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Cu-doped AlN: a dilute magnetic semiconductor free of magnetic cations from first-principles study

Q Y Wu[1], Z G Huang[1], R Wu[1] and L J Chen[2]

[1] Department of Physics, Fujian Normal University, Fuzhou 350007, People's Republic of China
[2] Department of Applied Physics, South China University of Technology, Guangzhou 510640, People's Republic of China

E-mail: nano@fjnu.edu.cn (R Wu)

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Abstract
The spin-resolved electronic structure of AlN doped with 6.25% Cu has been studied by first-principles calculations based on spin density functional theory. A single substitutional Cu impurity and its nearest neighbouring N atoms have a spin polarized state with a global magnetization of 2.00 μ_B. Band structures show a half metallic behaviour of Cu-doped AlN. Cu-doped AlN has a ferromagnetic ground state which can be explained by a p–d hybridization mechanism. These results indicate that Cu-doped AlN shows promise as a dilute magnetic semiconductor (DMS). This study give new clues to the fabrication of DMSs.

1. 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 [1–3]. Dilute magnetic semiconductors (DMSs), are thought to be ideal materials for this field [1] and alumina nitride (AlN) DMSs have been extensively studied because of the great interest in its wide gap (6.1 eV) and optical transparency. Magnetic transition metals atoms such as V, Cr, Mn, Fe, Co and Ni are frequently used to fabricate AlN DMSs and ferromagnetism at or above room temperature has been frequently observed [4–10]. However, while these magnetic transition metal atoms make the host AlN semiconductor ferromagnetic, the origin of this ferromagnetism is still somewhat difficult to explain. This because these transition metal atoms are intrinsically magnetic and thus their precipitates in the form of clusters or secondary phases in the host semiconductor may also contribute to the observed ferromagnetism. These precipitates may not be observable at small sizes. For example, the mean magnetic moments measured in some of these AlN DMSs are much smaller than expected and lie in a wide range [4, 7, 8], suggesting an inhomogeneous distribution of the magnetic dopants. A recent first-principles calculation by Cui *et al* [11] demonstrated that embedded

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clusters of Cr in GaN could contribute to the low mean magnetic moment in GaN DMSs. These clustering Cr atoms in GaN favour an anti-ferromagnetic (AFM) ground state and thus lower the total magnetic moment and hence the mean magnetic moment. This result can also be applied to explain the similar observations in AlN DMSs. Thus the origin of ferromagnetism in a DMS is difficult to identify when magnetic transition atoms are used as dopants.

To date the origin of the clustering tendency of magnetic dopants in semiconductors is not understood. However, non-magnetic metals alloyed into semiconductors do not suffer from the clustering problem. Indium dopants in GaAs distribute homogeneously [12, 13]. This might indicate the possibility of fabricating DMSs with alternative non-magnetic dopants to avoid the clustering problem in DMSs based on V, Cr, Mn, Fe, Co and Ni. An alternative dopant should first be intrinsically non-magnetic. Moreover, after being substitutionally incorporated into semiconductors, this kind of dopant can become spin-polarized with finite magnetic moments which can couple to each other ferromagnetically. Being free of magnetic precipitates, the observation of ferromagnetism in a DMS with such dopants will certainly classify such a material as an unambiguous DMS. Cu is such a dopant that has attracted both theoretical and experimental attention. Calculations based on density functional theory showed that a single Cu atom in ZnO favours a spin polarized state with finite magnetic moment (0.5 μ_B) and Cu dopants take a FM ground state [14–17]. The recent experimental observation of room temperature ferromagnetism of Cu-doped ZnO [18] confirmed these theoretical calculations. Besides Cu, Pd was also predicted as a potential non-magnetic dopant for GaN [19]. All these works suggest the possibility of fabricating DMSs using non-magnetic dopants.

2. Methodology

The possibility of Cu as dopant for group III–V semiconductors has not yet been explored, either theoretically or experimentally. In this paper, the feasibility of Cu as a non-magnetic dopant for AlN to form a DMS is examined by first-principles calculations based on density functional theory. The electronic properties of Cu-doped AlN at a concentration of 6.25% are studied in a $2 \times 2 \times 2$ AlN supercell with one Al atom substituted by Cu. All calculations are done using the plane-wave VASP package [20, 21]. The projector augmented wave (PAW) potentials are used to represent the interactions between the valence electrons and the core. For Cu, $3d^{10}4s^1$ are treated as valence states. The generalized gradient approximation (GGA) implemented in the PBE scheme [22] is adopted for the exchange–correlation potential. The electron wavefunction is expanded in plane waves with a cutoff energy of 500 eV, and a gamma-centred $6 \times 6 \times 4$ k-mesh is used to sample the irreducible Brillouin zone (IBZ). These parameters ensure a convergence better than 1 meV for the total energy. The atomic coordinates are fully relaxed using the conjugate-gradient algorithm [23] until the maximum force on a single atom is less than 0.02 eV Å^{-1}. The structural lattice constants are optimized to reach an energy minimum.

3. Results and discussions

The lattice constants a and c of AlN are calculated to be 3.13 and 5.02 Å, respectively, in agreement with experimental values (3.11 Å for a and 4.98 Å for c). When one Al atom in the $2 \times 2 \times 2$ AlN supercell is replaced by Cu, there are slight increases in the lattice constants to 0.013 Å for a and 0.024 Å for c after structural optimization. This increase is a result of the difference in atomic size between Cu and Al. The spin polarized state of the supercell is favoured over the non-spin polarized state by a difference of 80 meV in total energies. The spin

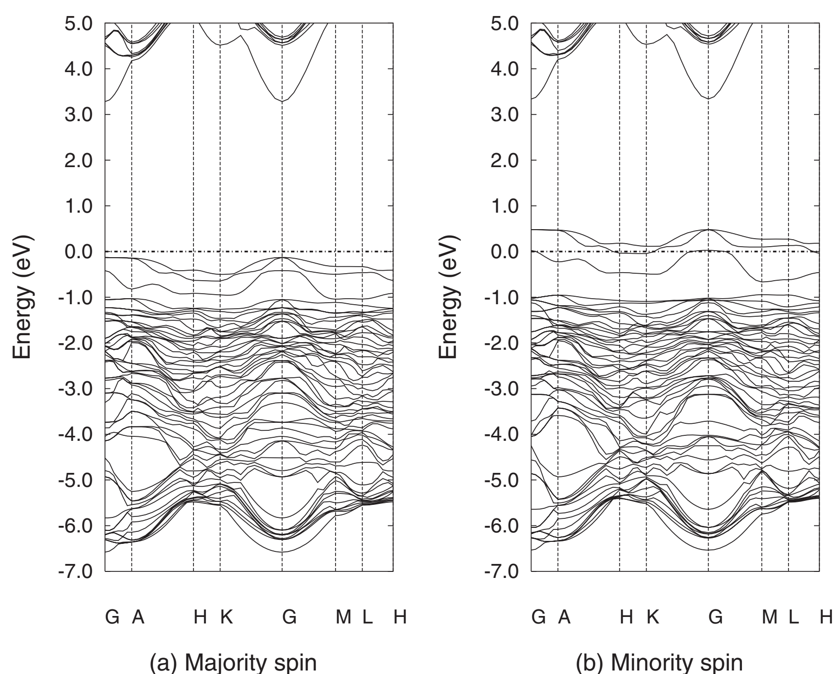

Figure 1. Band structure of the majority spin (a) and the minority spin (b) of AlN doped with 6.25% of Cu. The Fermi level is set to zero.

polarization results in a magnetic moment of 2.0 μ_B which is much larger than that of Cu-doped ZnO [17] (1.0 μ_B). Most of the magnetic moments are from the CuN_4 tetrahedron. The large total energy difference and the magnetic moment suggest an unambiguous spin polarization induced by Cu at the Al site. Figure 1 gives the spin-polarized band structures of the majority spin and the minority spin of the $2 \times 2 \times 2$ AlN supercell with an Al atom replaced by Cu. The majority spin is semiconducting with an energy gap larger than 3.0 eV. On the other hand, right on the Fermi level the minority spin has two unfilled bands. These two bands are dispersive, suggesting delocalized holes in the host semiconductor introduced by Cu. Thus in Cu-doped AlN, conduction carriers are 100% spin polarized, which is strongly desired for spin injection where a highly polarized spin current is desired [24, 25].

FM coupling of the spin polarized dopants is another important property for a DMS. In order to study how Cu dopants will couple to each other, two substitutional Cu atoms are put on positions with the largest possible distant of 6.0 Å between them and total energies are calculated with the two magnetic moments in ferromagnetic (FM) and antiferromagnetic (AFM) configuration along *c* direction. Comparison of the total energy between FM and AFM states shows a difference of 39 meV, with the FM state being the ground state. This value is very close to that of Cu-doped ZnO (42 meV) in Ye *et al*'s calculation [17]. Since a Curie temperature T_C of 350 K was observed in ZnO doped with 7% of Cu, room temperature ferromagnetism in AlN with the same concentration of Cu should be expected. Total energy calculation for a $3 \times 3 \times 2$ supercell with two Cu atoms (corresponding to a concentration of 5.5%) separated by a distance of 7.0 Å also shows that the FM state is favoured with a reduced energy difference of 30 meV. It is can be expected that with a lower concentration, the FM state will be less stable since the coupling between dopants will be weaker. Fortunately, from this study, the FM state can be stabilized within the typical concentration of a DMS.

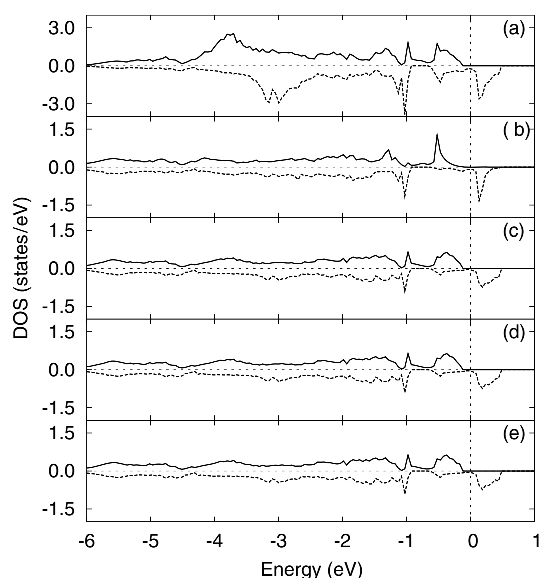

Figure 2. Spin DOS of Cu 3d (a) and N 2p of the N atom on the top (b) and at the bottom ((c), (d) and (e)) of the CuN_4 tetrahedron. The Fermi level is set to zero. Positive (negative) values correspond to the majority (minority) spin.

The stabilization of the FM state in Cu-doped AlN can be explained from its electronic structure. Regarding the electronic structure of a DMS, the stabilization of a FM state may result from Zener's double exchange or p–d hybridization mechanism [26], as explained by Sato *et al* [27]. When the magnetic dopant induces bands which are in the gap of the host semiconductor and are partially occupied, the FM state is stabilized by energy gain from bands broadening due to scattering between magnetic dopants. In this mechanism, bands in the gap are dominated by the magnetic dopant and anions connecting to the magnetic dopant are hardly spin polarized (see Mn-doped GaN [28]). On the other hand, if bands of the magnetic dopant hybridize with the valence bands of the host semiconductor, the host valence electrons are partially spin polarized with significant magnetic moments which couple ferromagnetically or antiferromagnetically to the magnetic dopant. Then other magnetic dopants in turn couple to the spin polarized host valence electrons in the same way for an energy gain. This results in an indirect FM coupling among magnetic dopants. This is the so-called p–d hybridization mechanism. These two mechanisms result in different relationship between the Curie temperature and the concentration of the dopants [27]. To study the mechanism that stabilizes the FM state in this Cu-doped AlN DMS, the projected density of state (DOS) is analyzed. Figure 2 shows the spin DOS of Cu 3d and N 2p (for the four neighbouring N atoms of Cu). As can be seen, in the majority spin channel the first peak of Cu 3d below the Fermi level overlaps with that of 2p of each N atom. While in the minority spin channel both Cu 3d and N 2p contribute to the unoccupied states above the Fermi level. These characteristics of the spin DOS suggest a strong hybridization between Cu 3d and N 2p and significant magnetization should be found in each of the neighbouring N atoms of Cu.

To further elucidate the p–d hybridization, the magnetization distribution in the CuN_4 tetrahedron is shown in figure 3. The atomic magnetization for Cu and N atoms is integrated with a radius of 1.6 Å. Significant magnetization is found in each N atom connected to a Cu atom. Each N atom carries about 0.25 μ_B. This value is of the same magnitude as that of Cu

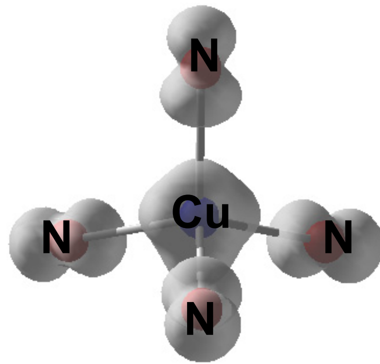

Figure 3. Isosurface of the spin distribution in the CuN_4 tetrahedron. The Cu atom is located at the centre.

(This figure is in colour only in the electronic version)

(0.7 μ_B) and is larger than that of Mn-doped GaN [28]. In Mn-doped GaN, each N connecting to Mn has a magnetization less than 0.02 μ_B in spite of the large magnetization of Mn (4.0 μ_B). All the neighbouring N atoms align their magnetization parallel to that of Cu. This is consistent with the spin DOS shown in figure 2. Since the unfilled states of Cu 3d and N 2p appear in the same minority spin channel, the resultant magnetizations (spin up–spin down) on Cu and N atoms should of course appear in the same majority spin channel and couple ferromagnetically to each other. Thus other Cu dopants also align their magnetization to the host N atoms in the same way to lower the total energy, resulting in an indirect FM coupling among all Cu dopants. This result also suggests that the FM state is stabilized by the p–d hybridization mechanism.

It is well known that as-grown AlN is intrinsically defective and impurity doping to control the electrical properties is challenging. However, in such a DMS, the concentration of the magnetic impurities is of the order of a few per cent, far greater than that of intrinsic defects [29]. So in principle the intrinsic defects will not have significant effect on the ferromagnetism of Cu-doped AlN.

4. Conclusions

To conclude, the electronic properties of Cu-doped AlN have been studied by DFT calculations. A single Cu dopant becomes spin polarized when substitutionally incorporated into an AlN semiconductor. This spin polarization further magnetizes the p electrons of its four connecting N atoms through p–d hybridization. This hybridization in turn renders an FM coupling state among all Cu dopants above a certain concentration. Thus Cu should be a promising non-magnetic dopant for AlN to form AlN DMSs.

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