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Electronic structure of Mn on the GaAs(001) surface

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The electronic structure of Mn adsorption on GaAs(001) surface is studied by using the linear muffin-tin orbital approach. The Mn adatom chemisorption on Ga-terminated surface and As-terminated surface are considered separately. A monolayer of S atoms is used to saturate the dangling bonds on one of the supercell surfaces. The layer projected density of states for a half monolayer of Mn atoms covered GaAs(001) surface are calculated and compared with that of the clean surface. The chemisorption energy and charge transfer are investigated. It is found that Mn-As interaction is stronger than Mn-Ga interaction and Mn atoms prefer to be adsorbed on the As-terminated surface. It is possible for the adsorbed Mn atoms to sit below the As-terminated surface resulting in a Mn-Ga-As mixed layer which is in agreement with the experimental results and our recent theoretical results. [S0163-1829(97)04135-0]

I. INTRODUCTION

Recently, epitaxial ferromagnetic metallic or metallic compounds thin films on semiconductor substrates attract much interest since it is anticipated that ferromagnet-semiconductor heterostructures can lead to the integration of magnetism with semiconductor electronics. It has been found that some of the Mn-based metallic compounds sharing common atoms with the underlying III-V compound semiconductors could be promising, such as MnGa, MnAs, and MnAl on GaAs(001).[1–5]

As the initial stage of interface formation, the chemisorption of Mn on the semiconductor surface is of importance for understanding the properties of the interface. Using a cluster model and the extended Hückel theory (EHT), Fu *et al.*[6] studied the chemisorption properties of a Mn atom on a GaAs(110) surface. In view of the integration of magnetic materials with compound semiconductors, the epitaxial magnetic films MnGa or MnAs on GaAs(001) substrate could have many potential applications. Recently, we have studied a single Mn atom chemisorption on GaAs(001),[7] and found that the preference adsorption sites are different for a Mn adatom on Ga face and on As face. A Mn atom prefers to be adsorbed at the fourfold hollow site on the Ga-face, and at the bridge site on the As face. It is also found that the Mn-As bond is much stronger than that of the Mn-Ga bond. For the As-face adsorption, the adsorbed Mn atom may penetrate into the surface and sit below the surface, resulting in a Mn, Ga, As mixed layer at the interface. These results are in agreement with the experimental observation.[8,9] In the previous study,[7] we emphasized the local properties of the interaction of a single Mn atom with the GaAs(001) surface by using a cluster model and the empirical EHT method. In this paper we perform a first-principles calculation with a slab model to deal with the cases of a slab of half monolayer Mn atoms chemisorption on GaAs(001) surface. The model and the calculation method are described in Sec. II. The calculated results and discussion are presented in Sec. III, and a brief summary is given in Sec. IV.

II. MODEL AND CALCULATION METHOD

In this paper, the electronic structure of a half monolayer Mn atoms adsorption on GaAs(001) surface is studied by using the linear muffin-tin orbital (LMTO) approach[10,11] based on the density function theory[12] within the local density approximation (LDA) using the Hedin-Lundqvist parametrization of correlation.[13] A standard supercell model shown in Fig. 1, named the Ga-face model, is used to describe the adsorption of a half monolayer Mn atoms on the Ga-face of the GaAs(001) surface. Figure 1(a) is the schematic diagram of the supercell which consists of four Ga atomic layers and three As atomic layers with a monolayer of sulfur atoms saturating one face of the slab, a half adsorbed monolayer of Mn, and four layers of vacuum. In the region of the slab, some empty spheres are introduced in the usual tetrahedral interstices. Figure 1(b) is the top view of the substrate slab which contains two atoms on each atomic plane. The model for the case of As-face adsorption, named the As-face model, can be obtained by exchanging the Ga and As atoms in the Ga-face model. The $4s$, $4p$ states of Ga, $4s$, $4p$ states of As, $3s$, $3p$ states of S, and the $3d$, $4s$ states of Mn are treated as valence bands.

The polar character of the GaAs(001) surface introduces some complications to the slab calculations. If the slab is not thick enough, the dangling bond states on the two sides of the slab might interact with each other and give rise to an artificial charge transfer from one face to the another. In the case of Si slab or Ge slab, for avoiding the charge transfer and decoupling the two sides of the slab, the dangling bonds can be saturated by H atoms. It is known that there are 0.75, 1.25 electrons for the Ga- and As-dangling bonds, respectively. Therefore the H saturation is not suitable for the GaAs slab. Ohno and Shiraishi[14] used fictitious H atoms with 0.75

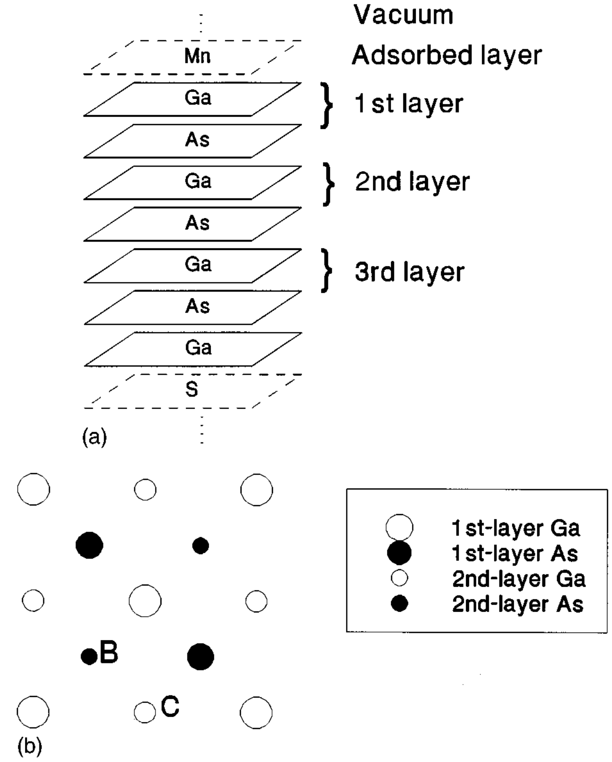

FIG. 1. (a) The schematic diagram of the supercell used for the adsorption of Mn on the Ga-terminated surface of GaAs(001). (b) The top view of the supercell. The supercell for the adsorption of Mn on the As-terminated surface of GaAs(001) can be obtained by alternating the Ga and As atoms. The label *C* denotes the adsorption site for Mn on Ga-terminated surface and *B* for the Mn- on As-terminated surface which includes one adsorption site above the As face (B_1) and one below the As face (B_2).

or 1.25 electrons to saturate the As- or Ga-dangling bonds. But the LMTO method cannot deal with fictitious atoms. In the present paper, a monolayer of sulfur atoms is introduced to saturate the dangling bonds on the slab. Since both the experimental[15,16] and theoretical[14,17] studies showed that, for the GaAs(001) surfaces, the number of electronically active dangling bond states can be dramatically reduced by the sulfur passivation, this method will be expected to improve the slab calculation for the GaAs systems.

In order to test the passivation effect, first, we take a monolayer of sulfur atoms as the adsorbed layer in Fig. 1(a), i.e., both faces of the slab are covered by one sulfur layer and the sulfur atoms are located at the ideal lattice sites for simplicity. Then we consider the clean surface by removing one of the sulfur layers. The calculated layer projected density of states (LPDOS) for the two cases are shown in Fig. 2 and Fig. 3, respectively. The density of states (DOS) for the bulk is shown by dashed line for comparison.

For the Ga-face model, it is found from Fig. 2(a) that all the LPDOS for the first, second, and third layers are quite bulklike, and there are no surface states in the energy gap when both sides of the slab are covered by a monolayer of sulfur atoms. Due to the LDA limitation, the calculated energy gap for the bulk GaAs is 0.95 eV by using the lattice constant $a = 5.65$ Å. The LPDOS for the clean surface is given in Fig. 3. It can be seen from Fig. 3(a) that, near the top of the valence band, the LPDOS for the first layer and the second layer is greatly different from that for the sulfur covered surface. A sharp peak (p) of surface states appeared near the edge of the valence band. This state is mainly contributed by Ga $4s$,$4p$ states and As $4p$ state, and damped rapidly on the second layer. The LPDOS of the third layer is still quite bulklike. These results show that the sulfur layer can effectively passivate the Ga-terminated GaAs(001) surface. Similar results has been reported by Ohno and Shiraishi.[14] Therefore the model shown in Fig. 1 can adequately simulate the Ga-terminated GaAs(001) surface. The position of the third layer is near the bottom of the slab, therefore, compared with a nonsaturation model, the sulfur passivation method is quite effective for the calculation using a smaller supercell (thinner slab and thinner vacuum) to

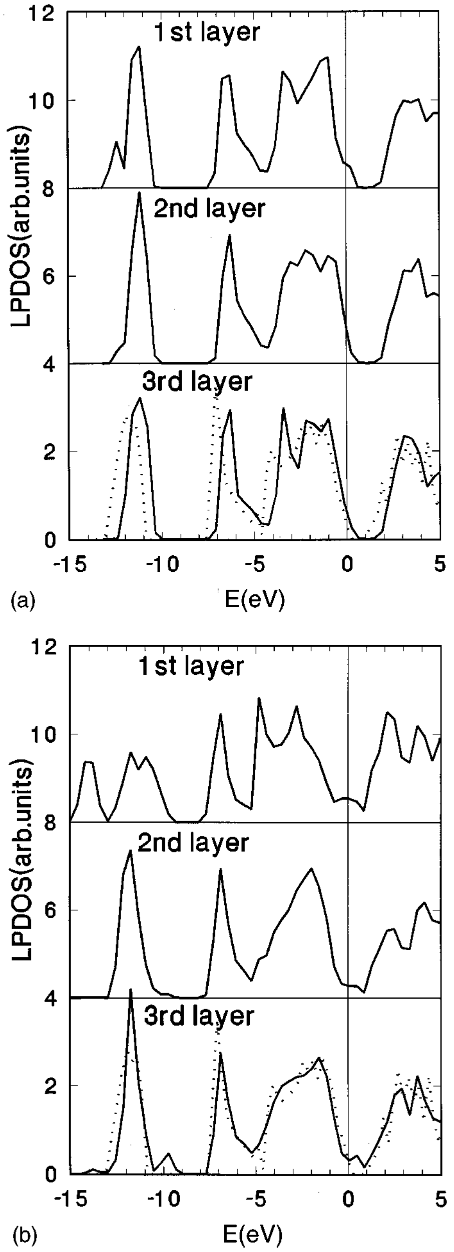

FIG. 2. The LPDOS for (a) the Ga-terminated supercell model and (b) the As-terminated supercell model with two saturation sulfur layers. The dashed line is the LPDOS for the bulk and the vertical line indicates the Fermi level.

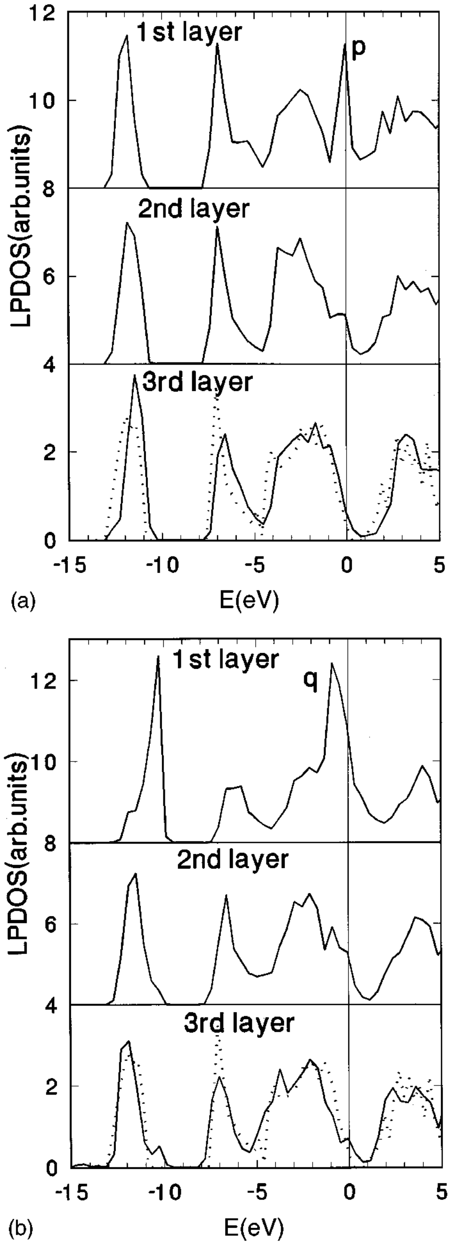

FIG. 3. The LPDOS for the clean Ga-terminated surface (a) and for the clean As-terminated surface (b). The dashed line is the LPDOS for the bulk and the vertical line indicates the Fermi level.

simulate the GaAs(001) surface and will make the calculation easier.

For the case of As-face model, the LPDOS for the above two cases are shown in Fig. 2(b) and Fig. 3(b). When both of the slab surfaces are terminated by S atoms, the LPDOS for the first layer has a large difference from that of the bulk. While the LPDOS for the second and the third layers are both bulklike. For the clean surface model, it also shows from Fig. 3(b) that the LPDOS near the top of the valence band for first layer and the second layer is very different from that of the bulk GaAs. A large sharp peak (denoted as q) appeared just below the top of the valence band with a large tail in the energy gap, which is a resonance state mainly contributed by the As $4p$ state (i.e., the dangling bond states of As). A few states coming from the interaction between S $3p$ and As $4p$ states exist in the gap. The above discussion indicates that the passivation effect of sulfur atoms on As face is not as good as that on Ga face. A similar result has also been pointed out by Ohno and Shiraishi.[14] However, the LPDOS of the third layer is also bulklike, therefore the sulfur saturated supercell for As-face model could be used for Mn adsorption on the GaAs(001) surface.

III. RESULTS AND DISCUSSION

For the adsorption of Mn on the GaAs(001) surface, our recent study[7] has shown that for the Ga-face adsorption, the stable position of Mn atom is at the fourfold hollow site, 0.23 Å above the surface [i.e., site C in Fig. 1(b)]. While for the As-face adsorption, the possible adsorption sites are bridge sites [i.e., site B in Fig. 1(b)], with a distance 1.19 Å above the surface (denoted as B_1) or 1.07 Å below the surface (denoted as B_2). Therefore we only consider the C site adsorption for a half monolayer Mn atoms on the Ga-face model and the B_1,B_2 sites adsorption on the As-face model. The positions of the Mn atoms for these adsorption sites are taken as the values given above.

A. Density of states

The LPDOS as well as the partial density of states (PDOS) of the adsorbed Mn after the adsorption of a half monolayer Mn on Ga-face and on As face are shown in Fig. 4. It is evident from Fig. 4(a) that the adsorption of Mn on Ga face has obvious effects on the LPDOS near the top of the valence band in the first layer. The surface state peak (p) for the clean surface was split into two peaks: one denoted as p_1 moves downward into the valence band and the other denoted as p_2 moves upward into the gap. These results are mainly attributed to the interaction of Mn $3d$ with Ga $4s$, $4p$ and As $4p$ in the first layer. Experimentally, Jin *et al.*[8,9] found a new state below Fermi energy after the deposition of Mn on the GaAs(001) surface. This state might correspond to the peak p_1 in our calculation. The LPDOS of the third layer remains bulklike, which indicates that the present model is reasonable. The narrow peak of the PDOS of the adsorbed Mn atom shows that adsorbed Mn is almost at its unperturbed atomic $3d$ states, which means that the interaction between Mn and the Ga face is very weak.

When a half monolayer of Mn adsorbed on the As face at B_1 site (above the surface), the LPDOS are shown in Fig. 4(b). It is found that the sharp As $4p$ resonance state peak q for the clean surface [Fig. 3(b)] disappeared, due to the fact that the adsorption of Mn atom has partly saturated the surface As-dangling bond. Due to the interaction of Mn $3d$ with As $4p$ states, part of the dangling bond states moved downward and merged into the valence band peak q_1 and the rest formed a new peak q_2 in the gap. The PDOS of the adsorbed Mn atom has a sharp peak with some dispersions. When the Mn atoms are adsorbed at B_2 sites (under the surface), the PDOS of Mn atom shown in Fig. 4(c) is split completely into two peaks which reflects an even stronger interaction of Mn with the substrate. The peak with lower energy corresponds to the bonding states and the one with higher energy corresponds to the nonbonding states. This splitting is induced by the strong interaction of the $3d$ state of Mn with the $4p$ states of As atoms around the Mn atom.

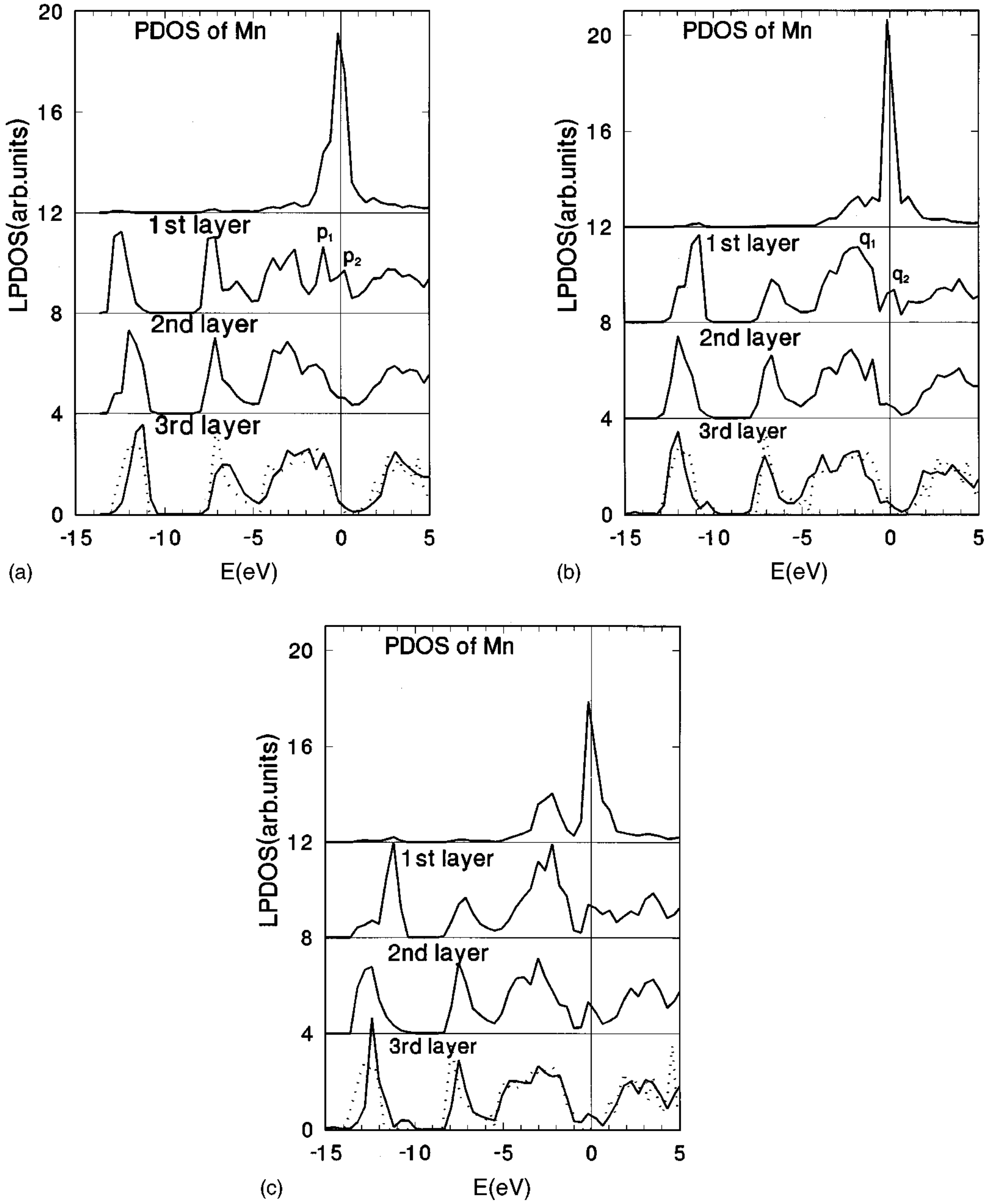

FIG. 4. The LPDOS as well as the partial density of states (PDOS) of the adsorbed Mn atom for Mn adsorption (a) on C site of Ga-terminated GaAs(001) surface; (b) on B_1 site above the surface; and (c) on B_2 site below the surface of the As-terminated GaAs(001) surface. The dashed line is the LPDOS for the bulk and the vertical line indicates the Fermi level.

B. Adsorption energy

The adsorption energy per Mn atom is calculated by the difference between the total energy of the adsorption system and the sum of the total energies of the clean surface and an isolated Mn atom.[18] The calculated adsorption energies for the C site adsorption on the Ga face and for the B_1,B_2 sites adsorption on the As face are -2.67 eV and -7.36 eV, -8.60 eV, respectively. The large difference between the adsorption energy for Mn on the Ga face and those for Mn on the As-face demonstrates that Mn on the As face is more stable than that on the Ga face. The lower adsorption energy of Mn atom at the B_2 site on As face shows that it is possible for Mn atoms to sit below the surface. Therefore a Mn, Ga, As mixed layer might exist at the Mn/GaAs(001) interface which has been observed by Jin *et al.*[8,9] These results are qualitatively in agreement with those of our recent study.[7]

C. Charge transfer

Usually, chemisorptions are accompanied by charge transfers between the adsorbates and the substrates. Table I gives the layer effective charges which are obtained from the sums of the effective charges of all atoms and empty spheres on the corresponding layers in the unit cell. From Table I, it can be seen that the effective charges on the third layers are almost not affected by the adsorption. For the case of the Ga-face adsorption, compared with the clean surface, the effective charge of the Ga-atomic layer in the first layer almost remains unchanged, while the As-atomic layer gains 0.38

TABLE I. The layer effective charges (in the unit of electron) in the unit cell. Here Ga (or As) denotes the sum of the effective charges of all atoms and empty spheres within the Ga (or As) atomic layer. The values in the brackets are those for the clean surfaces.

	Mn adsorbed at C site on Ga-terminated surface		
Atoms	First layer	Second layer	Third layer
Ga	0.98 (0.96)	0.30 (0.22)	0.27 (0.28)
As	−0.62 (−0.24)	−0.12 (−0.14)	−0.20 (−0.20)
	Mn adsorbed at B_1 site on As-terminated surface		
Atoms	First layer	Second layer	Third layer
As	−0.12 (0.58)	−0.18 (−0.16)	−0.16 (−0.14)
Ga	0.27 (0.08)	0.28 (0.30)	0.24 (0.24)
	Mn adsorbed at B_2 site on As-terminated surface		
Atoms	First layer	Second layer	Third layer
As	0.02 (0.58)	−0.42 (−0.16)	−0.14 (−0.14)
Ga	0.48 (0.08)	0.30 (0.30)	0.23 (0.24)

electrons per unit cell after the Mn adsorption. After deducting the part coming from the second layer, there are about 0.28 electrons transferred from Mn to the surface. For the As-face adsorption, when the Mn atom is adsorbed above the surface, it will make the As-atomic layer in the first layer gain 0.70 electrons and the Ga-atomic layer in the first layer lose 0.19 electrons. Therefore about 0.51 electrons are transferred from the adsorbed Mn atom to the first layer. When the Mn atom sits below the surface, it gives about 0.56 electrons to the As-atomic layer in the first layer and about 0.26 electrons to the As-atomic layer in the second layer, at the same time it will gain about 0.4 electrons from the Ga face in the first layer. Therefore there are totally about 0.42 electrons are transferred from the Mn atom to the substrate. The fact that more charge transferred from Mn to the substrate for the As-face adsorption than that for the Ga-face adsorption gives a clue about the reason for the large adsorption energies of Mn on the As-terminated surface. The charge transfer analysis also shows that the Mn-As interaction is stronger than the Mn-Ga interaction.

IV. SUMMARY

In summary, the chemisorption of Mn adatom on the GaAs(001) surface is studied by using the LMTO method with the atomic sphere approximation (ASA). An effective method of using a monolayer of sulfur atoms to passivate the dangling bonds of the slab was introduced in this study, which makes it possible to use a smaller supercell to simulate the GaAs(001) surface. This method is proved to be useful for the self-consistent calculation in the study of Mn adsorption on GaAs(001) surfaces. And, it seems that the sulfur saturation could be used to study other chemisorptions on GaAs surface with slab model. The Mn adatom adsorbed on both the Ga face and the As face are considered separately. The total energy calculation, charge distribution, and the analysis of the layer projected density show that the adsorption of Mn atoms on the As face is stronger than that on the Ga face which is due to the fact that Mn-As interaction is stronger than the Mn-Ga interaction. The calculations also show that the adsorbed Mn atoms might sit below the surface for the As-face adsorption. Therefore a Mn, Ga, As mixed layer might exist in the Mn/GaAs(001) interface region. These results confirmed the results of our recent study[7] by using the empirical EHT method with the cluster model and are in qualitative agreement with the experimental results.[8,9]

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