evidenced by the obvious overlap of electron clouds. One thing to note is that a compressive strain may induce buckling in the GPBN sheet (see the Supporting Information). The occurrence of buckling is found to not affect the characteristics of strain-induced local lattice reconstruction and transition in magnetic states, but can influence (albeit little) the exact values of strain at which those reconstruction and transition events occur.

For the case of $Zn-C_{SV}^B$, a C–B bond exists under strain-free condition, but is broken under sizable tensile strain (e.g., $\varepsilon_b =$ 5%), as shown in Figure 6e. This bond breakage causes $Zn-C_{SV}^B$ to become polarized, leading to a nonzero magnetic moment. Similar magnetism evolution phenomena and associated bonding reconstruction mechanisms have been observed in other TM-SV systems.

3.3.2. Electric Field Engineering. Meanwhile, external electrostatic field has also been proved as an effective method to engineer the electronic structure and magnetism of 2D semiconductors.^{34,60} The TM-GPBN systems with high-spin states can be regarded as a dipole where the TM atom is positively polarized while the SV-decorated GPBN sheet is negatively polarized. This brings the possibility of electric field engineering perpendicular to the GPBN sheet, as schematically illustrated in Figure 7a. Below we demonstrate the application of electric field engineering using the Cr-SV_N system as an example.



Figure 7. (a) Schematic illustration of electric field engineering of TM-GPBN system. (b) The magnetic moment of the $Cr-SV_N$ system as a function of the electric field EV, with the two inserted figures showing the polarization state at a small EV (i.e., 1 V/nm) and large EV (i.e., 2 V/nm) respectively. (c) DOS plots for the $Cr-SV_N$ system under different electric fields. E_{MA} and E_{mi} denote the majority bandgap and minority bandgap, respectively.

As seen in Figure 7, accompanying the increasing of electric field (EV), there is a transition from a low-spin state (magnetic moment of 3 $\mu_{\rm B}$) to to a high-spin state (magnetic moment of 5 $\mu_{\rm B}$). Different from strain engineering, electric field engineering does not really alter the local lattice configuration at a TM-SV. The change in the magnetic moment comes from the modification of overall polarization of the TM-GPBN system. Examining Figure 7b-d, one can see that, under relatively small electric field (<2 V/nm), polarization within the TM-GPBN system is localized and there is no change of the magnetic moment. As the electric field continues to increase (≥ 2 V/nm), the polarization propagates throughout the whole GPBN sheet, and the magnetic moment increases to 5 $\mu_{\rm B}$.

Meanwhile, as can be inferred from the DOS plots show in Figure 7c, electric field engineering also induces half metallicity. In particular, the bandgap for majority spin DOS ($E_{\rm MA}$) continues to decrease as the electric field increases while the

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bandgap for minority spin DOS ($E_{\rm mi}$) remains to be ~0.7 eV. The origin of half metallicity can be attributed to the electric field induced propagation of the polarization from interface into graphene domain, as illustrated by the inserted figures in Figure 7b. Similar phenomena have been previously reported for graphitic materials.^{21,24,61-63}

4. CONCLUSION

To conclude, first principle density functional theory calculations were employed to study the interplay between a series of transition metal (TM) atoms and single vacancies (SVs) at the armchair interface in an in-plane graphene/h-BN (GPBN) monolayer heterostructure. The TM-SV complexes were shown to give rise to a rich set of magnetic states. Through detailed analyses of band structures and charge transfer behaviors, the magnetism at those TM-SV complexes was shown to originate from the interactions between valence electrons of the TM atom with dangling orbitals at the SV. Moreover, it was demonstrated that, through the application of strain and electric field, the magnetic state at a TM-SV complex can be modulated. Such modulation can be attributed to deformation induced alteration in bonding configuration and electric field induced propagation of the polarization. The present findings suggest an integrated route combining TM doping, defect engineering, strain, and electric field engineering to enrich and manipulate the magnetic states of GPBN heterostructures, providing new information toward the design of tunable low-dimensional spintronic devices.

ASSOCIATED CONTENT

Supporting Information

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Benchmark tests of k-grid, supercell size, and exchangecorrelation functional adsorption energy definition and van der Waals interactions (PDF)

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Notes

The authors declare no competing financial interest.

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