Magnetism driven by surface dangling bonds in gallium nitride nanoclusters

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ABSTRACT

Magnetic properties of gallium nitride (GaN) semiconductor nanoclusters (NCs) of different sizes were systematically studied by using first-principles calculations. It is observed that the pure GaN NCs can be magnetic even without magnetic elements doping. Similar to the observed magnetism in undoped oxide NCs, the magnetism of the undoped GaN NCs is attributed to the spin polarization of the dangling bond electrons of the 2-coordinate surface nitrogen anions and originates from the spatially localized nature of the dangling bond states and associated on-site Hubbard interaction. It is demonstrated that the magnetism driven by the surface dangling bonds can be suppressed or enhanced via hydrogen passivation or structural design. These results indicate that it is promising to combine the surface magnetism of the GaN NCs with their unique optical properties to fabricate nanosized magneto-optical devices.

1. Introduction

Dilute magnetic semiconductors (DMSs) have attracted much attention in the last decade because of their potential applications in spintronics. Among various host materials for DMSs, GaN has been extensively studied since it was predicted to be a promising wide-band-gap semiconductor capable to achieve room temperature ferromagnetism [1]. Indeed, experiments have shown room temperature ferromagnetism in Mn-doped [2–4], Cr-doped [5], and Gd-doped [6,7] GaN, although the origin of the observed magnetism is still under debate as it has been argued that the nanoscale segregations due to spinodal decomposition of the magnetic dopants may be responsible for the observed magnetism in the DMSs [8–10].

The magnetic ordering in the DMSs requires not only the local magnetic moments in the DMSs but also the exchange coupling among them [11]. The traditional magnetic elements are not the sole source of the local magnetic moments in the DMSs and recently there has been increasing evidence that the magnetically ordered phases have been detected even in the absence of the traditional magnetic elements. For instance, the high temperature ferromagnetism was observed in the pure ZnO, CeO$_2$, SnO$_2$ nanoparticles (NPs) etc. even without magnetic element doping [12–16]. Theoretical studies revealed that the dangling bond electrons of defects play an essential role in local magnetic moments. In ZnO, it has been clarified that the neutral O vacancy is nonmagnetic while the Zn vacancy leads to the magnetism because of the local magnetic moments of the surrounding O 2p dangling-bond electrons [17].

It is noteworthy that a number of similar localized dangling bond states exist on surfaces of an oxide or nitride nanocluster, which may thus lead to a novel magnetism of the nanocluster. Indeed, undoped ZnO NCs have been observed to be magnetic by various groups [18–20] and our positron annihilation experiments and first-principles calculations have shown that the observed magnetism in the ZnO NCs has a definite relationship with their surface/interface dangling bond states [21,22]. Particularly, magnetic pure GaN NCs were observed as well [23]. Because the dangling bond induced magnetism does not require further magnetic elements doping, it is promising to combine the magnetism with unique optical properties of the well-established GaN nanodevices to fabricate nanosized magneto-optical devices.

For this reason, we systematically studied the magnetism of GaN NCs by using first-principles calculations. It is demonstrated that the pure GaN NCs can be magnetic even without magnetic elements doping. The magnetism of the undoped GaN NCs is attributed to the spin polarization of the dangling bond electrons of the 2-coordinate surface nitrogen anions, which is similar to the observed magnetism in undoped oxide NCs [18–22] and originates from the spatially localized nature of the dangling bond states and associated on-site Hubbard interaction. Furthermore, the calculations show that the surface magnetism can be enhanced via careful structural design or destroyed completely by H-passivation, indicating the magnetism of the GaN NCs is very sensitive to their chemical environments.

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2. Calculation details

2.1. Calculation method

Our first-principles calculations were carried out based on the density functional theory within the generalized gradient approximation (GGA) by using the Vienna ab initio simulation package (VASP). A supercell approximation was employed to simulate the free-standing NCs and in the supercell there are vacuum regions of 10 Å along the x, y, and z directions, respectively, which are large enough to avoid the interactions between the NCs. A plane wave basis set with a cutoff energy of 400 eV, the frozen core all-electron projector augmented wave pseudopotentials and the GGA exchange correlation potential of the Perdew-Wang-91 form, as implemented in VASP, were employed. Only the Γ point was sampled in the calculations and the atomic geometries were fully optimized until the Hellmann–Feynman forces were smaller than 0.01 eV/Å.

2.2. Structure of GaN nanoclusters

We firstly constructed five prototype stoichiometric GaN NCs consisting of two Ga layers and two N layers, i.e., Ga_6N_6, $Ga_{10}N_{10}$, $Ga_{13}N_{13}$, $Ga_{16}N_{16}$, and $Ga_{24}N_{24}$ (Fig. 1). It can be seen clearly that each nanocluster has a N-terminated (001) surface and a Ga-terminated $(00\bar{1})$ surface perpendicular to the c axis. There are two types of surface nitrogen anions in GaN NCs. The first type nitrogen anion (i.e., N_{II} in Fig. 1) bonds with two gallium cations, while the second type (N_{III} in Fig. 1) bonds with three gallium cations. It deserves to be mentioned that all 2-coordinate N_{II} anions are located at the edges of (001) surfaces of the NCs. In addition, a larger $Ga_{26}N_{26}$ nanocluster consisting of four Ga layers and four N layers was constructed to investigate the size effect along the c axis. Moreover, a huge tube-like $Ga_{72}N_{72}$ nanocluster was constructed to verify the exotic effect of the 2-coordinate N_{II} anions as discussed later. The structures of these two GaN NCs are shown in Fig. 2.

Both the non-spin polarized and the spin polarized calculations were performed for all the GaN NCs. Meanwhile, the effect of hydrogen
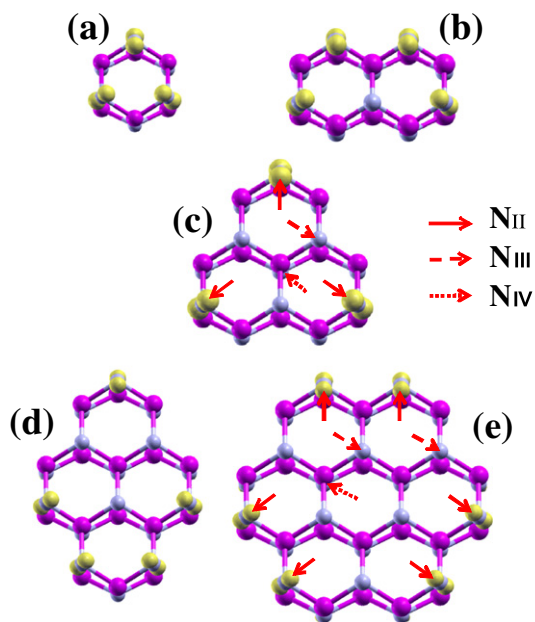

Fig. 1. (a)–(e) Atomic structures and spin density distributions of Ga_6N_6, $Ga_{10}N_{10}$, $Ga_{13}N_{13}$, $Ga_{16}N_{16}$, and $Ga_{24}N_{24}$ nanoclusters, respectively. Pink (dark cyan) balls represent Ga (N) atoms and N_{II}, N_{III}, and N_{IV} denote 2-, 3- and 4-coordinate nitrogen anions, respectively. The isodensity is $0.025\mu_B/a_0^3$.
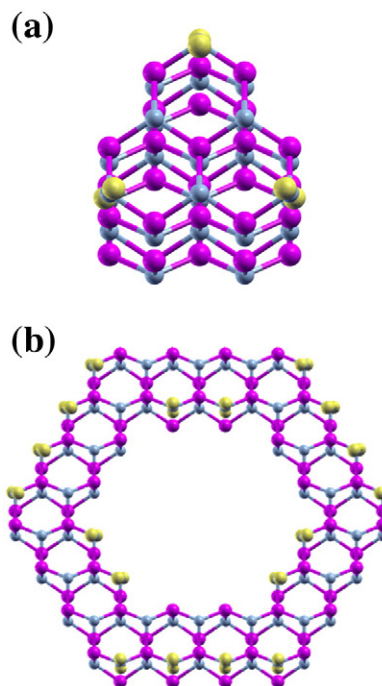

Fig. 2. Atomic structures and spin density distributions of a $Ga_{26}N_{26}$ nanocluster consisting of four Ga layers and four N layers (a) and of a tube-like $Ga_{72}N_{72}$ nanocluster (b). The meanings of the color balls are the same as Fig. 1. The isodensity is $0.025\mu_B/a_0^3$.

passivation to magnetism was also investigated by means of first-principles calculations.

3. Results and discussion

3.1. Spin density distributions

We performed both the non-spin polarized and the spin polarized calculations for all the GaN NCs and we found that the spin polarized calculations are always energetically favorable. The total energy of the spin polarized calculation is lower than that of the non-spin polarized calculation by 0.05, 0.10, 0.18, 0.42, and 0.88 eV for the Ga_6N_6, $Ga_{10}N_{10}$, $Ga_{13}N_{13}$, $Ga_{16}N_{16}$, and $Ga_{24}N_{24}$ NCs, respectively. Fig. 1 presents the calculated spin density distributions for the Ga_6N_6, $Ga_{10}N_{10}$, $Ga_{13}N_{13}$, $Ga_{16}N_{16}$, and $Ga_{24}N_{24}$ NCs.

The spin density distributions in Fig. 1 show clearly that magnetic moments of the GaN NCs mainly originate from the 2-coordinate N_{II} anions on the N-terminated (001) surfaces; while the contributions of the 3-coordinate N_{III} anions are rather small and the 4-coordinate nitrogen N_{IV} anions inside the GaN NCs are observed to be nonmagnetic. In addition, there are 2- and 3-coordinate gallium cations on the Ga-terminated $(00\bar{1})$ surfaces and 4-coordinate gallium cations inside the GaN NCs as well, however, all of them are found to be nonmagnetic as shown in Fig. 1. As a result, the obtained total magnetic moments of the GaN NCs highly depend on the numbers of 2-coordinate N_{II} anions in the NCs.

Table 1
Total magnetic moment (TMM), numbers of the 2-coordinate nitrogen (N_{II}) anions, and average magnetic moment (AMM) per N_{II} for various GaN nanoclusters.

Clusters	TMM (μ_B)	Number of N_{II}	AMM (μ_B)
Ga_6N_6	2.93	3	0.98
$Ga_{10}N_{10}$	4.00	4	1.00
$Ga_{13}N_{13}$	3.84	3	1.28
$Ga_{16}N_{16}$	6.24	5	1.25
$Ga_{24}N_{24}$	7.62	6	1.27