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Pd-doped AlN: A dilute magnetic semiconductor from first-principles study

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ABSTRACT

Electronic band structure and ferromagnetic properties of Pd-doped AlN were reseached wth the density functional theory (DFT). The Pd dopants and its nearest neighboring four N atoms have a spin polarized state with a net magnetic moment of 1.62μB. The results also show that the Pd-doped AlN presents a half metallic behavior and the Pd-doped AlN favors ferromagnetic ground state which can be explained by p-d hybridization mechanism. These results suggest that the Pd-doped AlN is a promising dilute magnetic semiconductor and can be used in the field of spintronics widely.

KEYWORDS

Pd-doped AlN;
Dilute magnetic semiconductor;
Density functional theory;
DOS.

INTRODUCTION

Spintronics devices, which utilize both the charge and the spin freedom of electrons to create new functionalities beyond conventional semiconductor devices, have attracted much attention recently. Dilute magnetic semiconductors (DMSs) formed by substituting a small amount of cations of the host compound semiconductors with magnetic dopants (magnetic transition metals such as Mn, Fe, Co and Ni), have attracted intense interest[1]. The ideal DMSs should exhibit ferromagnetism at room temperature for practical applications and have a homogeneous distribution of the magnetic dopants. AlN DMSs have been extensively studied because of the great interest in its wide gap (6.1eV) and optical transparency.

However, while using magnetic transition metals as dopants in the AlN, their precipitates will influence the ferromagnetism in the form of clusters or secondary phases in the host semiconductor because of the dopants' intrinsical magnetic. Recent researches indicated that In as dopant in GaAs was evenly distributed[2, 3]. This means that using nonmagnetic transition metals instead of magnetic transition metals as dopants is feasible and their precipitates can not induce any ferromagnetism. However, nonmagnetic transition metals will produce ferromagnetism by the interaction of spin-polarization with the finite magnetic moment when they are doped in the host semiconductor. Cu is such a dopant. It has caused great interests in both theory and experiment. The Cu atom doped in the ZnO produced a spin-polarized state with finite magnetic moment, and the Cu atom only exist ferromagnetism ground state[4-6].

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In recent years, Cu-doped ZnO based DMSs has been achieved at room temperature in experiment[7-10]. What's more, Cu, Pd and Mg were also predicted to be nonmagnetic dopants[11, 12]. All of these research indicated that it is possible to fabricate DMSs by using nonmagnetic dopants.

AlN, a new type semiconductor of III-V group, with a wide band gap of about 6.2eV[13], is of great importance in luminescent material fabricating[14]. Recently, AlN doped with different metallic elements had been studied carefully both in theory and experiment. First-principle calculation based on density functional theory(DFT) with pseudo-potential approaches has been used to simulate the properties of different materials widely[15, 16].

In this paper, the possibility of Pd as an intrinsically nonmagnetic dopant to fabricate AlN based DMSs is investigated by using first-principle calculation based on spin density functional theory.

COMPUTATIONAL METHODS

In this work, the first principle calculation was performed with the CASTEP code, based on DFT using ultrasoft pseudo-potentials[17]. The valence states of N, Al and Pd atoms are $2s^2 2p^3$(N), $3s^2 3p^1$(Al) and $4d^{10}$(Pd) respectively. The generalized gradient approximation(GGA) with the Perdew-Burke- Ernzerhof (PBE)[18] was used to investigate the band structure, density of states and magnetic properties of Pd. A plane wave energy cutoff of 370eV is used throughout the calculations. A *k*-point sampling using a Monkhorst-Pack grid[20] with parameters of 5×5×3 was used over the Brillouin zone. The atomic geometries were fully optimized by using Broyden-Fletcher-Goldfarb-Shannon (BFGS) forces on atoms and stresses on the supercell. The ionic coordinates were fully relaxed until the forces on the atoms were smaller than 0.01eV/Å, and the total energy was converged to lower than 5.0×10^{-6}eV/atom.

The calculated lattice constants of wurtzite AlN are $a=b=3.06$Å, $c=4.91$Å and $c/a=1.604$, the result of calculation is very close to the experimental values: $a=3.112$Å and $c=4.982$ Å[19]. The doping concentration is 6.25% as shown in Figure 1.

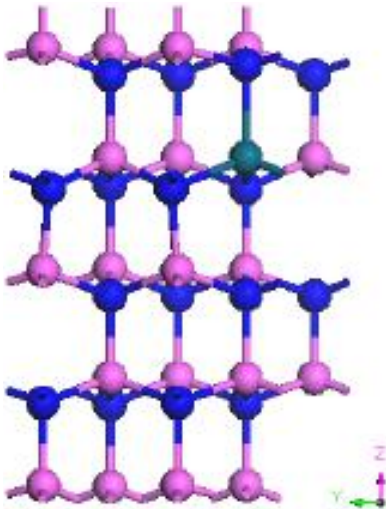

Figure 1 : AlN supercell with 32 atoms used in the calculations for 6.25% Pd concentration. Al, N, and Pd atoms are represented by pink, blue, and green spheres.

RESULTS AND DISCUSSION

For 6.25% concentration of Pd doping in AlN, the growth of lattice constants is 0.6% for *a* and 1.2% for *c*, this variation resulted from the difference in the atomic radius between Al and Pd. In this work, we considered both the spin polarized state and the nonspin polarized state for our model. By contrast the total energies of these two states, we find that the energy of the spin polarized state is 202 meV lower than the energy of the nonspin polarized state. This means that the spin polarized state is much more stable than the other state for Pd-doped AlN. This energy distinction is larger than that of Cu-doped GaN (103meV)[21], and Cu-doped AlN (174meV)[22]. And the supercell exhibit magnetism. The total magnetic moment is 1.7μB per supercell, while 1.0μB per supercell in Cu-doped ZnO[23], and 1.3μB per supercell in Pd-doped GaN[11].

The band structures and the densities of states (DOS) of the supercell for the spin polarized states are shown in the Figure 2 and Figure 3. It can be concluded that with the addition of Pd in the AlN, it introduced a new impurity gap which is near by the 0eV. Resulted in the reduction of the width of band gap (~3eV) between the bands of conduction and valence. The impurity gap was mainly caused by the hybridization of Pd-4*d* and N-2*p*. The Figure 3 indicated that the electrons of majority spin and minority spin appeared

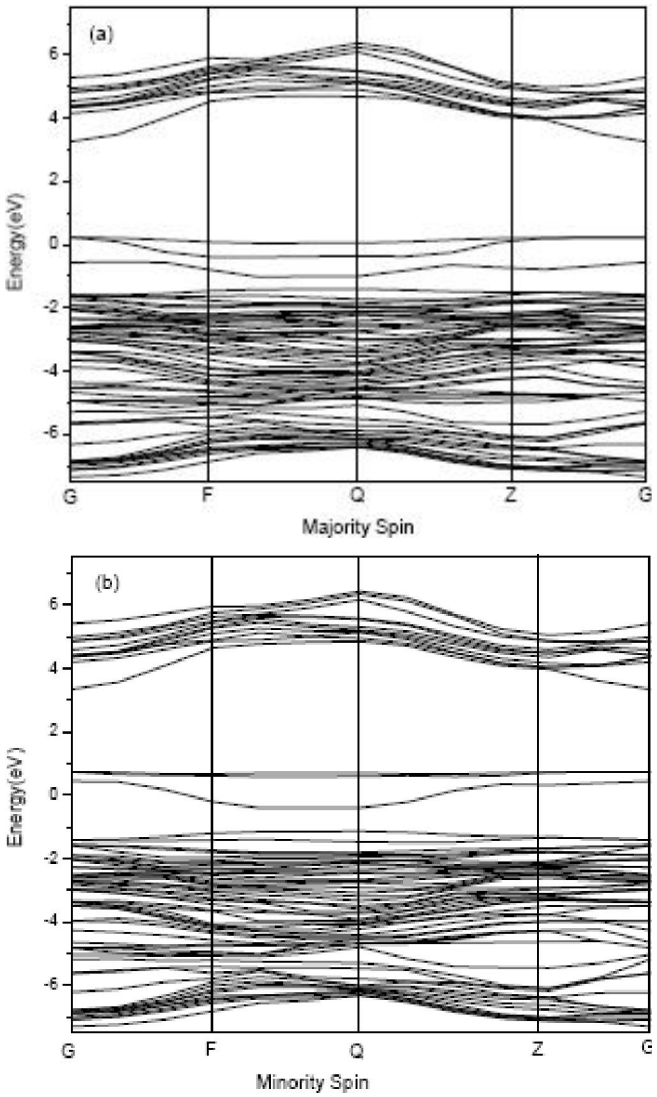

Figure 2 : Band structure of the majority spin (a) and minority spin (b) of AlN doped with 6.25% Pd.

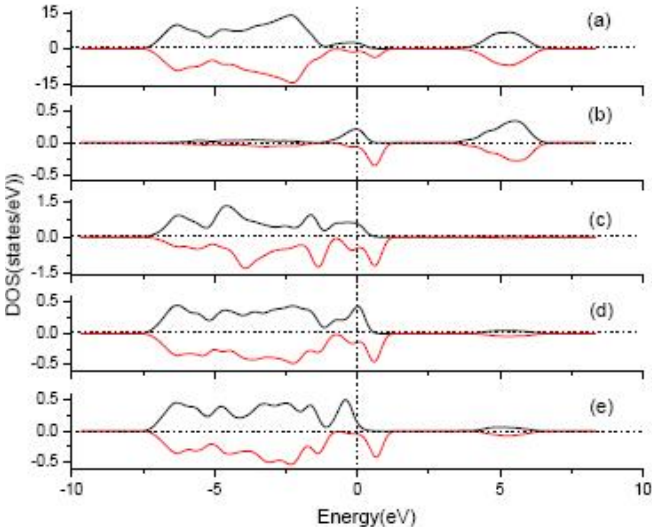

Figure 3 : (Color online) Spin DOSs of total(a), Pd-4*p* (b), Pd-4*d* (c), N-2*p* of the N atom at the basal plane (d) and N-2*p* of the N atom at the top (e) of the PdN_4 tetrahedron. Positive (black) values correspond to the majority spin, negative (red) values correspond to the minority spin.

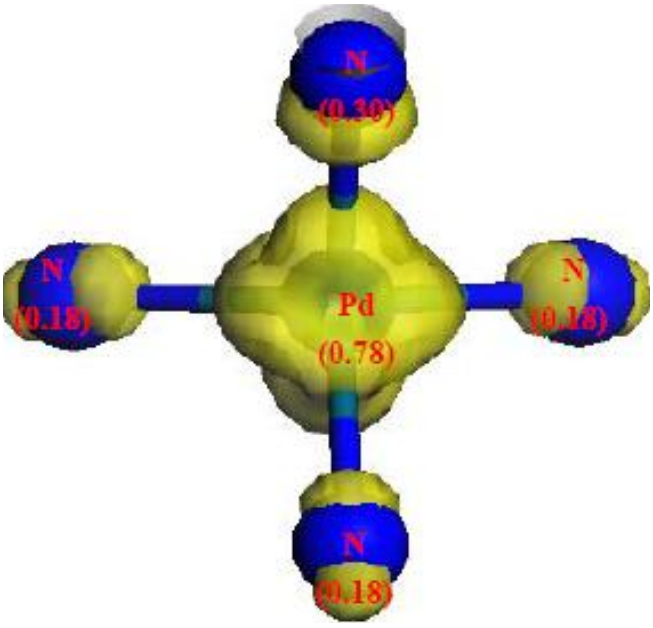

Figure 4 : Isosurface of the spin electron density distribution in PdN_4 tetrahedron and the Pd atom is placed at the center. Magnetic moment of each atom is marked out in the parentheses.

spin split around Fermi level. This is the reason why the supercell of AlN doped with Pd has a minor magnetic moment. In DOS of the minority spin we can find that there exist hybridization between the electrons of Pd-4*d* and N-2*p*. Based on the *p*-*d* hybridization theory for ferromagnetism in DMS[24, 25], the electrons of Pd-4*d* hybridizes strongly with the electrons of N-2*p* nearby, then the nearby anions(N) are spin polarized with magnetic moment. The magnetic moment is mainly come from the tetrahedron of PdN_4. In Figure 4 we marked out the magnetic moment of PdN_4 tetrahedron, three N atoms at the basal plane have a magnetization about 0.18μB, the N atom at the top has a larger magnetization about 0.30μB, the difference is mainly caused by the minor difference of the distances between the N-atoms and Pd atom, and the reason why the magnitude of the top N atom is larger than that of other N atoms is not clear. The Pd atom at the center has a magnetization about 0.78μB. The magnetization of Pd atom is larger than that of all four N atoms and no significant contribution was observed from other atoms.

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CONCLUSIONS

DFT based first-principles calculations were carried out to study the properties of Pd-doped AlN. Based on the results of the calculations, Pd dopants become spin polarized when doped in the AlN, and the *p* electrons of four nearby N atoms were magnetized by this spin polarization through *p-d* hybridization. Compared with conventional magnetic transition metal dopants DMSs, Pd-doped AlN doesn't produce any magnetic precipitate due to its intrinsically nonmagnetic. It is feasible to fabricate AlN based DMSs doped with Pd and the Pd-doped AlN will be useful both in applications and theoritical researches in DMSs.

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