Density functional study of ferromagnetism in Mn at GaN/$Al_xGa_{1-x}N$ interfaces

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It has been proposed that the ferromagnetic (FM) interaction between the Mn atoms placed at the GaN/$Al_xGa_{1-x}N$ interface might be enhanced due to the presence of a two-dimensional hole gas (2DHG) at the "N-face" interface. We examine this proposal by studying the magnetic interaction between two Mn atoms at this interface with density functional methods. The virtual crystal approximation is used to introduce a controlled number of electrons or holes at the interface in order to understand the variation in the magnetic interaction as a function of carrier concentration. Contrary to expectation, we find that the extra carriers diminish the strength of the ferromagnetic interaction rather than enhancing it. This can be understood within the double exchange model to be the result of the deviation from half filling of the crystal-field-split Mn *e* band, since the FM interaction is strongest at half filling. However, because the carrier density of the 2DHG is quite small, we predict no significant reduction in the magnetic interaction to occur.

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There is a long standing conjecture that the ferromagnetic transition temperature of the GaN:Mn dilute magnetic semiconductor (DMS) can be enhanced by placing the manganese atoms at the interface between GaN and $Al_xGa_{1-x}N$ due to the presence of a two-dimensional hole gas (2DHG).[1] Since holes in the DMS systems are thought to mediate the magnetic interactions better than electrons and since it is difficult to dope holes into bulk GaN, it is an interesting idea to examine the interface region for enhanced magnetism. A 2DHG occurs at the interface naturally due to the electric field discontinuity of the two bulk materials. This interaction may be understood through the double exchange model,[2,3] where an increase in the number of holes results in a stronger Mn-Mn interaction.[4–6] This idea is of considerable interest as this may help in ultimately producing a ferromagnetic dilute magnetic semiconductor at room temperature, which is an important goal of research in this area. In this brief report, we examine this conjecture from density functional calculations and derive results contrary to this expectation.

Improving the performance of DMS, which combine functionalities of semiconductors and magnetic materials, has been actively investigated recently both experimentally and theoretically.[7] Mn in GaN has received considerable interest[4,7–10] after Dietl *et al.*[2] used a Zener model to predict a Curie temperature (T_C) above the room temperature. There is considerable effort to enhance the magnetic interaction between Mn atoms to further increase T_C.[4,5]

With the advent of new experimental growth techniques, clean interfaces between lattice-matched materials can be formed with little disorder between the two materials. One such interface is that between GaN and $Al_xGa_{1-x}N$,[11–15] where the lattice mismatch is less than 3% in the plane perpendicular to the [0001] growth direction, so nearly lattice-matched interfaces can be grown.

Recent theoretical[13,16] and experimental[1,11,12,15] works have examined the electronic properties at this interface. As the wurtzite crystal structure of the two bulk materials lacks inversion symmetry, they can sustain a macroscopic electric field. The magnitude of the electric fields is a bulk property and therefore a discontinuity occurs at the GaN/$Al_xGa_{1-x}N$ interface resulting in a monopole charge. For the "N-face" interface, which is of interest to us here, the monopole charge is negative, which attracts the holes to compensate the monopole charge, resulting in a 2DHG, which resides on the GaN side. The "Ga-face" interface on the other hand leads to the formation of a two-dimensional electron gas (2DEG). This is indicated schematically in Fig. 1. The electron/hole concentration at the interface is of the order of $2 \times 10^{13}/\mathrm{cm}^2$ and spread over an area extending over a thickness of about 40 Å.[11] Since the in-plane lattice constant perpendicular to the interface is $a \sim 3.2$ Å, this density corresponds to approximately 0.005 carriers (electrons or holes) per interface Ga atom. The question we address here is whether the Mn atoms placed in the 2DHG or the 2DEG region will improve ferromagnetism.

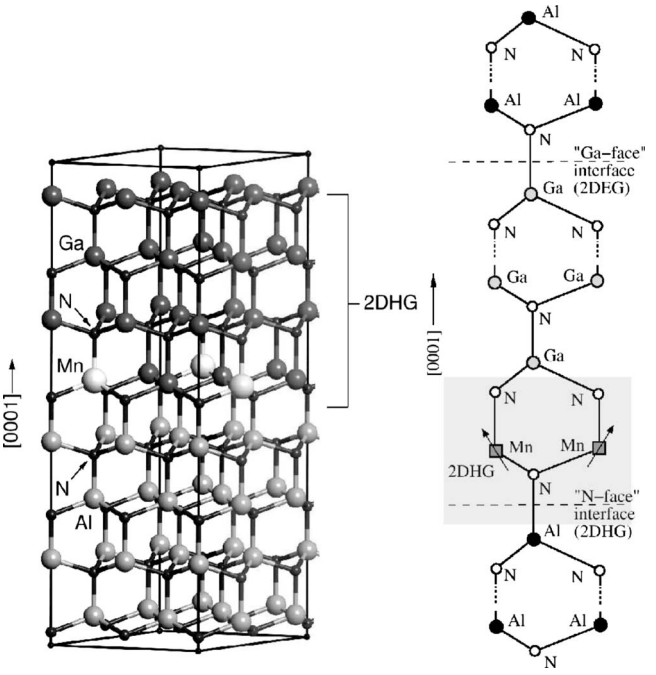

FIG. 1. The two-dimensional hole gas region at the GaN/AlN interface (schematic). The 2DHG region is actually about 40 Å thick and resides on the GaN side of the interface.

To address these issues, electronic structure calculations were performed within density functional theory[17] using the full-potential linearized augmented plane wave (FP-LAPW) program WIEN2K (Ref. 18) and the linear muffin-tin orbital method within the atomic spheres approximation (LMTO-ASA).[19] The magnetic exchange interaction was calculated using an 80-atom supercell $(Ga_4N_4)_5/(Al_4N_4)_5$ consisting of five layers of GaN alternating with five layers of AlN, with four formula units in each layer, and two Mn atoms replacing Ga at nearest-neighbor distances on the first GaN layer at the interface. This is the end member of the series $GaN/Al_xGa_{1-x}N$, with $x=1$. This supercell is used for the simplicity of the calculations and because the density of the 2DHG is highest for this structure.[1,16] The generalized gradient approximation (GGA) (Ref. 20) was used. For bulk GaN, the calculated lattice parameters are $a=3.202$ Å and $c=5.317$ Å, as compared to the experimental values of $a=3.192$ Å and $c=5.196$ Å, i.e., a 3% difference in volume, which is typical for results obtained from density functional calculations. For AlN, the calculated lattice parameters, $a=3.121$ Å and $c=5.044$ Å, more or less agree with the experimental values. In the supercell calculation, an average value of these calculated lattice constants was used. Since the unit cell repeats, both interfaces exist within the unit cell, so the Mn atoms can be placed at either the "N-face" or the "Ga-face" interface.

We need to simulate the rather "low density" of carriers (0.005 electrons or holes per interface atom) in the interface region. In the actual interface, these carriers are believed to come from surface states or defects from regions away from the interface. One may consider introducing the carriers by adding donor or acceptor dopants. There are two problems with this approach. First, in order to accomplish the small carrier concentration needed, the density of such dopants will have to be small, resulting in a huge supercell, making the calculations impractical. Second, the dopants themselves might introduce localized states that are not available as carriers that might mediate magnetism between the Mn atoms. Therefore, we model the extra carriers in our calculations by using the virtual crystal approximation (VCA),[21] where the number of electrons can be changed continuously to correspond to a small density of electrons or holes. To accomplish this, the nuclear charge is changed by a small noninteger value ΔZ from the original charge and the enforcement of the charge neutrality condition produces automatically the desired number of carriers. If ΔZ is small, no perceivable change in the valence or conduction band structure occurs, and the Fermi energy shifts in more or less a rigid-band fashion. To add electrons, we increase the atomic numbers of both Ga and N on the GaN side (typical value $\Delta Z=0.01$, so that $Z_{Ga}=31.01$ and $Z_N=7.01$) and to add holes, we reduce the atomic numbers in a similar fashion. The extra electrons or holes are spread in the entire GaN part mimicking the extra carriers at the actual interface.

Figure 2 shows the layer-projected density of states (DOS) for the superlattice with a single Mn substitutional atom replacing a Ga atom at the "N-face" interface. The Mn d states lie in the gap region with the electron occupancy being $(d^4\uparrow, d^0\downarrow)$, which is quite similar to the Mn states in the bulk GaN.[22] However the Mn d states of the bulk GaN are split further due to the reduction of symmetry at the interface.

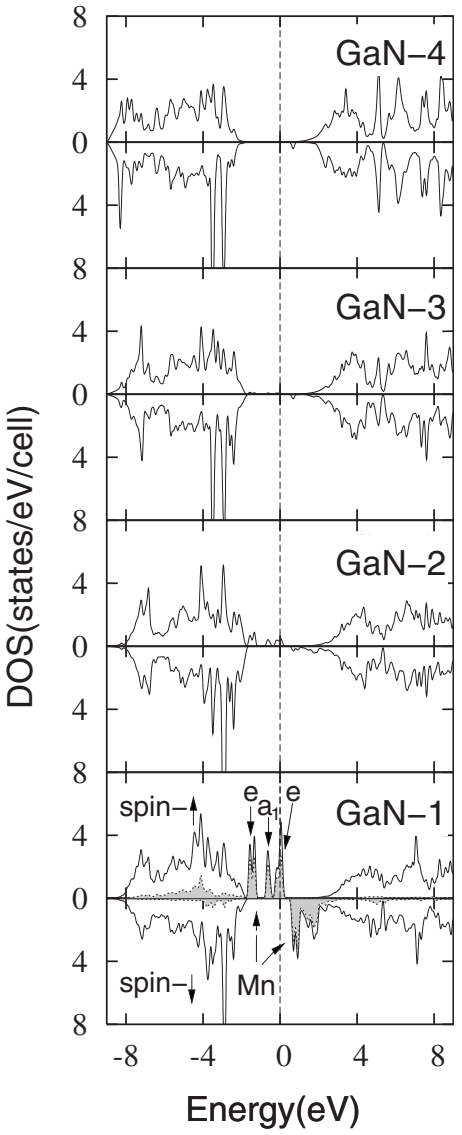

FIG. 2. The layer-projected electron density of states obtained using LDA-LMTO for the supercell consisting of four layers of GaN and four layers of AlN with one Mn atom placed in the 2DHG region, on a substitutional Ga site in the first interface layer (GaN-1), closest to the interface.

This splitting of the Mn d states can be understood by considering symmetry arguments. The point group symmetry around a single Mn atom at the substitutional site in GaN is tetrahedral T_d, so that the Mn states split into the lower energy, doubly degenerate e_g state and the higher energy, triply degenerate t_{2g} state.[22] For Mn at the interface, the tetrahedral symmetry is lost due to the lack of inversion symmetry perpendicular to this interface. The T_d symmetry now reduces to C_{3v}, splitting the t_{2g} state into a singly degenerate a_1 and a doubly degenerate e state. This can be seen in the calculated density of states (Fig. 2), where the five Mn d states have split into two e and one a_1 states, with a doubly degenerate state of e symmetry lying at the Fermi energy E_F. This state is half filled and extra electrons or holes at the interface

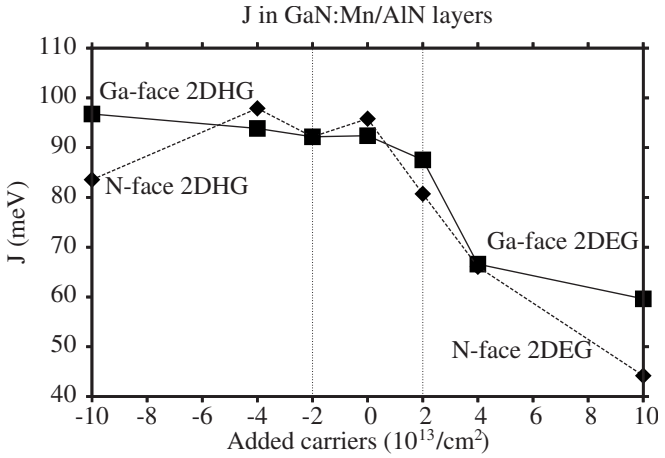

FIG. 3. The calculated J values as a function of the sheet carrier density σ. The experimental carrier concentration (given by the horizontal lines) at the GaN/AlN interface is about 2×10^{13} cm^{-2}, which is too small to significantly alter the magnetic interaction.

further populate or deplete this band, changing the number of carriers in this band. These carriers serve as the itinerant carriers within the double exchange model,[3] which mediate the ferromagnetic interaction between the remaining Mn d electrons, the "t_{2g}" electrons with $S=3/2$, usually treated as classical spins localized at the Mn sites.

Two Mn atoms lying at nearest-neighbor Ga sites are used to compute the exchange interaction J from the total energy difference between the ferromagnetic and the antiferromagnetic configurations: $J=(E_{AFM}-E_{FM})/2$. With this definition, J is positive for a ferromagnetic interaction. For the Mn-Mn interaction in bulk GaN, we found from our 80-atom supercell calculations a J of 88 meV, which agrees with previous calculations.[4,23] We then computed J in the GaN/AlN superlattice. Mn at the "N-face" and the "Ga-face" interfaces yielded values of $J=92$ and 96 meV, respectively. This is about the same as in the GaN bulk, which is expected since the gross electronic structure is about the same. These differences are too small to explain any changes in T_C, so we look to changes in J as a function of hole and electron carrier concentration.

Using the VCA, the added sheet carrier density per interface area σ is given by $\sigma=N\Delta Z/A$, where $N=38$ and A is the area of one interface in the supercell. These added carriers occupy the partially filled Mn bands at the Fermi energy, affecting the ferromagnetic double exchange interaction between the Mn t_{2g} core spins (split into $e+a_1$ in Fig. 2). So, instead of these extra carriers spreading out over a few nanometers at the GaN/AlN interface without the Mn atoms, now they occupy the Mn states. In either case, the monopole charge arising out of the electric field discontinuity[16] at the GaN/AlN is compensated exactly by these extra carriers.

The calculated exchange energy J as a function of the sheet carrier density σ is plotted in Fig. 3. The horizontal lines correspond to the experimental carrier concentration.[1] In addition to the case for the 2DHG for the "N-face" interface, which is of our main interest here, we have also shown the results for the other situations. In particular, the case of 2DEG at the "Ga-face" interface is also experimentally relevant, as a 2DEG does form at this face as does the 2DHG at the "N face." There are two main conclusions. First is that the strength of the exchange interaction J is reduced from the case of no extra carriers ($\sigma=0$), contrary to the conventional wisdom that extra carriers should enhance the ferromagnetic double exchange. Second is that the deviation of J is small at the range of experimental sheet carrier densities. These are the main points of the paper. Even though we have performed the concrete calculations of the magnetic exchange with the two Mn atoms at specific sites in the lattice, we expect the extra carriers to leave the magnetic interaction more or less unchanged, even though the strength of the Mn-Mn exchange itself would depend on their positions in the lattice.[4] These calculations suggest that increased hole concentration at the interface cannot explain (and is likely not the mechanism for) any increase in T_C seen experimentally[1] in layered semiconductors.

The reduction in the magnetic exchange between the two Mn moments is easily understood within a simple rigid-band model of the filling of the degenerate Mn d e band, which crosses E_F as seen from Fig. 2. We model this band simply by a constant density of states spreading over the band width W from $-W/2$ to $W/2$. The energy arises from two terms: an antiferromagnetic term J_{AF} arising because of the superexchange between the Mn core spins and a ferromagnetic double exchange term arising out of the itinerant carriers, which we are modeling by the constant density of states. The strength of the double exchange is given by $-2t\cos(\theta/2)$, where θ is the canting angle between the two Mn spins and t is the hopping integral, so that $W=2\nu t$, ν being the number of nearest neighbors. The energies for the ferromagnetic and the antiferromagnetic alignments of the two Mn spins are then given by

$$E_{\uparrow\uparrow}=J_{AF}-W(x-x^2)/2,$$

$$E_{\uparrow\downarrow}=-J_{AF}, \tag{1}$$

where x is the band filling parameter $0\le x\le 1$. The itinerant electrons do not contribute to $E_{\uparrow\downarrow}$ because of the zero effective hopping due to the $\cos(\theta/2)$ factor. The resulting exchange interaction

$$J=E_{\uparrow\downarrow}-E_{\uparrow\uparrow}=-2J_{AF}+W(x-x^2)/2 \tag{2}$$

has a parabolic maximum (maximum ferromagnetic) for the half filling of the itinerant band, which corresponds to the case with no added electrons or holes. This qualitatively agrees with the calculated J curve of Fig. 3. The calculated J (Fig. 3) does peak for half filling (no added carriers) and decreases for the case of added holes or electrons to the system. However, the change in J is not symmetric with respect to the addition of electrons and holes, which is due to the approximation of a rigid band, as well as a constant density of states. The shape of the real density of states for the itinerant band would lead to different behaviors for the hole and electron filling. Differences also exist between the densities of states for Mn on the "Ga face" and "N face," even though the gross features of the electronic structure are the same. However, this simple picture does contain the essential physics of the behavior of the calculated J, that the ferromag-

netic double exchange is maximum at the half filling of the itinerant band.

In summary, we studied the magnetic exchange interaction between two Mn atoms placed at the 2DEG or the 2DHG region of the GaN:Mn/AlN interface and concluded that the ferromagnetic interaction is not significantly altered as compared to the bulk GaN:Mn.

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