Structural, electronic, and magnetic properties of transition-metal atom adsorbed two-dimensional GaAs nanosheet*

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By using first-principles calculations within the framework of density functional theory, the electronic and magnetic properties of 3d transitional metal (TM) atoms (from Sc to Zn) adsorbed monolayer GaAs nanosheets (GaAsNSs) are systematically investigated. Upon TM atom adsorption, GaAsNS, which is a nonmagnetic semiconductor, can be tuned into a magnetic semiconductor (Sc, V, and Fe adsorption), a half-metal (Mn adsorption), or a metal (Co and Cu adsorption). Our calculations show that the strong p–d hybridization between the 3d orbit of TM atoms and the 4p orbit of neighboring As atoms is responsible for the formation of chemical bonds and the origin of magnetism in the GaAsNSs with Sc, V, and Fe adsorption. However, the Mn 3d orbit with more unpaired electrons hybridizes not only with the As 4p orbit but also with the Ga 4p orbit, resulting in a stronger exchange interaction. Our results may be useful for electronic and magnetic applications of GaAsNS-based materials.

Keywords: GaAs nanosheet, adsorption, transition-metal atom, magnetic properties

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1. Introduction

Since graphene was found by Novoselov *et al.*,[1] it has drawn a lot of attention because of its unique properties such as high electron mobility, "massless" Dirac electrons near the *K* point, and anomalous quantum Hall effect at room temperature.[2,3] Inspired by graphene, other two-dimensional (2D) layered crystalline materials with atomic thickness have attracted great research interests in recent years, such as silicene,[4–7] phosphorene,[8,9] borophene,[10,11] metal oxides,[12,13] transition-metal dichalcogenides,[14–17] and III–V compounds.[18,19] Among the III–V compounds, GaAs nanosheets (GaAsNSs) based materials have been studied extensively both experimentally,[20,21] and theoretically.[19,22] According to the work of Şahin *et al.*,[22] the pristine GaAsNS is a nonmagnetic semiconductor with an estimated indirect bandgap of 1.29 eV. So if we can induce a controllable magnetism to GaAsNS, it could be utilized as another potential dilute magnetic semiconductor system.

It is known that transition metal (TM) atoms adsorption is an effective approach to modulate the magnetic properties of grapheme-like 2D materials. There are a large number of studies on the interaction between graphene and transition metal,[23–28] especially, perfect[28–30] and defective[31] graphenes with a single TM adatom have been found to exhibit interesting magnetic behaviors. Recently, the adsorption effects on the magnetic properties of monolayer phosphorene were also studied using first-principles calculations.[32] However, theoretical work has rarely been reported on the magnetic properties of 3d TM atoms adsorbed GaAsNSs. Based on these facts, here we present the structural, electronic, and magnetic studies of 3d TM atoms adsorbed GaAsNSs with first-principles calculations. To make a comprehensive comparison, all 3d TM atoms from Sc to Zn are studied. It is found that the 3d TM atoms decorated GaAsNSs show different magnetic properties depending on the different species of TM atoms.

2. Method

The calculations were performed using the spin-polarized density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP).[33] The projector augmented wave (PAW) pseudopotentials[34] were used to describe the electron–ion interactions and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)[35] was used to treat the exchange–correlation interaction between electrons. In our calculations, the kinetic-energy cutoff for the plane-wave expansion was set to 400 eV. All atoms in the unit cell were fully relaxed until the force on each atom was less than 0.01 eV/Å. Electronic energy minimization was performed with a tolerance of 10^{-4} eV. The Brillouin zone (BZ) sampling was performed using a $5\times5\times1$ grid for static calculations and density of state (DOS) calculations. A vacuum layer thicker than 16 Å perpendicular to the sheet (along the *z* axis) was applied to avoid the interaction between the

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sheets caused by the periodic boundary condition.

3. Results and discussion

The top and side views of the structure under consideration are presented in Figs. 1(a) and 1(b), respectively. A 4 × 4 supercell of 2D GaAsNS is composed of 16 Ga atoms and 16 As atoms, which are repeated along the x and y directions. As the hollow site (center of the hexagonal ring formed by 3 Ga atoms and 3 As atoms) was found to be energetically favorable when 3d TM atoms adsorbed on silicene,[36] phosphorene,[32,37] and graphene nanosheets,[29,38] in our calculations, we are mainly interested in the 3d TM atoms adsorbed on the hollow site. We put the TM atoms at the center of the hexagonal ring formed by 3 Ga atoms and 3 As atoms and in the same plane with GaAsNS. To discuss the stability of different 3d TM atom adsorbed GaAsNS systems, we calculate the binding energy with the following equation:

$$E_{\mathrm{b}} = E_{(\mathrm{GaAsNS})} + E_{(\mathrm{atom})} - E_{(\mathrm{atom-GaAsNS})}, \qquad (1)$$

where $E_{(\mathrm{GaAsNS})}$ is the total energy of the isolated GaAsNS, $E_{(\mathrm{atom})}$ is the total energy of the corresponding adsorption atom in its ground state, and $E_{(\mathrm{atom-GaAsNS})}$ is the total energy for the optimized equilibrium configuration of the TM–GaAsNS system. For instance, a larger adsorption energy means a stronger binding of the 3d TM atom to the surface of GaAsNS.

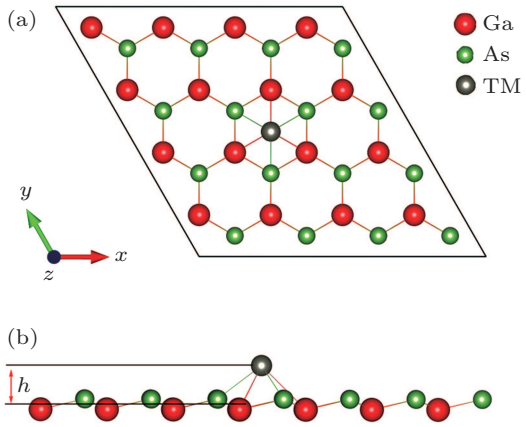


Fig. 1. (color online) (a) Top view and (b) side view of the model of 3d TM atom adsorbed GaAsNS.

The optimized structures are displayed in Table 1. As the TM atomic radii are larger than those of the Ga and As atoms, the metal atoms displace outwards from the GaAs plane in the range of 0.237 Å (for Cr) to 2.744 Å (for Zn). As shown in Fig. 2(a), the elevation h and bond lengths decrease from Sc to Mn as the atom size decreases, and go up from Fe to Zn as the bonding becomes weaker. By analyzing the bond length, we also find that the adsorbed TM atom is slightly getting closer to the Ga atoms and farther away from the As atoms as the atomic number of the TM atom increases.

Table 1. The calculated TM atom elevation h, TM–Ga and TM–As average distances (bond lengths), binding energy, magnetic moment, and conductivity of different TM atoms adsorbed GaAsNS systems.

Adatom	h/Å	TM–Ga/Å	TM–As/Å	E_{b}/eV	M/μ_{B}	Conductivity
Sc	–2.046	2.83	2.62	4.30	1	semiconductor
Ti	–1.128	2.64	2.47	4.55	0	semiconductor
V	–0.657	2.53	2.40	3.25	1	semiconductor
Cr	–0.237	2.41	2.35	1.07	0	semiconductor
Mn	–0.272	2.38	2.36	1.19	1	half-metal
Fe	–0.341	2.37	2.39	2.97	2	semiconductor
Co	–0.578	2.38	2.46	3.24	0	metal
Ni	–0.808	2.40	2.54	2.86	0	semiconductor
Cu	–1.010	2.52	2.59	1.82	0	metal
Zn	–2.744	3.42	3.82	0.13	0	semiconductor

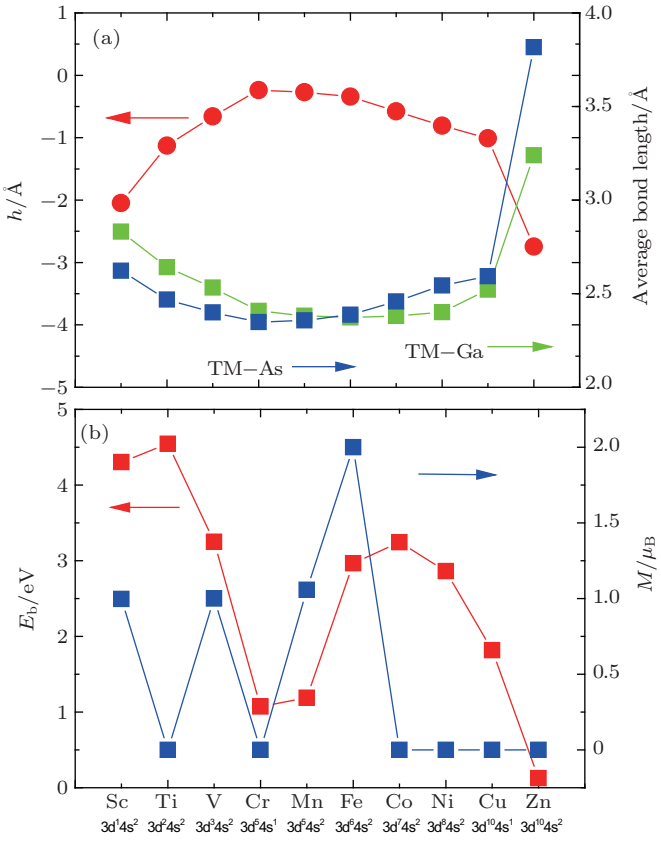


Fig. 2. (color online) (a) TM atom elevation h and TM–As, TM–Ga average bond lengths of 3d TM atoms adsorbed GaAsNSs (red, blue, and green curves, respectively). (b) Binding energy and magnetic moment of 3d TM atoms adsorbed GaAsNSs (red and blue curves, respectively). The lines are to guide the eyes.

From Fig. 2(b), we can see that when the 3d-shell of the adsorbed TM atoms becomes half-full or full, the binding energy of the TM atom adsorbed GaAsNS system reaches a minimum. As a result, the full d-shell Zn atom adsorbed GaAsNS system does not have a considerable binding, its binding energy is 0.13 eV, which suggests that the Zn atom easily diffuses on the surface of GaAsNS; this is in accordance with the largest elevation h of the Zn atom. On the contrary, the binding energies of Sc, Ti, V, Fe, Co, and Ni are relatively higher, and

the Sc and Ti adsorptions are the most energetically favorable ones.

An important aspect of TM atoms adsorption on 2D materials is the magnetic behavior of the adsorbed systems. In Fig. 2(b), we plot the calculated total magnetic moments of the TM-adsorbed GaAsNSs. It is noted that in Sc to Mn adsorbed situations, an oscillated behavior occurs: for Ti and Cr with even numbers of valence electrons, the corresponding adsorbed systems are nonmagnetic, while for Sc, V, and Mn with odd numbers of valence electrons, the corresponding adsorbed systems are magnetic. In Fe to Zn adsorbed situations, except the total magnetic moment of the Fe adsorbed system is $2\mu_B$, the Co, Ni, Cu, Zn adsorbed systems are nonmagnetic.

To clarify the origin of magnetism induced by TM atoms adsorption, the Fe adsorbed system with the largest moment is further investigated as an example. It is well known that a free Fe atom possesses a magnetic moment of $4\mu_B$,[39] when it is adsorbed on GaAsNS, the magnetic moment of the Fe atom is reduced to about $2\mu_B$. The isosurface of electron spin density of the Fe adsorbed GaAsNS is plotted in Fig. 3(a). It is shown that the magnetic moment of the system is contributed mainly by the Fe atom. To give a further insight of the electronic structure and magnetic properties, the spin-polarized total and partial DOS of the Fe adsorbed GaAsNS are plotted in Fig. 3(a). It is obvious that the adsorption of Fe atom induces a certain impurity state within the band gap of the pristine GaAsNS. The 3d orbit of Fe in the spin-up channel induces a large peak and a small peak at 3.2 eV and 0.5 eV below the Fermi level, respectively, and several strong peaks between these two peaks. It indicates that the spin-up channel of the 3d orbit of Fe is mostly occupied, while the spin-down channel is less occupied compared with the spin-up channel. So the 3d orbit of Fe makes a distinct contribution to the magnetic property of the Fe adsorbed GaAsNS. It is noticed that there are several pairs of equal-energy Fe 3d peaks and As 4p peaks located below the Fermi level on both spin channels, which indicates that the hybridization of Fe 3d and As 4p orbits results in the adsorption of Fe atom on GaAsNS by chemical bonds, not only by physical interaction. From the DOS, we can see that the p–d hybridization may play important roles in the magnetism of the Fe adsorbed GaAsNS. Similar results are found for Sc and V adsorbed GaAsNSs. The high magnetic moment of the TM atoms adsorbed GaAsNSs may be useful for spintronic devices.

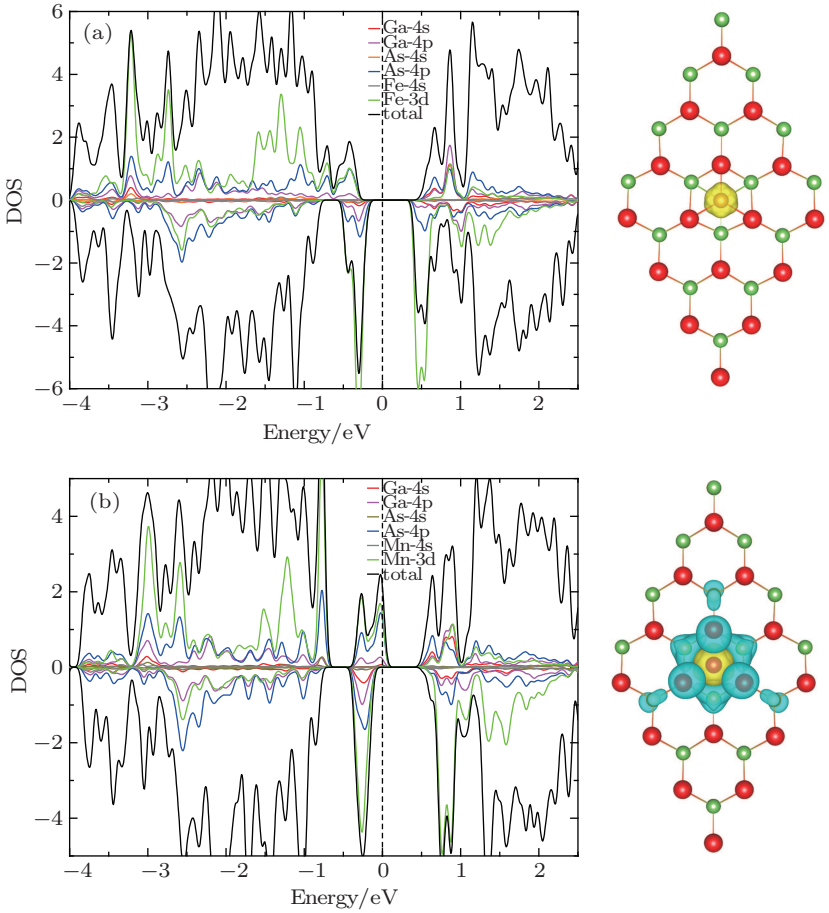


Fig. 3. (color online) The spin-polarized total and partial DOS (left panel) and the isosurface of spin density (right panel) of (a) Fe-adsorbed and (b) Mn-adsorbed GaAsNSs. The vertical dotted line indicates the Fermi energy level. The yellow and glaucous isosurfaces correspond to the spin-up and spin-down densities, respectively.

As to the Mn adsorbed GaAsNS, things become more interesting. The spin-polarized DOS analysis reveals that the Mn adsorbed GaAsNS is half-metallic, i.e., the spin-up channel behaves as a metal, while the spin-down channel acts as a semiconductor, as shown in Fig. 3(b). Spin polarization $P_{(\mathrm{EF})}$, based on the definition[40]

$$P_{(\mathrm{EF})} = (D_{(\mathrm{EF},\uparrow)} - D_{(\mathrm{EF},\downarrow)})/(D_{(\mathrm{EF},\uparrow)} + D_{(\mathrm{EF},\downarrow)}), \qquad (2)$$

where $D_{(\mathrm{EF},\uparrow)}$ and $D_{(\mathrm{EF},\downarrow)}$ represent the DOS of the spin-up channel and the spin-down channel at the Fermi level, is found to be 100%. As most transport phenomena take place around the Fermi level, this high spin polarization ensures a high degree of passage of the preferred spin. Thus, the Mn adsorbed GaAsNS seems to be a good candidate for spintronic applications. As the spatial spin density shown in Fig. 3(b), the Mn atom induces small negative magnetic moments in its three nearest Ga atoms and three nearest As atoms, which is different from the Fe adsorbed system. From a further analysis of the spin-polarized DOS distribution, we find that the Mn 3d orbit hybridizes not only with the As 4p orbit but also with the Ga 4p orbit strongly, in other words, the p–d hybridization between the TM 3d orbit and Ga 4p orbit in the Mn adsorbed system is stronger than that in the Fe adsorbed system, which may be attributed to the fact that the Mn atom possesses more unpaired valence electrons than the Fe atom.

Next we discuss the nonmagnetic situations. The spin-polarized total and partial DOS for six nonmagnetic TM adsorbed GaAsNSs are shown in Fig. 4. We can see that the Co and Cu adsorbed GaAsNSs exhibit metallic electronic structures as certain bands cross the Fermi level, while the Ti, Cr, Ni, and Zn adsorbed GaAsNSs act as semiconductors. As shown in Fig. 4, it is obvious that the energy range occupied by the TM 3d orbit moves from high energy to low energy as

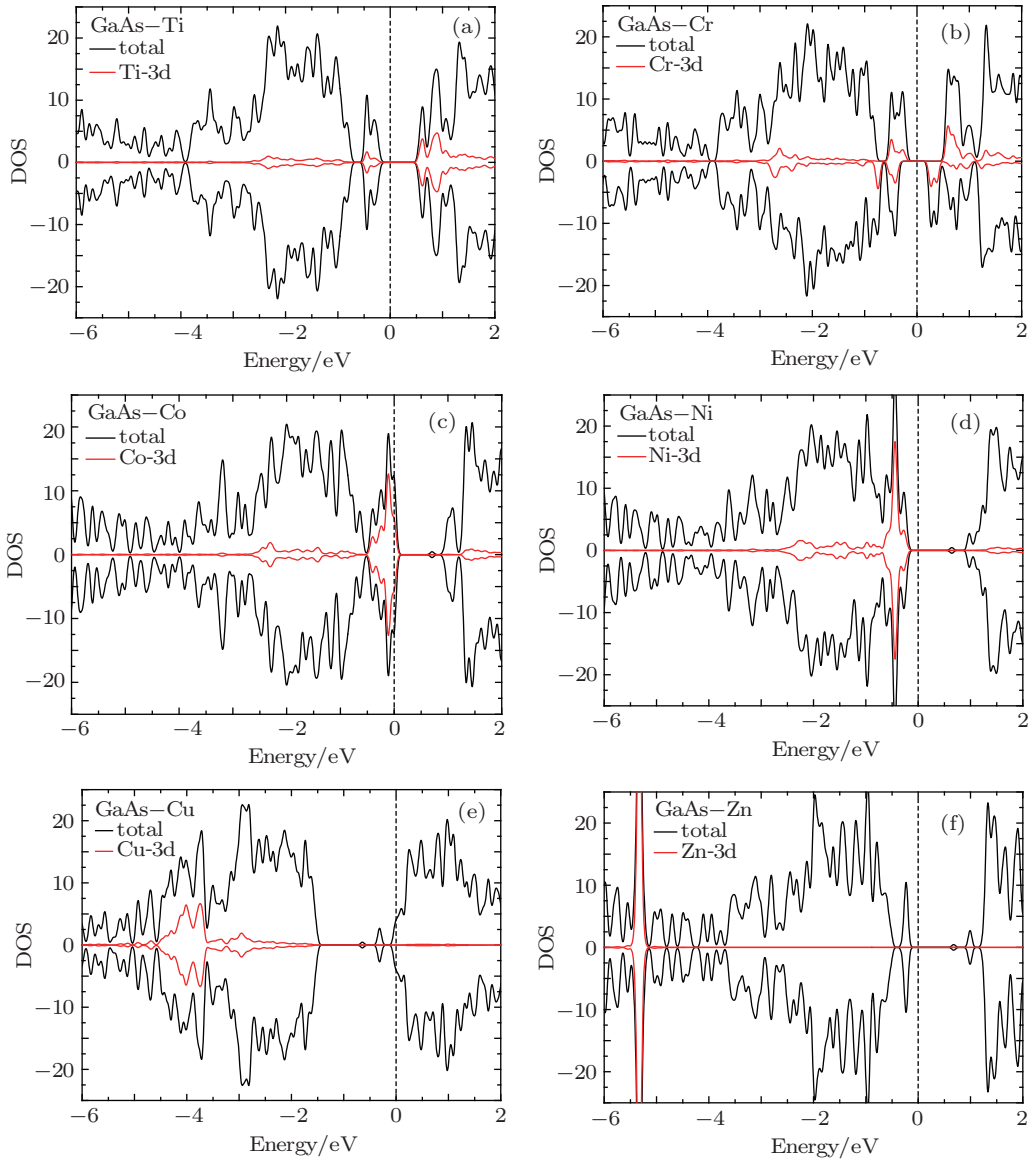


Fig. 4. (color online) The spin-polarized total and partial DOS of (a) Ti-adsorbed, (b) Cr-adsorbed, (c) Co-adsorbed, (d) Ni-adsorbed, (e) Cu-adsorbed, and (f) Zn-adsorbed GaAsNSs. The vertical dotted line indicates the Fermi energy level.

the atomic number of the TM atoms increases. The Ti 3d orbit hybridizes well with the conduction bands while the Cr 3d orbit hybridizes with both valence and conduction bands. The energy range mainly occupied by the 3d orbits of the Co, Ni, Cu, Zn atoms decreases from −0.2 eV to −5.3 eV below the Fermi level. A possible reason is that the Co, Ni, Cu, and Zn atoms have $3d^7$, $3d^8$, $3d^9$, and $3d^{10}$ electronic configurations, respectively, when the 3d shell approaches the full configuration, the activity of the 3d electron is weakened, so the lower energy range is occupied. We should note that there is no spin polarization in the nonmagnetic situations except the Cr adsorbed GaAsNS. In the Cr adsorbed situation, the spin-up and spin-down channels are asymmetrical, but the spin split does not induce any magnetic moment. This case suggests an antiferromagnetic-like coupling between the Cr atom and its surrounding Ga, As atoms.

4. Conclusion

We perform first-principles calculations on the electronic and magnetic properties of 3d TM atoms adsorbed monolayer GaAsNSs. We focus on the trend of the structural, electronic, and magnetic properties of GaAsNSs adsorbed with different types of TM atoms. We do not include the Hubbard U correction, because if the selected U is inappropriate, the trend of the physical properties may be inaccurate. The calculated results indicate that the TM atom can induce a magnetic moment in the nonmagnetic GaAsNS, and the magnetic moment localizes mainly on the 3d TM atom and its neighboring Ga or As atoms. The DOS analysis indicates that the Mn adsorbed GaAsNS is half-metallic, and its spin-up or spin-down electronic states are 100% spin polarization; this hybrid structure can therefore be applied to circuits that demand preferential transport of electrons with a specific spin. From the total DOS, we also find that the Co and Cu adsorbed GaAsNSs exhibit metallic electronic structures. The tuning of the electronic and magnetic properties in the TM atoms adsorbed 2D GaAsNSs may be useful in potential applications of spintronics.

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