First-principles investigation of Mn δ -layer doped GaN/AlN/GaN (0001) tunneling junctions

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Highly spin polarized diluted ferromagnetic semiconductors are expected to be widely used as electrodes in spintronic devices. Based on density functional theory calculations, we investigate the feasibility of using Mn-doped wurtzite GaN/AlN/GaN(0001) trilayer junctions for tunnel magnetoresistance (TMR) devices. We address some key issues affecting the degree of spin polarization and spin tunneling transport with the aim of realizing the appealing half-metallicity and large TMR ratio. We propose digital δ -Mn layer doping in GaN, close to the GaN/AlN interfaces for enhanced performance. Layer-resolved band structure and density of states calculations reveal that Mn dopants produce local metallic or half-metallic states surrounded by the host semiconductor materials. Spin polarized electrons can transport across the interfaces, free of the conductivity mismatch problem owing to the strong hybridization between Mn 3d states and the states of surrounding host atoms. The calculated TMR ratio is found to depend sensitively on the dopant concentration. Half-metallicity and large TMR ratios are predicted for “low” dopant concentrations (1/2 and 1/4 monolayers), while a high concentration (1 monolayer) produces metallic states and thus a decreased TMR ratio. Very thin AlN barrier layers are predicted to yield low TMR ratios. We also study the role of two types of structural defects close to the Mn atoms at the interfaces, namely, atomic mixing (Al replaces Ga and vice versa), and N and Ga vacancies. While the studied atomic interdiffusion defects have little effect on the TMR ratio, both N and Ga vacancies are found to destroy the half-metallicity and lead to a substantial reduction of the TMR ratio, and thus should be eliminated for enhanced device performance. © 2009 American Institute of Physics.

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I. INTRODUCTION

The last two decades have witnessed a remarkable impact on the information technology revolution by utilizing magnetoresistive effects—the change in electrical resistance in response to applied magnetic fields—in the ever-growing field of spintronics (or transport spin electronics). In 1988, the discovery of the giant magnetoresistance (GMR) effect¹ of magnetic metal multilayers, such as Fe/Cu/Fe, has led to the miniaturization and enhanced hard disk performance.² The magnetic tunnel junction (MTJ) is another type of spintronic device using the tunnel magnetoresistance (TMR) effect, for applications in nonvolatile magnetic random access memory, magnetic sensors in hard disk drives, as well as in field-programmable logic circuits and biochips.³

A MTJ device consists of two layers of ferromagnets (electrodes) separated by an ultrathin layer of an insulator (spacer), typically with a thickness of a few nanometers or less. The insulating layer is so thin that electrons can tunnel through the barrier if a bias voltage is applied between the two metal electrodes. The TMR effect refers to a dramatic change of the tunneling current in MTJ when the relative magnetizations of the two ferromagnetic (FM) layers change their alignments (for reviews on MTJs and TMR see Refs.

3–5). The amplitude of the TMR ratio is key quantity in applications of MTJs, which is commonly defined as,

$$\text{TMR} = \frac{R_{\text{AP}} - R_{\text{P}}}{R_{\text{P}}}, \quad (1)$$

where R_{P} and R_{AP} are the electrical resistance for the parallel (P) and antiparallel (AP) magnetization alignments, respectively.

Jullière⁶ first discovered the TMR effect in 1975 with a ratio of up to 14% in Fe/Ge/Fe and Fe/Ge/Co junctions at 4 K. Two decades later, experimental studies obtained TMR ratios with values exceeding 15% at room temperature for Co/AIO_x/Co tunnel junctions.^{7,8} Inspired by the success of GMR, this has triggered a surge of research in this field. Currently, two complementary avenues are followed so as to realize large (giant) TMR ratios using MTJs. One approach is to evaluate different tunnel barrier materials with an aim to increase the quality of the sample entering the limit of coherent tunneling. This means that for favorable systems, the interface between the FM electrode and the barrier acts as a spin filter and can increase the polarization of the tunneling electrons. Within this framework, large TMR values, greater than 1000% were first predicted theoretically for MTJs based on crystalline MgO tunnel barrier layers epitaxially grown on (001) Fe electrodes.^{9,10} This prediction was followed by experimental realizations of MTJs utilizing both epitaxial

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and textured Fe and Fe–Co alloy electrodes,^{11,12} which showed greater than 180% and 220% TMR ratios at room temperature, respectively (for a review on Fe/MgO/Fe MTJs, see Ref. 13). These achievements have triggered further interest in MTJs and the phenomenon of TMR.

The other strategy aiming for large TMR is to use highly spin polarization (SP) electrodes.¹⁴ Such a choice is evident from the model of Jullière,⁶ which quantifies the magnitude of the TMR ratio in terms of the SP of the FM electrodes,

$$\text{TMR}^J = \frac{2\text{SP}_L \times \text{SP}_R}{1 - \text{SP}_L \times \text{SP}_R}, \quad (2)$$

where SP_L and SP_R are the SP of the left (L) and right (R) electrodes, respectively, which can be determined by the spin-up ($\uparrow$) and spin-down ($\downarrow$) electronic density of states (DOS), $N(E_F)$, at the Fermi energy, E_F , of two FM layers. SP is normally defined as

$$\text{SP} = \frac{N^\uparrow(E_F) - N^\downarrow(E_F)}{N^\uparrow(E_F) + N^\downarrow(E_F)}. \quad (3)$$

Obviously, then, one would expect the largest TMR values for materials with the largest tunneling SP, i.e., the so-called “half-metallic” (HM) ferromagnets with a perfect 100% SP.^{15–17} Indeed, using some HM Heusler compounds, such as Co_2MnSi , high TMR ratios of up to 580% were reported^{18–20} at low temperature. A record giant TMR ratio of 1800% was demonstrated with electrodes of the manganite $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) at low temperature.²¹ This extreme TMR value was attributed to the half-metallicity of LSMO. Moreover, Tezuka *et al.*²² reported a TMR ratio of 175% at room temperature using $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ full-Heusler alloy electrodes with large SP and high thermal stability.

For both approaches, it is well known that interfaces play a vital role in determining the SP and hence the TMR ratio.^{23–26} Experiments²⁷ and simulations²⁸ indicated that tunneling electrons come from the top few monolayers of the FM electrodes. Therefore, the TMR effect in MTJs is expected to be strongly influenced by the atomic structure and bonding at the interfaces between the FM electrodes and the insulating barrier. It is further suggested that the SP is primarily determined by the electronic structure of the ferromagnet/insulator interfaces rather than by their bulk properties.²⁶ Based on theoretical arguments, it was proposed that, in order to exploit HM ferromagnets in TMR junctions, it is crucial to eliminate interface states at the Fermi level within the HM gap.²⁹ However, it is usually rather difficult to establish a high degree of SP at the interface even using some bulk half-metals. One possible reason for this is the poor quality of the half-metal/barrier interfaces, which result in a dramatic reduction of the SP and/or a detrimental effect of thermal fluctuations on the SP.^{30,31} Moreover, for some cases, even the formation of ideal epitaxial interfaces may damage the half-metallicity of the bulk systems. For example, it was theoretically predicted that for the $\text{Co}_2\text{MnSi}/\text{GaAs}(001)$ heterostructure, only certain interface morphologies can conserve the HM character.³²

Apart from using traditional ferromagnets, such as Fe, Co, or Heusler compounds, the so-called diluted magnetic

semiconductors (DMSs), which are frequently predicted to be half-metals, are expected to be used as electrodes in MTJs and other spintronic devices and have the advantage of a better integration in a semiconductor structure.^{14,33} Furthermore, because DMS and nonmagnetic semiconductors have more compatible growth conditions as well as closer DOS and conductivity, it can in principle overcome the chemical reactivity between metals and semiconductors and the so-called “conductivity mismatch” encountered in metal/insulator interfaces, which will dramatically reduce the SP in the regime of diffusive electron transport.^{4,14} In addition, it is expected that semiconductor-based spintronics could eventually combine storage, detection, logic and communication capabilities on a single chip to produce a multifunctional device that could replace several components.^{34,35} DMS based MTJs also open the way to new effects such as tunneling anisotropic magnetoresistance.³⁶ Thus, DMS-based MTJs share the virtues of being both fascinating to basic research and potentially important in many practical applications.

It is fair to say that using traditional metal based MTJ devices, such as Fe/MgO/Fe, has reached a certain stage of maturity, although theoretical understanding of the mechanism of TMR is currently under intense investigation.^{26,37} By contrast, magnetoelectronic devices based on DMS as electrodes are at a much earlier stage of development, largely due to the lack of an efficient means of injecting spin-polarized charge. The p -type Mn-doped GaAs system has been an archetypal DMS that has been extensively studied. Like its metal counterpart, MTJs based on (Ga,Mn)As, such as (Ga,Mn)As/AlAs/(Ga,Mn)As and (Ga,Mn)As/GaAs/(Ga,Mn)As, show TMR effects.^{38–42} The highest TMR ratios so far obtained are 75% and 290% for an AlAs and a GaAs intermediate barrier layer, respectively. However, Mn-doped GaAs systems suffer from the limitation that the Curie temperature, T_C , is too low (173 K for a thin layer⁴³ and up to 240 K for δ -doped systems⁴⁴), which precludes its practical use in room temperature devices.

Mn doped III-nitrides, usually n -type DMSs, on the other hand, were theoretically predicted⁴⁵ and experimentally demonstrated^{46,47} with ferromagnetism well above room temperature. Although the microscopic origin and the mechanism of the ferromagnetism is still a subject under intense research,^{48,49} there has been some encouraging progress using Mn-doped III-nitrides DMS as electrodes for room temperature spintronic devices. Recently, Ham *et al.*⁵⁰ demonstrated electrical spin injection from room-temperature FM (Ga, Mn)N in III-nitride based spin-polarized light-emitting diodes. The anomalous Hall effect provides proof of spin-dependent transport, confirming the intrinsic FM ordering. However, very low spin injection efficiency was obtained—the electroluminescence polarization saturates at around 8 T and reaches maximum values of approximately 1.3% and 0.8% at 150 and 300 K, respectively. Since the occurrence of TMR can be regarded as spin dependent transport involving spin injection from one electrode and spin detection (or spin extraction) by the second electrode and the physics of spin injection and spin extraction is similar,⁵¹ one would expect that Mn-doped III-nitride DMSs

could exhibit a room temperature TMR effect, as is the case for the epitaxial GaCrN/AlN/GaCrN trilayer heterostructure, where the AlN layers behave as a tunnel barrier.⁵²

Clearly, an improved understanding of the dependence of the materials used, and the nature of the interfaces will provide essential input for device design optimization. This is a particularly imperative subject in view of the large deviation between theoretical expectation and the hitherto unsatisfactory performance obtained in experiments, namely, very low spin injection efficiency⁵⁰ and low TMR ratio (0.1%).⁵² One of the main motivations of this paper, therefore, is to shed some light on the correlation between “structure and properties” with an aim for enhanced performance. In particular, regarding the often theoretically predicted HM in III-nitrides based DMS,^{53,54} we notice that experiments showed that Mn:GaN^{55,56} is in fact semiconducting or highly insulating. Such poor conductivity could be a major obstacle for applications using DMS as electrodes in spintronic devices. We argue that one of the key issues concerns the spatial distribution and electronic states of the doped ions. First, the electrical conductivity competition between HM, semiconducting, or metallic character sensitively depends on concentration and dopant distribution^{49,57} and charged states, particularly for Mn-doped III-nitrides under *n*-type conditions.⁴⁹ Second, we will show below that the doped Mn atoms or ions will create *local* metallic or HM states surrounded by semiconducting host atoms. Third, total energy calculations show dopants prefer to form embedded clusters-incorporated with the host matrix,⁴⁹ and synchrotron radiation microprobe experiments reveal that such clusters prefer to form *along* the epitaxial growth direction.⁵⁸ Evidently, such clustering of dopants is detrimental to the realization of the *extended ferromagnetism* and could be difficult to avoid completely under nonequilibrium conventional epitaxial growth conditions due to the attractive interaction among dopants. To eliminate such an effect, we propose δ -layer epitaxial doping of Mn *perpendicular* to the growth direction. Technically, it has been well established that digital δ -functionlike doping profiles can be obtained in III-V semiconductors by growth-interrupted impurity deposition during molecular beam epitaxy.⁵⁹ Such an approach has been demonstrated for achieving higher values of T_C for various samples since it helps to realize extended ferromagnetism, albeit limited to two dimensions. Moreover, it has been established that in Mn doped AlN/GaN(0001) interfaces, Mn atoms prefer to segregate into the GaN region and reside close to the interface,⁶⁰ substituting Ga sites.⁴⁹ Hence in this study, we focus on substitutional sites on Ga close to the interfaces, representing δ -Mn-layer doped systems.

We address some key issues affecting the HM and the TMR ratio, namely, the interface properties, dopant concentration, barrier thickness, and nonoptimal growth defects, such as atomic interdiffusion and nitrogen and gallium vacancies at the interfaces. Our results reveal that spin polarized electrons can transport across the interfaces via hybridization between the dopants and host atoms, free of the conductivity mismatch problem. The SP and TMR ratio depend sensitively upon the dopant concentration. Very thin AlN barrier layers are predicted to produce low TMR ratios.

FIG. 1. (Color online) Geometry of the $(1 \times 2):(\text{GaN})_5/(\text{AlN})_6/(\text{GaN})_5(0001)$ heterostructure. Substitutional sites considered for Mn atoms are labeled as “Ga1” and “Ga’1.” The two vertical dashed lines represent the two types of interfaces. “L” and “R” indicate the left and right GaN regions, respectively. Small (yellow) spheres indicate N atoms and large light (green) and dark (red) spheres, indicate Ga and Al atoms, respectively.

With regard to native defects, while HM is found to be rather robust against isovalent atomic interdiffusion, N and Ga vacancies at the interface will typically destroy the HM and substantially reduce the TMR ratio.

The present paper is structured as follows. In Sec. II, we describe the computational details. The main results and discussions are presented in Sec. III. After a brief study of the pure trilayer superlattices (without Mn), we study various ideal (defect-free) Mn-doped GaN/AlN/GaN (0001) junctions, in which the mechanism of TMR at the atomic level and the effects of dopant concentration and barrier thickness are also reported. We then study various defect-containing junctions, involving two types of defects at the interfaces, namely, atomic interdiffusion and neutral N and Ga vacancies. The conclusions are given in Sec. IV.

II. COMPUTATIONAL DETAILS

We perform all-electron density functional theory (DFT) calculations using the generalized gradient approximation⁶¹ for the exchange correlation functional as implemented in the DMol³ code.⁶² The wave functions are expanded in terms of a double-numerical quality localized basis set with a real-space cutoff of 9 bohr. Polarization functions and scalar-relativistic corrections are incorporated explicitly. Full relaxation, including lattice constants and atomic positions, is performed for undoped systems. After doping, the lattice constants are kept unchanged, while the atomic positions are free for relaxation.

The Mn δ -layer doped GaN/AlN/GaN (0001) junctions are modeled using (1×1) , (1×2) , and (2×2) supercells of $(\text{GaN})_5/(\text{AlN})_n/(\text{GaN})_5(0001)$ trilayer superlattices, corresponding to a dopant concentration of 1 ML (monolayer), 1/2 ML, and 1/4 ML, respectively in the “electrodes” (GaN region). To model the effects of barrier thickness, we choose $n=2, 4, 6$ and 8; corresponding to thickness values ranging between 0.5–2.0 nm. As an example, Fig. 1 shows the 1/2 ML $(\text{GaN})_5/(\text{AlN})_6/(\text{GaN})_5(0001)$ structure. For short, we label it the “ $(1 \times 2):5+6+5$ ” junction. It contains two asymmetric Mn-doped GaN regions, where the Mn atoms are substitutionally doped at Ga1 and Ga’1 sites, serving as two (left and right) FM electrodes (as shown below) connected by a six double-layer AlN regions, and involves two different interfaces, “type A” and “type B.” The Brillouin-zone integrations are performed using a $6 \times 6 \times 2$ grid for the 128-atom 1/4 ML doped 5+6+5 trilayer junction. For the other supercells, the grids are obtained such that the same/similar sampling of reciprocal space is obtained.

TABLE I. Lattice constants a and c , and band gap at the Γ -point, E_g^Γ , for the $(1 \times 1):(\text{GaN})_5/(\text{AlN})_n/(\text{GaN})_5(0001)$ ($n=2, 4, 6$, and 8) heterojunctions.

$5+n+5$	a (Å)	c (Å)	E_g^Γ (eV)
5+2+5	3.199	31.182	1.95
5+4+5	3.186	36.189	1.93
5+6+5	3.180	41.207	1.89
5+8+5	3.176	46.057	1.71

III. RESULTS

A. Pure trilayer superlattices

It is instructive to start from the parent compounds-bulk wurtzite AlN and GaN. The calculated in-plane lattice parameters of pure AlN (3.134 Å) and GaN (3.228 Å) differ by 2.91%, compared with the experimental value of 2.48% (The corresponding experimental values of AlN and GaN are 3.111 and 3.190 Å, respectively⁶³). Our calculated direct band gaps at the Γ -point are 4.15 and 1.82 eV, compared with experimental values 6.02 and 3.34 eV for AlN and GaN,⁶³ respectively. Such underestimation of band gaps is typical for standard DFT calculations. After forming the trilayer superlattices, the semiconducting behavior is retained. The fully relaxed lattice constants and band gaps of the pure free-standing (1×1) junctions are listed in Table I. As expected, the calculated in-plane lattice parameters of the heterojunctions are found to be in between the corresponding values of pure AlN and GaN, and to slightly decrease with increasing thickness of the AlN region. Interestingly, the calculated band gaps also decrease with the number of AlN layers, but are not limited to the band gaps of the parent semiconductors. Due to periodic boundary conditions, these

trilayer junctions are equivalent to 2+10, 4+10, 6+10, and 8+10(AIN)_m/(GaN)_n superlattices. The decreasing band gaps with increasing superlattice thickness is due to the built-in electric fields in the polar superlattice, as found in Refs. 60 and 64. Like the parent semiconductors, in each nitride layer of the junctions, the conduction band minimum (CBM) at the Γ point is predominantly of Al 3*p* and 3*s* (or Ga 4*s*) character and the valence band maximum is predominantly of N 2*p* hybridized with Al 3*p* and 3*s* (or Ga 4*p* and 4*s*) states.

B. Defect-free Mn-doped junctions

For each Mn-doped junction, we model both the P and AP magnetization alignments by calculating FM and antiferromagnetic (AFM) coupling between the two electrodes. The calculated Mn magnetic moments (MMs), SP values at the two interfaces, the energy difference between the P and AP configurations, ΔE_{P-AP} , and the estimated TMR ratio⁶⁵ are summarized in Table II. These results allow the following conclusions. (i) The trilayer junction, under P and AP magnetizations, represents a bistable system as indicated by the negligible total energy differences between these configurations (The P configuration being very slightly lower in energy). The largest ΔE_{P-AP} values, -11.7 and -13.3 meV/cell, which are already well below the room temperature thermal energy (25.8 meV at 300 K), are found for a high Mn concentration (1 ML) and with a thin AlN barrier (i.e., smallest Mn_{Ga1}–Mn_{Ga'1} separation). MTJs operate under applied P and AP magnetic fields. These small ΔE_{P-AP} values indicate that the changing of the magnetic field orientations can readily switch the magnetic structures of these two electrodes. This, in turn, demonstrates the feasibility of modeling the P and AP configurations using FM and AFM coupling

TABLE II. Mn MM (in μ_B), SP (in %) of two interfaces SP_L and SP_R, energy difference between P and AP configurations (ΔE_{P-AP} , in meV/cell), and the estimated TMR ratios (in %) for various defect-free and defect-containing Mn-doped trilayer junctions. Al_{Ga} and Ga_{Al} denote junctions containing the mixing antisite defects and V_N and V_{Ga} for junctions containing two N and Ga vacancies at the interfaces (see text). For HM systems, the absolute DOS at the Fermi level is also shown in parenthesis, in units of states/per cell-eV.

	P			AP			ΔE_{P-AP}	TMR ratio
	MM	SP_L	SP_R	MM	SP_L	SP_R		
Mn-doped ideal 5+6+5 junction								
1 ML	(3.87, 3.67)	69	57	(3.83, -3.51)	64	-59	-11.7	57
1/2 ML	(3.96, 3.77)	HM (82)	HM (78)	(3.96, -3.77)	HM (80)	HM (-77)	-0.16	∞
1/4 ML	(3.98, 3.69)	HM (89)	HM (81)	(3.98, -3.69)	HM (91)	HM (-80)	-0.14	∞
1/2 ML 5+n+5 junction with various layer thickness								
5+2+5	(3.96, 3.79)	HM (77)	HM (72)	(3.96, -3.76)	HM (73)	HM (-70)	-13.3	∞
5+4+5	(3.95, 3.78)	HM (82)	HM (77)	(3.95, -3.77)	HM (82)	HM (-75)	-0.21	∞
5+8+5	(3.97, 3.78)	HM (83)	HM (76)	(3.96, -3.78)	HM (82)	HM (-78)	-0.13	∞
1/2 ML 5+4+5 junction with interdiffusion defects								
Al _{Ga}	(3.91, 3.75)	HM (72)	HM (74)	(3.89, -3.74)	HM (73)	HM (-74)	-1.1	∞
Ga _{Al}	(3.95, 3.72)	HM (81)	HM (79)	(3.95, -3.71)	HM (82)	HM (-81)	0.78	∞
1/4 ML 5+4+5 junction with vacancy defects								
V _N	(4.01, 4.03)	35	27	(4.04, -4.02)	31	-21	2.9	14
V _{Ga}	(1.62, 1.50)	HM (47)	...	(1.62, -1.50)	HM (45)	...	-0.35	0

Another important issue affecting device performance concerns the possible charged states of the doped ions in Mn doped III-nitride systems. It has been shown that for Mn-doped bulk GaN (Ref. 49) and GaN/AlN interfaces,⁶⁰ charged electronic states will not help in achieving the appealing ferromagnetism with HM character. In particular, under the usual *n*-type growth conditions, Mn dopants prefer to exist as Mn^{2+} ions (-1 charge state), whose magnetic ground states are in fact AFM for all concentrations considered. For the theoretically predicted Mn^{4+} ions ($+1$ charge state) under *p*-type conditions, although ferromagnetism is maintained, the degree of SP is dramatically decreased as compared to the corresponding neutral systems.⁶⁰ Such a behavior is found to be robust for all doping concentrations considered and is in accordance with the band coupling model.⁷² Because of the weak interaction between the two interfaces involved in the junction, we expect similar behavior, in terms of stable charged states and magnetic coupling, in the Mn-doped GaN/AlN/GaN junctions, as that in Mn-doped AlN/GaN interface systems.⁶⁰ Consequently, charged states of the Mn ions are predicted to degrade TMR performance in Mn doped III-nitride junctions.

C. Defect-containing junctions

So far, we have only considered ideal, i.e., defect-free junctions, for which very large TMR ratios are predicted under certain conditions. This shows the potential to realize giant TMR effects by using III-nitride based MTJs. However, it is well established that the properties of III-nitrides are strongly influenced by the presence of defects, such as vacancies.⁷³ The same is expected to apply for III-nitride based junction systems, particularly around the interfaces. Moreover, during the epitaxial growth process, chemical mixing might happen at the interfaces, which will affect the sharpness/roughness of the interfaces and perhaps the TMR ratio. Indeed, it has been proposed that device performance can be improved by preparing junctions with flat and smooth interfaces.^{50,52} To shed some light on the possible effect of structural defects on the TMR, we consider two types of common defects at the interfaces. One is the atomic mixing (interdiffusion) defects, i.e., Al (Ga) atoms diffuse to the GaN (AlN) region and occupy Ga (Al) sites; the other involves vacancies, i.e., the N vacancy, V_N , and Ga vacancy, V_{Ga} .

We model the mixing (antisite) defects by employing $(1 \times 2):5+4+5$ junctions. Two atomic mixing possibilities are studied, namely, at the type A interface, where a Ga1 atom is substituted by an Al atom called $\text{Al}_{\text{Ga}1}$, and at the type B interface, where an Al2 atom is replaced by a Ga atom called $\text{Ga}_{\text{Al}2}$. The simulation of junctions containing V_N or V_{Ga} is done by employing larger $(2 \times 2):5+4+5$ junctions. Based on DFT calculations, it has been proposed that in Mn doped GaN bulk systems, both V_N and V_{Ga} prefer to be located close to the Mn ions.^{74,75} Thus, in this study, vacancies are modeled close to the Mn atoms at the two interfaces, e.g., at N1 and N3 sites for V_N and at $^*\text{Ga}1$ and $^*\text{Ga}'1$

sites for V_{Ga} in Fig. 1, respectively. The calculated MMs, SP at the interfaces, and estimated TMR ratios are summarized in Table II.

It is evident that the TMR performance is rather robust against the chemical mixing of Al and Ga atoms at the interface. Indeed, the calculated DOS for junctions containing the intermixing defects is similar to the ideal junctions (not shown). In particular, the presence of $\text{Al}_{\text{Ga}1}$ and $\text{Ga}_{\text{Al}2}$ does not destroy the HM nature of the corresponding ideal junctions for either the P or AP configurations. Furthermore, the calculated SP and TMR ratios are found not to change much compared to the corresponding ideal junctions, see Table II. This behavior is not surprising due to the similarity of the chemical properties of Al and Ga. This is another advantage of using DMS over traditional metals as electrodes in MTJs. For example, in Fe/MgO/Fe systems, it was predicted that an atomic layer of iron oxide at the interface will significantly reduce the TMR.⁷⁶

By contrast, the presence of vacancies is found to have profound effects on predicted TMR performance. Introducing V_N or V_{Ga} close to the Mn ions (and the interfaces), results in strong interactions between them and, due to chemical bonding, the formation of $V_N + \text{Mn}_{\text{Ga}}$ or $V_{Ga} + \text{Mn}_{\text{Ga}}$ complexes, respectively.^{74,75} Consequently, there are significant changes in the atomic and electronic structure around the complexes. Kang and Chang⁷⁴ reported that a charge transfer occurs from the Mn *d* band to the acceptor levels of V_{Ga} , and strong MnN bonds are formed between the Mn ion and the N atoms in the neighborhood of V_{Ga} in Mn-doped GaN. Larson and Satpathy⁷⁵ found that both V_{Ga} and V_N are detrimental for ferromagnetism in Mn:GaN. Both studies are based on neutral charge state investigations.

From our investigations of the vacancies in the Mn-doped heterojunctions, it is found that the presence of V_{Ga} at the two interfaces leads to similar local structural changes to each other. The bond lengths of Mn_{Ga} to the in-plane neighboring N atoms ($\text{Mn}_{\text{Ga}1}-\text{N}1$ and $\text{Mn}_{\text{Ga}'1}-\text{N}3$) change from about 1.95 to about 1.72 Å. Interestingly, introducing V_N leads to very different structural changes at the two interfaces. At the type A interface, the bond lengths of Mn to in-plane neighboring Ga atoms ($\text{Mn}_{\text{Ga}1}-^*\text{Ga}1$) increases from 3.19 to 3.39 Å, and the bond length of $\text{N}1-\text{Al}1$ decreases from 1.92 to 1.88 Å (see Fig. 1). In contrast, at the type B interface, the corresponding bond length ($\text{Mn}_{\text{Ga}'1}-^*\text{Ga}'1$) decreases from 3.19 to 2.94 Å, and the bond length of $\text{Mn}_{\text{Ga}'1}-\text{N}4$ increases from 1.95 to 2.06 Å. Such a difference is manifested in the corresponding electronic structures. It is found that both complexes will introduce defect-states within the band gap and destroy the half-metallicity of the ideal 1/4 ML junctions. The Mn DOS (for simplicity, only the AP alignments) for junctions without and with the vacancies are shown in Fig. 6. Specifically, $V_N + \text{Mn}_{\text{Ga}}$ will lead to a metallic, rather than a HM state at the interfaces, as seen from the Mn DOS in Fig. 6(b), where the DOS at E_F are also reduced substantially. This results in a dramatic reduction of the TMR ratio, namely, from virtually infinity to 14%. For $V_{Ga} + \text{Mn}_{\text{Ga}}$, although the half-metallicity survives, it does so with a decreased DOS at E_F for the spin-up channel at the type A interface (from 89 to 47 states/

FIG. 6. Mn atomic DOS for Mn-doped $(2 \times 2):(\text{GaN})_5/(\text{AlN})_4/(\text{GaN})_5$ junctions (a) without defect and (b) with two nitrogen vacancies, V_N , and (c) with two gallium vacancies, V_{Ga} under AP magnetization alignments. Left and right columns correspond to the Mn atoms at the left (type A) interface and the right (type B) interface, respectively.

per cell-eV for the P alignment and from 91 to 45 per cell-eV for the AP alignment). At the type B interface, it changes from HM to semiconducting under both P and AP configurations, leading to a zero TMR ratio [see Fig. 6(c)]. Interestingly, we notice that the Mn MMs do not change significantly after forming $V_N + \text{Mn}_{\text{Ga}}$; by contrast, the Mn moments change from $\sim 4 \mu_B$ to $\sim 1.5 \mu_B$ after forming the $V_{\text{Ga}} + \text{Mn}_{\text{Ga}}$ complex, suggesting there is charge transfer from the Mn ion to V_{Ga} , which is in agreement with the findings in Ref. 74.

A thorough charged states study of the defect-containing (as well as other impurities such as oxygen⁷³) junctions, which is beyond the scope of current paper, will likely change the details of the electronic structure and the calculated TMR ratio. Here we are interested in the general role of defects on TMR performance. Our present results highlight that V_N or V_{Ga} vacancies at the interfaces, at least for the neutral systems, will play a destructive role in realizing HM ferromagnetism and giant TMR, and thus should be eliminated as much as possible by preparing flat interface systems. Similar behavior is also predicted for the neutral O vacancy in Fe/MgO/Fe junctions.⁷⁷

IV. CONCLUSION

Making room temperature DMS-based giant TMR devices a reality requires a substantial amount of fundamental materials development, together with the experimental characterization of spin properties in complex junctions. Unlike

using traditional metals as electrodes, to fulfill the potential of DMS for spin injection and optimal performance, one needs to consider various different aspects and challenges. It is difficult to control the properties of DMS materials in the bulk form, and even more so when the material is deposited in a thin film, as is required when fabricating a MTJ device. Here we propose doping δ -Mn-layers close to the interfaces to partially overcome the formation of clusters along the epitaxial growth direction. Our present results highlight that this scheme will also help to realize the appealing half-metallicity in a more controllable way, compared to traditional doping approaches. Moreover, the energetically favorable δ -Mn-layers close to the interfaces is particularly useful for TMR devices, since it is known that the tunneling electrons come from the top few monolayers of the electrodes.^{27,28}

Based on extensive first principles DFT calculations, we investigated the underlying mechanism of the TMR effect in Mn-doped GaN/AlN/GaN(0001) junctions at the atomic level. The role of each component, namely, interfaces, electrode, and barrier, was studied. Mn dopants produce local metallic or HM states surrounded by the host semiconductors. Spin polarized electrons can transport across the interfaces, free of the conductivity mismatch problem. The calculated TMR ratio was found to depend sensitively on the dopant concentration. Half-metallicity and large TMR ratios were predicted for low dopants concentrations (1/2 and 1/4 ML), while high concentration (1 ML) produces metallic states and thus a decreased TMR ratio. Very thin AlN barrier layers were predicted to produce a low TMR ratio. With regard to the effects of structural defects at the interfaces, our results show that while atomic interdiffusion antisite defects (Al replaces Ga and visa versa) have little effect on SP and TMR ratios, both neutral N or Ga vacancies destroy the half-metallicity and lead to a substantial reduction of the TMR ratio.

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