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First-principles study on ferromagnetism in C-doped AlN

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ABSTRACT

First-principles calculations are performed to study the electronic structures and magnetic properties of C-doped AlN. Both generalized gradient approximation (GGA) and GGA + U calculations show that a substitutional C atom introduces magnetic moment of about 1.0 μ_B, which comes from the partially occupied 2p orbitals of the C, its first neighboring Al and first neighboring N atoms (GGA) or out-of-plane first and fifth neighboring N atoms (GGA + U), among which the atomic moment of the C is the biggest. The U correction for the anion-2p states obviously changes the magnetic moment distribution of Al and N atoms and transforms the ground state of C-doped AlN to insulating from half-metallic. The C atoms can induce ferromagnetic ground state with long-range couplings between the moments in C-doped AlN. The ferromagnetic coupling can be explained in terms of the two band coupling model.

1. Introduction

Diluted magnetic semiconductors (DMS) have attracted much attention for their potential applications in the field of spintronics. Such applications require the DMS to be ferromagnetic above room temperature. High-temperature ferromagnetism has been reported by many researchers in several types of transition-metal (TM)-doped semiconducting oxides and nitrides [1–6]. However, the origin of the ferromagnetism observed in TM-doped semiconductors is still under debate. It was found that the magnetic TM dopants in TM-doped DMS segregate to form ferromagnetic clusters, precipitates or secondary phases [7–9], which are obstacles for the practical applications of DMS. To avoid these extrinsic magnetic behaviors, many researches have been focused on investigating the effect of nonmagnetic ion doping in semiconductors to obtain high temperature ferromagnetic semiconductors based on nonmagnetic ion dopants. Besides the discovery of ferromagnetism in nonmagnetic cation doped semiconductors, the experimental researches demonstrated that high temperature ferromagnetism also can be obtained in nonmagnetic anion C- and N-doped ZnO and TiO_2 and C-doped GaN [10–19]. Furthermore, first-principles calculations reported that anion C or N substitutions in several oxides, sulfides and nitrides can induce ferromagnetism and the ferromagnetism is intrinsic [18–34].

AlN is one of the most promising semiconductors for optoelectronic devices, and realization of high temperature ferromagnetism in TM-doped AlN makes it attractive for multifunctional devices. It has been reported that nonmagnetic cation Cu- and Sc-doped AlN are ferromagnetic at temperatures above 300 K [35–37]. Due to the frequent usage of C as dopant of III–V nitrides, many works have been made to study the structural and electronic properties and the formation energies of substitutional C impurities in AlN [38–42]. So far, there has not been a detailed report on the magnetic properties of nonmagnetic anion C-doped AlN. In order to explore possible magnetic properties of C-doped AlN, we investigate the effects of nonmagnetic C dopants on the electronic structures and magnetic properties of C-doped AlN by first principles calculations.

2. Computational details

The calculations were performed using Vienna ab-initio simulation package (VASP) [43,44]. The exchange–correlation potential was treated with the generalized gradient approximation (GGA) [45] and the strong correlation effects were introduced by means of GGA + U scheme [46]. It has been known that electronic correlation effects are important for the structural, electronic and magnetic properties of systems involving localized 2p orbitals of first-row anions, and inclusion of the correlation effects for the anion-2p electrons by means of the local spin-density approximation (LSDA) + U or GGA + U scheme can give improved results [31–33]. For the GGA + U calculations, the on-site Coulomb and exchange parameter for anion-2p states was taken as $U = 5.6$ eV and $J = 1.2$ eV, respectively, which is almost the same as the value used in Refs. [31] and [32] and is close to the estimated values from spectroscopic measurements in oxides [47–49]. The electron–ion interaction was described by the projector augmented wave method. The electronic wave function was expanded in plane wave

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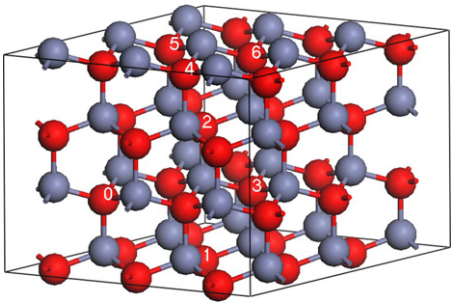

Fig. 1. (Color online.) 72-atom $3 \times 3 \times 2$ supercell of AlN. The red and gray balls represent N and Al atoms, respectively. The positions of N substituted by C are denoted by 0–6.

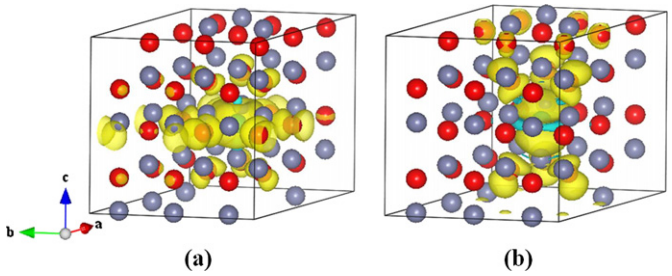

Fig. 2. (Color online.) The spin density distribution in the relaxed $3 \times 3 \times 2$ supercell containing a substitutional C atom calculated by GGA (a) and GGA + U (b). The yellow and blue isosurfaces correspond to the majority- and minority-spin densities. The red, gray and green balls represent N, Al and C atoms, respectively.

Table 1
The magnetic moments of the C atom (M_C), its four nearest neighboring Al atoms (M_{Al}) and all of N atoms (M_N).

	M_C (μ_B)	M_{Al} (μ_B)	M_N (μ_B)
GGA	0.276	0.043	0.231
GGA + U	0.280	0.041	0.250

up to a cutoff energy of 400 eV, and a $5 \times 5 \times 3$ Monkhorst–Pack k-point grid was used to sample the Brillouin zone.

AlN crystallizes in the hexagonal wurtzite phase under ambient conditions. The C-doped AlN system was modeled with a supercell built of $3 \times 3 \times 2$ wurtzite unit cells (see Fig. 1). Since the ionicity of C is closer to that of N, than Al, it is expected that C will occupy predominantly N site in C-doped AlN. Indeed, theoretical investigations showed that in C-doped AlN the substitution of C at N site is preferred [38–42]. As mentioned above, first-principles calculations suggested that substitutional C or N at anion site can induce ferromagnetism in several oxides, sulfides and nitrides. In this work C atoms substitute N atoms in the supercells. The cell and atomic relaxation were carried out until the residual atomic forces were smaller than 0.05 eV/Å. The optimized lattice parameters of wurtzite AlN are $a = 3.126$ Å and $c = 5.011$ Å, in agreement with experimental values [50].

3. Results and discussion

The C-doped system $Al_{36}CN_{35}$, in which one N atom is substituted by one C in the supercell, is first investigated. Due to the larger atomic radius of C, the Al and N atoms around the C move outward and the displacement is not isotropic. After GGA and GGA + U relaxation the C–Al bond length along the hexagonal c axis increases about 0.012 and 0.142 Å, and the other three C–Al bonds increase about 0.061 and 0.046 Å, respectively. As a result, the C–Al bond length along the c axis is smaller than that of other C–Al bonds for GGA relaxation, while it is opposite for GGA + U relaxation. The total energy of spin polarized state calculated by GGA and GGA + U is lower than that of non-spin polarized state by about 62.1 and 135.5 meV, respectively, which indicates that the ground state of C-doped AlN is magnetic. Both of the magnetic moments of the supercell calculated by GGA and GGA + U are 1.0 μ_B. Table 1 lists the magnetic moment distribution on the C, Al and N atoms in $Al_{36}CN_{35}$. It can be seen that the moment is mainly contributed by the substitutional C atom, its first neighboring Al atoms and some N atoms, among which the atomic moment of C is the biggest. The remaining moments are mainly located in the interstitial region around these atoms. Similar moment distributions have been found in C-doped GaN [19], ZnO [22], TiO_2 [24] and ZnS [25]. Figs. 2(a) and 2(b) show the space distribution of spin density in the relaxed supercell calculated by the GGA and GGA + U, respectively. The distribution in Fig. 2 reveals that the spin density is mainly localized on the vicinity of C atom and the first neighboring N atoms or out-of-plane first and fifth neighboring N atoms, with a small contribution from the first neighboring Al atoms. Different from GGA calculations, which show that the spin polarizations of Al and N atoms are mainly located on 3 first neighboring Al atoms in the hexagonal plane and 12 first neighboring N atoms, respectively, GGA + U calculations show that the polarizations are mainly located on the first neighboring Al atom along c axis and 6 out-of-plane first neighboring and 6 fifth neighboring N atoms, and the polarizations of the out-of-plane first neighboring N are much larger than that of the fifth neighboring N atoms. Therefore, the U correction obviously changes the magnetic moment distribution of Al and N atoms. Figs. 3(a) and 3(b) show the total density of states (DOS) of $Al_{36}CN_{35}$ and the partial DOS of 2p states of C atom, a first neighboring Al atom and a first neighboring N atom calculated by GGA and GGA + U, respectively. It can be seen that the C substitution induces the spin splitting impurity states above the top of the valence band. Similarly, the calculations by Bogusławski et al. [38,39] showed that substitutional C at N site creates impurity-induced levels above the top of the valence band. The impurity states are mostly formed by 2p states of the C and its first neighboring N atoms or out-of-plane first and fifth neighboring N atoms, whereas 2p states of first neighboring Al atoms also provide small contribution. This indicates that all of the magnetic moment comes from 2p orbitals, in which a majority of the moment comes from partially filled 2p orbitals of C atom and its first neighboring N atoms or out-of-plane first neighboring and fifth neighboring N atoms. Comparing Figs. 3(a) and 3(b) one can see that Fermi level passes through the minority-spin impurity states for GGA calculation, while the U correction obviously enlarges splitting between the occupied and unoccupied minority-spin 2p states of C, its first neighboring Al and the first and fifth neighboring N atoms, which consequently open a gap of about 0.5 eV between the occupied and unoccupied minority-spin impurity states. Accordingly, the U correction transforms the ground state of C-doped AlN to an insulating state.

Next, the system $Al_{36}C_2N_{34}$, in which two N atoms are substituted by C in a supercell, is investigated to study the magnetic coupling between the moments induced by C doping. We consider six different C–C positions in the supercell, where the first C atom is fixed at site 0 and the second C occupies one of sites 1 to 6, as shown in Fig. 1. Hereafter, $Al_{36}C_2N_{34}$ systems with the six C–C positions are named configurations (0, 1), (0, 2), (0, 3), (0, 4), (0, 5) and (0, 6). For each configuration, the spin-polarized GGA and GGA + U calculations were performed, considering ferromagnetic (FM) and antiferromagnetic (AFM) coupling of the moments induced by C doping, respectively. The energy difference between FM and AFM states for each configuration, $\Delta E_m = E_{FM} - E_{AFM}$, is listed in Table 2. For the magnetic ground state of each configura-