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Enhanced Ferromagnetic Stability in Cu Doped Passivated GaN Nanowires

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Density functional calculations are performed to investigate the room temperature ferromagnetism in GaN:Cu nanowires (NWs). Our results indicate that two Cu dopants are most stable when they are near each other. Compared to bulk GaN:Cu, we find that magnetization and ferromagnetism in Cu doped NWs is strongly enhanced because the band width of the Cu t_d band is reduced due to the 1D nature of the NW. The surface passivation is shown to be crucial to sustain the ferromagnetism in GaN:Cu NWs. These findings are in good agreement with experimental observations and indicate that ferromagnetism in this type of systems can be tuned by controlling the size or shape of the host materials.

PACS numbers:

Dilute magnetic semiconductors (DMSs) have attracted wide interest recently because they possess both semiconducting and magnetic properties at the same time, thus suitable for spintronic applications. One of the major focus in this important research field is to produce DMSs with Curie temperatures (T_c) at or above room temperature. It has been predicted that the use of wide band-gap semiconductors, e.g., GaN, as the host material for DMSs can lead to high T_c [1]. However, experimental studies on transition-metal (TM)-doped bulk GaN have led to conflicting results. For example, some experiments have shown the existence of ferromagnetism in $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ but with T_c varying between 8 K [2] and 904 K [3] at $x = 0.06$. In contrast, a magneto-optical study [4] suggested that $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ is paramagnetic. Theoretical studies also show that the magnetic properties of bulk $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ is quite unique: depending on the Mn concentration, carrier density, and pressure, it can change from ferromagnetism to antiferromagnetism [5, 6].

Recently, Wu *et al.* [7] predicted that two Cu ions in a configuration about 6.2 Å from each other in bulk GaN are coupled ferromagnetically with the total moment 2 μ_B/Cu . Subsequently, room temperature ferromagnetism was found in Cu-implanted GaN samples, although with a much smaller saturation magnetization (from 0.01 to 0.27 μ_B/Cu), and the results are very sensitive to the annealing temperature [8, 9]. A more recent calculation by Rosa and Ahuja [10] points out that the ferromagnetic coupling in bulk GaN:Cu is much weaker than expected from previous calculation [7] because the magnetic moment on Cu is very sensitive to the Cu-Cu distance; it becomes much smaller when Cu-Cu becomes nearest neighbor. However, a recent experimental study by Seong *et al.* reported that room temperature ferromagnetism can be achieved in $\text{Ga}_{1-x}\text{Cu}_x\text{N}$ nanowires (NWs) synthesized in a chemical vapor transport system under flow of NH_3 and the saturation magnetic moment is significantly higher than that in bulk GaN ($\sim 1.00 \mu_B/\text{Cu}$ at 5 K) [11]. The dramatically different satu-

ration magnetic moment of Cu in bulk GaN and GaN NWs suggest that the magnetic behavior of Cu doped GaN could be manipulated by tuning the size or shape of host. However, the mechanism of the enhanced magnetic coupling in GaN:Cu NWs is not known, including what is the effect of the surface passivation in the NWs.

In this Letter, we perform a comprehensive first principles study to understand the structural and magnetic properties of Cu doping in bulk GaN and GaN NWs. Both bare and passivated GaN NWs are studied. Our first-principles spin-polarized density functional theory (DFT) calculations were performed on the basis of the projector augmented wave method [12] encoded in the Vienna ab initio simulation package [13] using the generalized-gradient approximation (GGA) [14] and the plane-wave cutoff energy of 400 eV. For relaxed structures, the atomic forces are less than 0.02 eV/Å.

For bulk GaN, the optimized wurtzite lattice constants are $a = 3.218$ Å and $c = 5.240$ Å with the internal parameter $u = 0.3767$ (experimental values: $a = 3.189$ Å, $c = 5.186$ Å, and $u = 0.377$). The calculated band gap for bulk GaN is 1.72 eV. The GaN NWs are orientated along the [0001] direction with a diameter about 1 nm, as shown in Fig. 1(a) and (b). For passivated NWs, pseudo-hydrogen is used to saturate the dangling bond of the NW surface. In the simulation, the NW axis is along the c direction, and the lateral supercell size is chosen so that the closest distance between two neighbor NWs is larger than 8 Å. After optimization, the diameters of the GaN NWs become slightly smaller, and consequently, to minimize the strain, the lattice constant c is increased by 0.018 Å and 0.046 Å for passivated and bare GaN NWs, respectively, as in the case of bare ZnO NWs [15]. Both bare and passivated NWs are found to have a direct band gap (1.67 eV and 3.25 eV, respectively) at Γ . The small band gap of the bare wire is due to the formation of surface defect levels. In case of Cu doping in NWs, we use a $1 \times 1 \times 2$ supercell with a $1 \times 1 \times 4$ k-mesh. For comparison, Cu doping in bulk GaN is also studied by using a $3 \times 3 \times 2$ supercell (shown in Fig. 1(e)) with a $4 \times 4 \times 4$

k-mesh. The lattice constants of the doped systems are fixed to those of the undoped hosts since substitutional Cu changes only marginally the lattice constant [7, 9].

To compare the dopability of Cu in bulk GaN and GaN NWs and identify stable dopant position, we first calculate the formation energy of Cu substitution for Ga in GaN host as

$$\begin{aligned}\Delta H_f &= E(\text{GaN : Cu}) - E(\text{host}) + \mu(\text{Ga}) - \mu(\text{Cu}) \\ &= \Delta E + \mu(\text{Ga}) - \mu(\text{Cu})\end{aligned}\quad (1)$$

where $E(\text{GaN : Cu})$ is the total energy of the doped system, $E(\text{host})$ denotes the total energy of the GaN host for the same supercell in the absence of the defect, $\mu(\text{Ga})$ and $\mu(\text{Cu})$ are the chemical potential for Ga and Cu, respectively. We note that the absolute formation energy depends on $\mu(\text{Ga})$ and $\mu(\text{Cu})$. However, it is sufficient to calculate ΔE for the purpose of comparing the relative stability of Cu in GaN host. For a NW as shown in Fig. 1(a) and (b), there are three inequivalent Ga positions, i.e., A, B, and C. In all cases, we confirm that Cu will not form AX center in GaN due to the delocalization of the Cu 3d related defect bands. Our results are reported in Table. I. For bare GaN NW, we find that the formation energy of Cu_{Ga} is smaller than that in bulk GaN, because Cu_{Ga} can relax more easily in the NW than in the bulk. The lowering of the formation energy is most dramatic at the surface of the NW, where the formation energy is about 0.96 eV smaller. For the passivated GaN NW, we find that the formation energy of Cu_{Ga} is about 0.3 eV larger than that in bulk GaN and is most stable at the A site. This result follows the general trends observed in nanocrystal quantum dots [16] suggesting that the increased formation energy for this non-isovalent dopant is mainly due to the quantum confinement-induced band gap increase, but not sensitive to the shape of the quantum structure. The above results show that the doping ability of Cu in GaN NW depends sensitively on the surface termination of the NW. We also find that in all cases with an isolated Cu atom in GaN hosts, the total magnetic moment is $2 \mu_B$ and the local moment on Cu is about $0.65 \mu_B$ due to the strong Cu 3d and N 2p hybridization [7].

Experimentally, the valence state of Cu in Cu doped GaN NW is found to be close to that of Cu in CuO [11]. To confirm this theoretically, we calculate the charge transfer in Cu doped NWs using atoms in molecules (AIM) theory [17]. We find that the valence state of Cu dopant in bare (passivated) GaN NW is about 0.84 (0.88). For CuO and Cu_2O , the calculated Cu valence state is 0.99 and 0.55, respectively. So, the valence state of Cu dopant in GaN NW is indeed close to that in CuO. The calculated valence state is not close to the nominal value due to the strong covalency in the system. The results also indicate that Cu occupies Ga site in the experimental sample [11].

To investigate the interaction between Cu dopants in GaN NWs, we substitute two Ga atoms with two Cu atoms. The most stable configuration of two Cu atoms in GaN NWs is shown in Fig. 1. We can see that two Cu atoms tend to be next to each other, i.e., they are bonded to the same N atom. This is due to the strong bonding interaction between Cu 3d t states. In case of passivated NW, both Cu atoms occupied A positions. In contrast, these Cu atoms occupied C positions for the bare GaN NW case. This is understandable since an isolated Cu atom prefers to occupy the C (A) position in case of bare (passivated) GaN NW.

The spin exchange interaction between Cu 3d moments in GaN NWs is studied through calculating different spin states, i.e., ferromagnetic (FM) and antiferromagnetic (AFM) states. In case of Cu doped passivated GaN NW (Fig. 1(d)), the FM state with a total moment $2.8 \mu_B$ is more favorable over the AFM state by 90 and 31 meV for the unrelaxed and relaxed structures, respectively. Surprisingly, for the doped bare GaN NW as shown in Fig. 1(c), it is a non-magnetic semiconductor with a gap of 0.44 eV within the d bands. To probe the origin of the different nature of magnetism in these two cases, we plot the density of states (DOS) in Fig. 2. To facilitate the analysis, the DOSs of the systems with an isolated Cu dopant are also shown. In both cases, we can see that there is a band gap in the spin up component. In case of the passivated NW, the spin down t orbitals (in the crystal field of a wurtzite system, 3d orbitals are split into low-lying two-fold e states and three nearly degenerated t orbitals) are partially occupied. However, when a Cu atom occupies the surface position [position C in Fig. 1(a)] of the bare GaN NW, the different crystal field arising from a missing neighbor N atom at the surface will split the t orbitals into a low-lying one-fold a and a high-lying two-fold e' sets. The presence of the band gap is consistent with the stability of the surface Cu atom. When the two Cu dopants are next to each other [Fig. 1(c)], the coupling between two Cu t -derived orbitals will result in a splitting between the bonding and anti-bonding orbitals. Since the distance between two Cu atoms in bare NW is only 2.93 Å (the Cu-Cu distance in bulk GaN and passivated GaN NW are 3.13 Å and 3.12 Å respectively), the splitting will be larger than the spin exchange splitting, resulting in the low spin non-magnetic state. Similar results are observed in GaN:Mn, where pressure or surface strain can turn the system from a high-spin to a low-spin configuration, diminish the ferromagnetism [5, 18]. Our calculations reveal that passivation of the surface is crucial in this system to obtain ferromagnetism for Cu doped GaN NWs. It is noted that previous theoretical studies focused only on TM (Mn [19] and Cr [20]) doped GaN *bare* NWs. In addition, the coupling between a pair of Cr atoms substituted in unsaturated GaN nanoholes was found to be FM [21].

To compare the different magnetic behavior of Cu dop-

TABLE I: Relative formation energy ΔE of an isolated Cu_{Ga} defect in bare and passivated GaN NWs. Please refer to Fig. 1 for the definition of positions A, B, and C. ΔE is related to the absolute formation energy ΔH by Eq. 1. For bulk GaN, ΔE of an isolated Cu_{Ga} defect is 3.33 eV.

	site A	site B	site C
Bare NW	3.05	3.27	2.37
Passivated NW	3.52	3.68	3.52

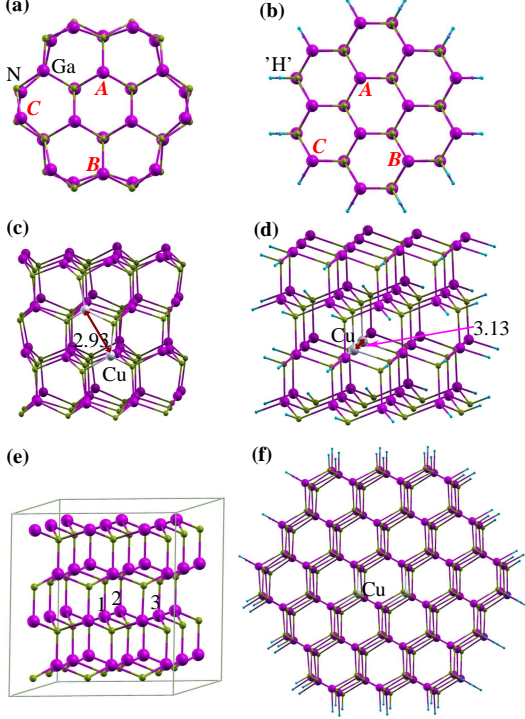


FIG. 1: (a) Top view of a bare GaN NW with a diameter about 1.0 nm, (b) top view of a GaN NW passivated by pseudo H atoms, (c) side view of the most stable configuration of two substitutional Cu atoms in the bare GaN NW, (d) side view of the most stable configuration of two substitutional Cu atoms in a passivated GaN NW, (e) side view of a $3 \times 3 \times 2$ bulk GaN supercell, and (f) top view of a configuration of two substitutional Cu atoms in a passivated GaN NW with a larger diameter 1.6 nm. A, B, and C in (a) and (b) denote three inequivalent Ga positions. The numbers in (c) and (d) give the distance (in Å) between two Cu dopants. Number 1, 2, and 3 in (e) label different Ga atoms in the supercell.

ing in bulk GaN and GaN NW, we also study the Cu-Cu interaction in bulk GaN. First, we find that Cu dopants in bulk GaN also tend to be nearest neighbor. The most favorable configuration is that two Cu atoms occupy the in-plane nearest neighbor positions [positions 1 and 2 in Fig. 1(e)] with a magnetic moment of $0.6 \mu_B/\text{Cu}$. However, the energy difference between the FM and the AFM state in this configuration is only -1.6 meV (the value for the unrelaxed structure is 10.5 meV), which is much

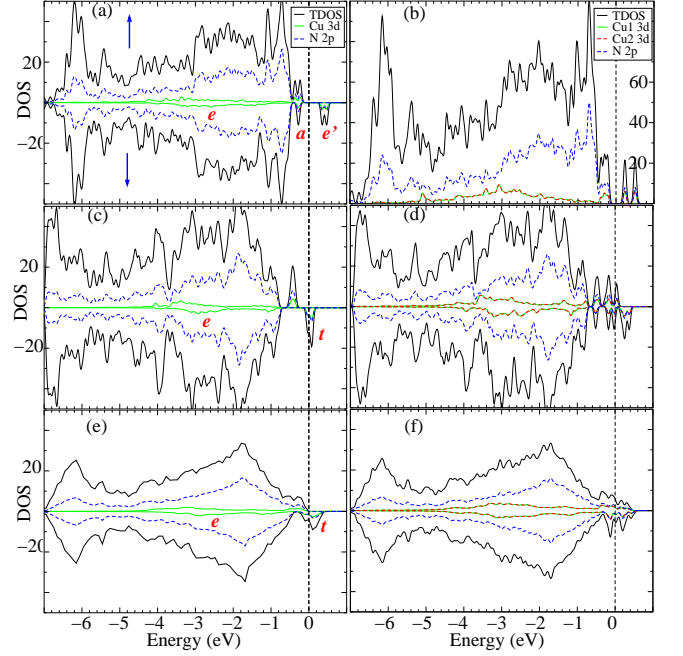


FIG. 2: DOS of (a) a bare GaN NW with an isolated Cu dopant at the C position (Fig. 1(a)), (b) a bare GaN NW with two Cu dopants (Fig. 1(c)), (c) a passivated GaN NW with an isolated Cu dopant at the A position (Fig. 1(b)), (d) a passivated GaN NW with two Cu dopants (Fig. 1(d)), (e) an isolated Cu dopant in a bulk GaN supercell (Fig. 1(e)), and (f) two Cu dopants at positions 1 and 2 in a bulk GaN supercell (Fig. 1(e)), respectively. Here, high energy conduction bands of GaN hosts are not shown.

smaller than that in passivated NW and in the case when the Cu-Cu distance is about 6.2 Å [7]. In some other configurations, we find that the AFM state could be even more stable than the FM state. For instance, if two Cu atoms occupy positions 1 and 3 [Fig. 1(e)], the FM state has higher energy by 41 meV. These results indicate that FM in Cu doped bulk GaN is not robust, which is consistent with experimental observations and the recent calculations of Rosa and Ahuja [10].

To unravel the origin of the different behavior of Cu dopants in bulk GaN and passivated GaN NWs, we illustrate the DOS of the t orbitals near the Fermi level in Fig. 3. For the isolated Cu dopant, the main difference between bulk GaN:Cu and GaN:Cu NW is that the bandwidth of the t states is smaller in NWs than that in bulk GaN (0.13 eV v.s. 0.53 eV) due to the quasi-1D nature of NWs. The DOSs for an isolated Cu in bulk GaN and GaN NWs resemble those shown in Fig. 3(a) and (d), respectively. When two Cu dopants are close to each other, the t orbitals in the same spin will couple to each other, resulting in a low-lying bonding set and a high-lying anti-bonding one in the FM state, broadening the band. This stabilizes the FM state over the AFM state due to the more occupation of the spin-down bond-

ing orbitals than the anti-bonding state [6, 22]. However, it also increases the overlapping between the spin-up and spin-down bands, causing electron transfer from the spin-up states to spin-down states as shown in [Fig. 3(b) and (e)], reducing the magnetic moment. The transfer is large in bulk GaN than in GaN NW because the band width in bulk GaN is wider. The reduced magnetic moment further leads to a reduced exchange splitting and more charge transfer. The final DOSs of the FM state for two Cu atoms in bulk GaN is shown in Fig. 3(c). This explains why Cu-Cu pairs in bulk GaN has a very small magnetic moment when the Cu-Cu distance is small and why the magnetic interaction is weak in bulk GaN. This is because for bulk GaN:Cu, when Cu-Cu distance is small, the coupling between Cu d orbital is large, but the magnetic moment is small. When the Cu-Cu distance is large, the magnetic moment is recovered, but the d orbital coupling becomes small. On the other hand, the Cu t orbital band width is much smaller in GaN NW, thus the charge transfer and reduction of magnetic moment is small in GaN:Cu NWs even when the Cu-Cu distance is small [Fig. 3(f)]. This explains why magnetization and ferromagnetism is enhanced in GaN:Cu NWs.

Due to the configurational entropy, Cu dopants might have many different configurations in GaN NWs under experimental growth condition. Here to examine the dependence of the magnetic properties on the configuration, we study all possible inequivalent configurations (102 configurations in total) of two Cu atoms in passivated GaN NW. To reduce the computational amount, no structural relaxation is performed. It turns out that in all cases, FM is always preferred over the AFM state, as shown in Fig. 4. Interestingly, the maximum magnitude of the energy difference occur at some configurations with the Cu-Cu distance about 6 Å, instead of the nearest neighbor configurations. This is because when the Cu-Cu distance is smaller than 6 Å the magnetic moment start to decrease, thus reducing the magnetic interactions, as discussed above. However, unlike in bulk GaN:Cu, the energy difference is still negative and large at nearest neighbor Cu-Cu distance. Thus FM in Cu doped passivated GaN NW is robust with respect to Cu configurations in GaN NWs.

In the experimental work by Seong *et al.* [11], the diameter of the GaN NW is larger than that of the NW we discussed above. Here to investigate the magnetic interaction between Cu dopants in larger GaN NWs, we also consider two Cu dopants in passivated GaN NW with a diameter about 1.6 nm, as shown in Fig. 1(f). From our calculation, the FM state is more stable by 75 and 54 meV than the AFM state for the unrelaxed and relaxed structures, respectively. So the change of exchange interaction between Cu atoms in GaN NW is not very significant when the diameter of the NW changes.

In summary, we explained why the ferromagnetism of GaN:Cu is enhanced in passivated GaN NWs. We show

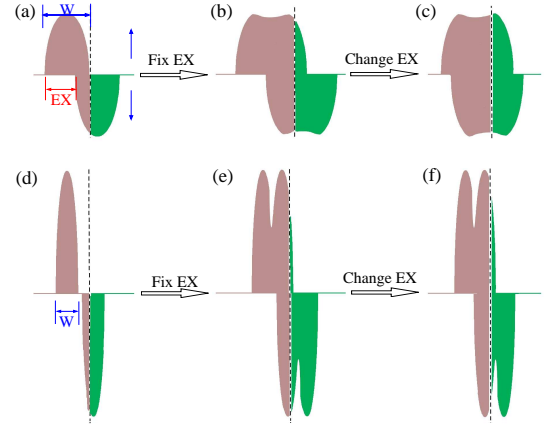


FIG. 3: Schematic illustration of the origin of the different magnetic behavior between Cu doped passivated GaN NW and Cu doped bulk GaN. (a) shows the DOS for the t orbitals of an isolated Cu atom in bulk GaN, (b) and (c) are the DOSs of two in-plane neighbor Cu atoms in bulk GaN in the FM state with the exchange splitting (EX) fixed and varied, respectively. (d), (e), and (f) are the corresponding DOSs for Cu in a passivated GaN NW (Fig. 1(d)). “W” denotes the band width.

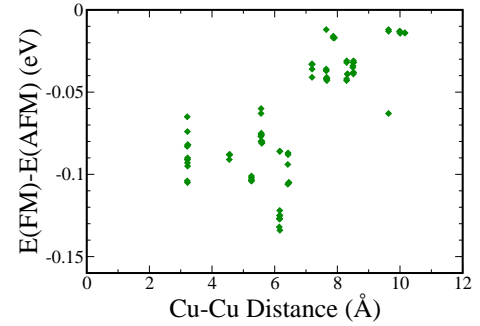


FIG. 4: Energy difference between the AFM and FM state for all possible inequivalent configurations of two Cu dopants in a passivated GaN nanowire as shown in Fig. 1(b).

that due to the 1D nature of the NW, the band width of the Cu t_d band is reduced, thus increases the magnetization. It is found that passivation of the nanowire surface has a significant impact on the substitutional position, and thus on the magnetic properties: For the bare GaN NWs, Cu tends to substitute Ga on the surface, and the strong direct interaction between two neighboring surface substitutional Cu atoms results in a non-magnetic semiconducting state. However, when the surface is passivated, Cu tends to substitute Ga inside the NW, and leads to ferromagnetism arising from the d - d exchange interactions. Our findings, thus, indicate that surface passivation of the NW is crucial to sustain the FM state.

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