ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 22, No. 4. 2016

First-principle Studies on Ferromagnetism of Fe-doped AlN Diluted Magnetic Semiconductors

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crossref http://dx.doi.org/10.5755/j01.ms.22.4.10750

Received 20 March 2015; accepted 03 October 2015

We have studied the electronic structures and magnetic properties of Fe-doped AlN by first-principles calculations within density functional theory. The calculated results show that AlN crystals doped by double Fe atoms display ferromagnetic properties, and the total magnetic moment is 10.0 μB per 72-atom supercell (3 × 3 × 2). The calculated energy differences between the antiferromagnetic (AFM) and ferromagnetic (FM) phases are 207 meV, which means FM state is a stable state. It is also found that the 3d-states of Fe dopants and the 2p-states of N atoms bonding to Fe dopants are the main contributors to the density of states at the Fermi level.
Keywords: first-principles, AlN, doping, magnetism, structure.

1. INTRODUCTION

Diluted magnetic semiconductors (DMSs) are attractive materials for the spintronics, as they can have the inherent properties of both semiconductor and ferromagnetic materials. Aluminum nitride (AlN), as a new generation semiconductor material, has a wide direct-bandgap (6.2 eV), the good dielectric strength, the low thermal expansion coefficient, excellent piezoelectric properties, high thermal conductivity and stability. It can be used in emitting in the UV, light detecting acoustic surface wave devices. [1 – 3] With the same time, the theoretical predict has shown that transition metal element (e.g., Fe) doped AlN can show well ferromagnetic at room temperature, which means the promising application in spintronics devices [4, 5].

First principles calculations are one of the most usual methods to investigate the ground-state properties of native or doped semiconductor materials. However, the doping usually has strong influence in the properties of semiconductors. With different impurities, the electronic, magnetic and optical properties of crystals can be modified and even a few new potential applications can be realized. [6 – 8] Although AlN-based DMS materials have been modeled and studied, [4, 9 – 11] it is absent for deep analysis on the electronic structure of magnetic properties of transition metal (TM) element doped AlN. For example, the magnetic coupling among the Fe dopants in AlN is seldom considered and investigated. So most calculations usually use one Fe atom to substitute one Al atom in the AlN supercells to study the magnetism of Fe-doped AlN [12 – 14].

In this paper, we have performed the first-principles calculations within density functional theory to investigate the structural, electronic and magnetic properties in a couple of Fe atoms doped AlN supercells. Considering the magnetic coupling among the Fe dopants, we studied and understood the mechanism of magnetic properties. Finally, the stability of ferromagnetism (FM) states and antiferromagnetism (AFM) states in a couple of Fe atoms doped AlN supercells were investigated.

2. METHOD OF CALCULATION

The unit cell of wurtzite AlN with experimental lattice parameters of 0.3112 nm for *a* and 0.4982 nm for *c* contains two Al atoms and two N atoms. Based on the experimental lattice constants, the 3 × 3 × 2 AlN supercell model encompassing 72 atoms was built. To investigate magnetic coupling among the Fe dopants, we substitute two Al atoms by Fe atoms in the supercell. In doped model as shown as Fig. 1, two Fe atoms are replaced Al atoms on the base of the supercell ($Al_{36}N_{36}$) to build the doped supercell ($Al_{34}Fe_2N_{36}$). Several other doped configurations (e.g., the two Fe atoms were placed in 1and 2 sites or in 2 and 3 sites) were also constructed and investigated. Thus, both the parallel and antiparallel arrangement of spins on the Fe atoms were considered.

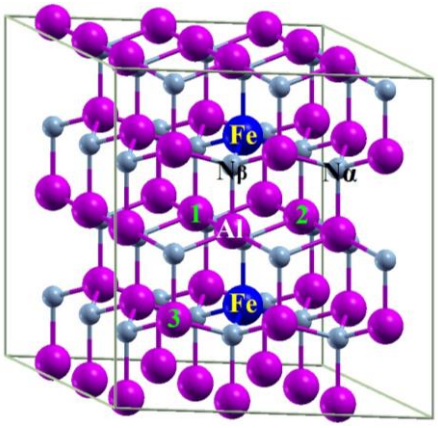

Fig. 1. The Fe-doped AlN supercell (3 × 3 × 2) is used in the calculation. Violet (gray) balls indicate Al (N). Red balls are Fe substituting Al. Nβ (Nα) does (not) bond to Fe atom

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Based on density functional theory (DFT) with the generalized gradient approximation (GGA) as implemented in the WIEN2K code, [15] the calculations were performed. Relaxation of atomic positions for model defects in AlN was described by the full-potential linear augmented plane wave (FP-LAPW) method. The GGA was used to treat exchange-correlation effects. The electrons are divided into core and valence electrons. The Al (3s2 3p1), N (2s2 2p3) and Fe (3p6 3d6 4s2) states are treated as valence electrons.

The muffin-tin radii of Al, N and Fe atom are set to 1.77, 1.66 and 1.87 a.u., respectively. The $R_{min} \times K_{max}$ parameter defines the basis set size in the FP-LAPW method, where R_{min} is the minimal muffin-tin sphere radius and K_{max} is the maximal reciprocal lattice vector in the plane wave. The plane wave expansion of the electronic eigen functions in the interstitial region is cutoff with $R_{min} \times K_{max} = 7.0$. The G_{max} as the largest vector for the Fourier expansion of charge density, is taken to be 12.0 $Ry^{1/2}$. The maximum value of lattice harmonics for wave expansion in the atomic sphere is $l_{max} = 10$. The $4 \times 4 \times 3$ *k*-point meshes in the scheme of Monkhorst-Pack are used for the Brillouin zone integration, where there are 9 special *k*-points. The convergence of self-consistent calculations is assumed as the change of the total energy was less than 1.0×10^{-4} Ry.

3. RESULTS AND DISCUSSION

First, the geometry optimizations of structure were performed to obtain the most stable AlN supercell which has the minimum energy and volume. With the calculated forces on the nuclei to determine the equilibrium positions of all constituent atoms, structural parameters were modified. After geometry optimizations, we can find that the supercell doped by two Fe atoms as shown as Fig. 1 has the less lattice distortion. The doping unit cell lattice parameters of 0.3112 nm for *a* and 0.4982 nm for *c* were changed to 0.3172 nm and 0.5080 nm, respectively. The change was less than 2 % and can hardly be considered. So, we pay more attention to study of the doping structure (as Fig. 1) which means also the parallel arrangement of spins on the Fe atoms.

Band structures (seen as Fig. 2) show spin splitting between the spin up and the spin down channels near the Fermi level, which implies the Fe dopants can order magnetism in the AlN crystals. Furthermore, the valence as well as conduction bands do not cross the Fermi levels and hence they behave like semiconductors. For both the spin down and the spin up, Fe-doped AlN crystal is still the direct band gap semiconductor, with direct gap at the point Γ.

Fig. 3 shows the spin-polarized total density of states (DOS) of Fe-doped AlN supercell for both spin up and spins down. Asymmetrical distributions of the DOS between the spin up and the spin down channels also mean the magnetism of Fe-doped AlN doped system. To find which contribute mainly to the magnetism among the atoms, we calculate the partial DOS of Al, Nα, Nβ and Fe atoms and plot them in Fig. 4. It can be seen from the Fig. 4 that the Fe dopants significantly change the DOS near the Fermi level and lead to the spin polarization of the valence band. Furthermore, Nβ (N atoms bonding with Fe dopants) differing from Nα influences on the magnetism too.

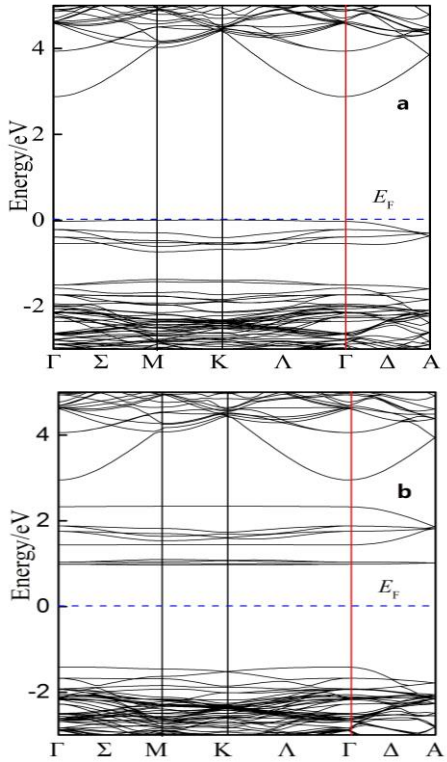

Fig. 2. The band structures of Fe-doped AlN are plotted: a and b represent spin up and spin down channel, respectively. Fermi level is indicated by the dotted horizontal line (blue)

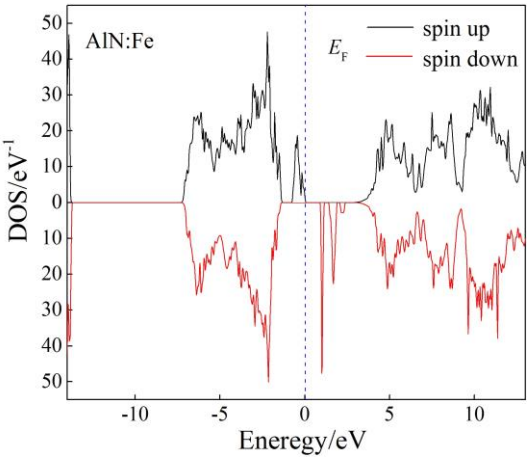

Fig. 3. The spin-polarized total DOS for Fe-doped AlN supercell is shown

More detailed discussion about the functions of Fe and N atoms are obtained by the spin-polarized partial DOS of Fe-4s, Fe-3p, Fe-3d, Nβ-2s and Nβ-2p in Fe doped AlN, shown as Fig. 5. Only both the Fe 3d orbitals and Nβ 2p orbitals DOS overlap near the Fermi energy. There are significant interaction between the Fe-3d states and the Nβ-2p states. The strong hybridization leads to the localization of the impurity wave function and the ferromagnetic coupling in Fe-doped AlN. The partial DOS indicates that the Fe 3d orbitals are the main providers for the magnetic moments and 2p-states Nβ attribute to them

too. So the largest contributions to the density of states at the Fermi level are provided by d-states of Fe atoms and p-states of neighboring N atoms.

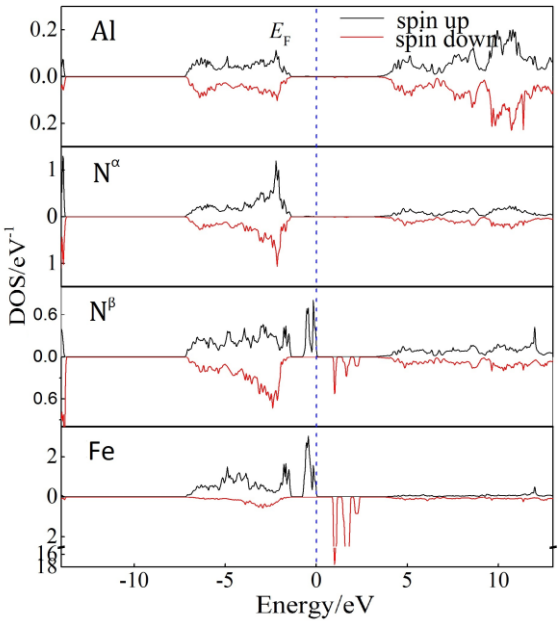

Fig. 4. The spin-polarized partial DOS of Al, Nα, Nβ, Fe in Fe-doped AlN are shown

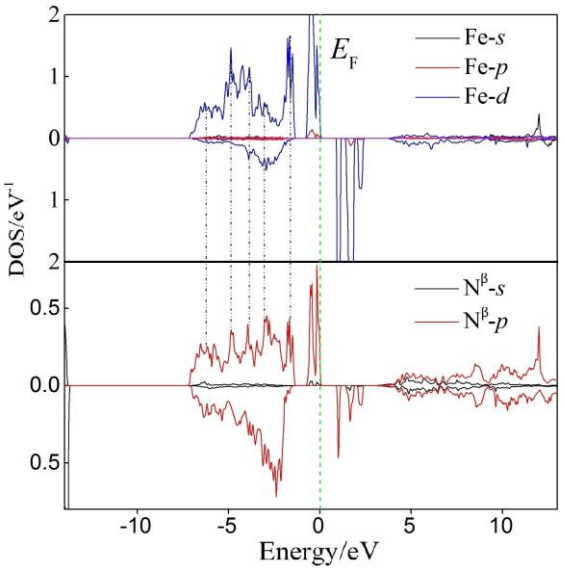

Fig. 5. The spin-polarized partial DOS of Fe-4s, Fe-3p, Fe-3d, Nβ-2s and Nβ-2p in Fe doped AlN are shown

With the theoretical investigations on magnetic properties of in the supercells of $Al_{15}Fe_1N_{16}$, $Al_7Fe_1N_8$ and $Al_3Fe_1N_4$ by Syrotyuk et al. [12], all of the total magnetizations of the supercells are 5.0 μ_B, which do not change for the concentrations of Fe atoms and the sizes of doping surpercells. Even for Fe-doped AlN nanosheets ($4 \times 4 \times 1$ supercell system including 32 atoms, i.e., $Al_{15}Fe_1N_{16}$) investigated by Shi et al. [14], the calculated total magnetic moments are also 5.0 μ_B. the magnetic moments of Fe are reduced due to strong p-d hybridization between 3d of Fe and p (N) states. Fe atoms are the main contributor (~ 3.4 μ_B /Fe) and N atoms contribute about 0.7 μ_B. In our work, spin-polarization calculations show the total magnetic moment is 10.0 μ_B for the AlN supercell ($Al_{34}Fe_2N_{36}$) with a couple of Fe atoms. Fe atoms are the main contributor (7 μ_B /Fe) and N atoms (Nβ) around Fe provide 1.6 μ_B. Other atoms hardly contribute to the total magnetic moment. The results are almost in accord with the above discussions on DOS. Thus the magnetic coupling among the Fe dopants in AlN exists and affects the magnetic properties. To determine the stability of the ferromagnetic state, spin-polarization calculations are performed. [16, 17] The energy differences ($\Delta E = E_{AFM} - E_{FM}$) between the antiferromagnetic (AFM) and ferromagnetic (FM) phases evaluated by GGA are calculated. According to the definition, a positive value means that FM state is a stable state in the corresponding systems while a negative value indicates a stable AFM state. [14] The value of ΔE in a couple of Fe atoms doped AlN is 207 meV, which indicates FM state is a stable state. That is to say, the ferromagnetic coupling is energetically favorable for Fe substitutions in AlN crystals.

4. CONCLUSIONS

To summarize, first-principle calculations based on DFT-GGA are employed to investigate the structural, electronic and magnetic properties of Fe-doped wurtzite AlN crystals. Our calculations suggest that by Fe doping AlN can exhibit ferromagnetism with a stable ferromagnetic ground state. The magnetic coupling among Fe dopants exists and affects the magnetic properties of AlN. Moreover, the Fe dopants and the neighboring N atoms in AlN determine to the DOS at the Fermi level and contribute mainly to the magnetic properties.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Grant Nos. 61136001, 61440028 and 11447029,), the Science & Technology Bureau of Shenzhen (Grant Nos. 20120821110533437 and 20140418095735610) and Natural Science Foundation of SZU (Grant No. 201451).

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