First-principles study of ferromagnetism in Pd-doped and Pd-Cu-codoped BN

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Abstract. In this paper, we aimed at probing the ferromagnetism properties of Pd and Pd-Cu-codoped supercell BN based on the first-principles methods. The formation energy, lattice constants, energy band structures, spin density of state, energy difference between ferromagnetism (FM) and antiferromagnetism (AFM) orderings were calculated. Formation energy calculations showed that Pd atom tended to replace B atom in the supercell. Pd-doped BN exhibited a half-metallic ferromagnetic. And the ferromagnetism arised from the strong hybridization between the Pd4d and N2p state. Pd-Cu-codoped BN also displayed a half-metallic ferromagnetic. The incorporation of Pd and Pd-Cu induced some impurity energy differences between FM and AFM orderings. It also showed that FM state was the ground state, and room temperature ferromagnetism may be expected. These results pointed out the possibility of fabricating BN based on dilute magnetic semiconductors (DMS) by doping with Pd and Pd-Cu.

1. Introduction

Recently, people have expected to achieve signal processing and information storage capabilities in the same device. The dilute magnetic semiconductors (DMSs) were considered to be an ideal material for the manufactures of such semiconductors. At present, it has become a hot topic. Nanoscale materials exhibit a variety of unique properties that could be used in a wide of advanced technological applications. BN has a lot of similar characteristics with AlN which has many useful properties, such as physical and chemical properties, especially involving the electronic and magnetic properties. As we know, element doping is a promising approach to controllably modify the electronic structures and magnetic behaviors. Since the discovery of AlN, many theoretical and experimental studies about the doping of metal atoms have been conducted [1-3].

The BN is a wide band gap and large band energy of the semiconductor [4]. BN had four structures, which are named as cubic BN (c-BN), hexagonal BN (h-BN), rhombohedral BN (r-BN) and wurtzite BN (w-BN). The c-BN and h-BN are steady state structure, but r-BN and w-BN are not. Within reported cubic structure BN, similar to rhombus, the bonding manner of the cubic BN sheet is sp3 hybridization, and it has several properties including high melting point, high thermal conductivity, and high chemical hardness. Currently, the research was mainly focused on the mechanical properties and thermal properties of BN, while the researchers rarely focused on the optical and magnetic properties. Back in 1999, the experiments [5,6] showed that the deficient BN exhibited ferromagnetic at room temperature. Zhou and Liu [7,8] made some calculations for the ferromagnetism of the semi-
metallic Cr-doped BN, and Pd doped BN had been reported [9] in the experiment, but the studies on DMS had not been reported. First-principles calculation method had been widely used in material simulation [10-12]. This paper carried out geometry optimization based on density functional theory plane wave pseudopotential (PWP) method for Pd-doped BN supercell system. And the results were analyzed to study electronic structure and optical properties of the Pd-doped BN. It explored the feasibility of obtaining Pd-doped BN based on the DMS.

2. Calculation model and methods
The space group of cubic BN semiconductor was F-43m. The experimental lattice constant was 0.3615nm [13]. 2 × 2 × 2 of the supercell system containing 64 atoms was built. In all calculations, one or two Pd atoms replace the B atoms in the supercell system. Where \( x = 0.03125, 0.0625 \) represent two different doping concentrations (\( \text{Pd}_x\text{B}_{1-x}\text{N} \)). Pd atom, as a substitute, replaces bits in supercell high symmetry center point. Two Pd atoms, as an alternative, substitute bit option in the center of the high symmetry, and the other alternative place Pd at the four corners. For each configuration, it was optimized before calculating the average structure. Structural optimization was calculated by the CASTEP package [14]. The Perdew-Burke-Ernzerh (PBE) of the generalized gradient approximation (GGA) [15] was chosen to describe the effects of the electronic exchange-correlation interaction. In these calculations, the cutoff energy of the plane wave basis set was 380eV. The Monkhorst-Pack scheme K-point grid sampling was set as 6×6×1 for the irreducible Brillouin zone. Structural optimization was continued until the energy converged to \( 1 \times 10^{-5} \) eV/atom, the forces on the atoms had converged to less than 0.03eV/Å, the stress had converged to 0.05GPa and the atom displacement had converged to \( 1 \times 10^{-3} \) Å. Integral spin density and spin density absolute value integrator were analyzed. If the two numbers were very close and very small, the system was paramagnetic; provided that the two numbers were close and limited, the system was ferromagnetic; should the absolute value of the spin density integration was limited and the spin density integration itself was close to zero, the system was antiferromagnetic; when the two numbers were limited and the D-value was limited, the system was ferrimagnetic.

3. Results and discussion
3.1. Optimized Structures
To assess the accuracy of our computation method, we performed a series of calculations for BN supercell optimization. The equilibrium lattice constant after optimization is \( a=b=c=3.615 \), which is in good agreement with the experimental results (\( a=b=c=3.615 \)) [16], hence it ensures the reliability of our method. We have calculated that the lattice constant of pure BN, the lattice constant is 0.3615 nm, and this value is exactly the same with the experiment. When using a Pd atom instead of one of the B atoms, the calculated lattice constants are 0.3615 nm, which indicates that Pd atoms do not affect the size of the lattice. However, the Pd-N bond increases compared with the B-N bond of the pure BN and the surrounding bond-length changes subsequently. This is because that the Pd atomic radius is larger than that of the B atoms leading to the redistribution of the electrons. Under the situation where the direction of the electron spin was not set, we made analysis for the integral of the spin density and spin density absolute value integrator by calculation. We found that pure BN exhibits antiferromagnetic, and Pd doped BN system is calculated for the magnetic moment of ferromagnetic 2.62 μB. This shows that the Pd-doped BN can produce a magnetic spin polarization.

3.2. Electronic Structure
When the electronic calculations are done, the valence electron configuration of the main selection has B: \( 2s^22p^6 \), and N: \( 2s^22p^3 \). The pure BN was calculated, in order to compare with the case of doped BN. Fig. 1 is a band structure and a partial density of states (DOS) diagram of BN. Fig.1a shows that the calculated BN band gap is 4.492eV. This value is lower than the experimental values of 6.0eV. That is mainly attributed to the generalized gradient approximation (GGA) that cannot accurately calculate the
band gap value \[17\]. But this does not affect the theoretical analysis of the electronic structure of BN. Fig.1b should be deviation, because the generalized gradient approximation (GGA) may calculate eigenstates in time, will produce a deviation. Fig. 1b shows that the valence bonds could be divided into the upper -22eV to -14eV and -11eV to 0eV band composition. It can be seen that valence band is mainly composed of B2s2p and N2p, the upper valence band is mainly composed of N2p, lower valence band is mainly composed of B2s2p and N2s which consist of a strong localized states at -15eV. The conduction band with a small amount of B2s and N2s is mainly composed of B2p and N2p.

**Figure 1.** The band structure (a) and PDOS(b) of the pure BN
Figure 2. Spin-polarized down (a) and Spin-polarized up (b) band structures of BN doped with 3.125% of Pd-doped

Fig.2 shows a concentration of 3.125% Pd-doped BN spin polarization energy band diagram. It can be seen from the Fig. 2, whether the spin up or spin down of the energy band diagram, there is a band gap, which indicates that Pd doped BN does not destroy the overall properties of the semiconductor. In the energy band diagram of the spin, or the rendering semiconductor properties, the band gap reaches 2.436eV, it is smaller than the above calculated pure BN of 4.492eV. Under spin down, there are two full valence bands above the Fermi level, which exhibit a certain degree of metallic nature. Therefore, the whole (B, Pd) N exhibits semi-metallic nature. It is also consistent with the above calculated energy spin polarization conclusion and the experimental results. The role of these two discrete filled valence bands is like a free hole. Therefore, in the Pd-doped BN, we can theoretically
achieve 100% spin polarization, which shows that (B, Pd) N possible spin injection is used. On the whole, the band gap is significantly reduced after the doping.
Fig. 3 shows the spin density of states of the total Pd-doped BN, partial wave density of states, and Pd, N spin density of states. Because the density of states near the Fermi level division determines the magnetic properties of matter, we focus on studying the density of states near the Fermi level. Fig. 3(a) shows the splitting up of the electronic density of states of spin-up and spin-down state density distributions appearing obviously in the vicinity of the Fermi surface, which suggests that the system of electrons by spin exchange interactions have emerged in order. Spin-up electrons across the Fermi surface show the metallic nature; and spin-down electrons in the Fermi surface open a gap show semiconducting, which is consistent with the above analysis of the energy band diagrams. Therefore, Pd-doped BN has a half-metallic nature. The total density of states distribution is different when the electron spin is up or down. It exhibits the asymmetry. In the occupied states under the Fermi level (vertical dashed line in Figure 3a), we found that the number of the spin-up electrons is larger than that of the spin-down electrons after a calculation of the density of states by integral computation. The spin-up electrons exhibit a net magnetic moment in the outside, which shows ferromagnetism.

Fig. 3(b) shows the density of states of B31PdN32, the peak of the lower valence band mainly coming from N2s electrons, the peak of the conduction band mainly from B2p electrons too, and the peak of the upper valence band mainly from B2p electrons, N2p electrons and Pd4d electrons. As can be seen from Fig. 3(c), Pd4d, B2p and N2p electrons below the Fermi level correspond to a few peaks, which indicates that Pd4d electronic and B2p, N2p have strong hybrid electronic effects. There are B31PdN32 B2p (a), N2p electron density of states (b) and Pd4d electron density of states (c) in the electronic density, as shown in Fig. 3. From the comparison, we can know that three peaks overlap each other in the plurality, strong hybrid peak can be found in Fig. 3a, the density of states near the Fermi surface is mainly composed of B2p, N2p and Pd3d electrons, all of which indicate the electronic states of Pd4d, B2p and N2p state electron mutual hybrid role. The calculations show that the number of occupy states below the Fermi level at the middle or on the electronic density of states Pd4d, B2p and N2p electronic integrating are much larger than that of spin-up electron spin-down electrons, suggesting that both Pd, B and N interaction are ferromagnetic state, nearest neighbor N atoms 2p electrons tend to be Pd4d electrons ferromagnetic order arrangement. These results indicate that Pd-doped BN ferromagnetic state can be obtained through the mechanism of the formation of hybrid p-d.
Many classes of computer simulation have two doped impurity element. In order to make the two elements doping together, we selected 3x2x2 supercell for co-doped Cu-Pd of BN. The density of states is shown in Fig. 4. Because of the density of states near the Fermi distribution determining the magnetic properties of matter, we focused on investigating the charges density of states near the Fermi distribution. Electronic density of states and splitting state density distribution of the spin-down can be seen from Fig.4, and in the vicinity of the Fermi surface, the spin-up is so obvious that it indicates the system in the electronic interaction taking place through the exchange of spin ordered. Spin-up electrons across the Fermi surface exhibit metallic nature; and spin-up electrons at the Fermi level lead to the opening of a gap, which exhibits semiconducting. That is consistent with the above analysis of the energy band diagram. Therefore, Cu-Pd co-doped BN has a half-metallic nature. There is an offset in spin-up and spin-down electron density of states. That also indicates the presence of magnetic ordering. There is a difference in the electronic density of states of spin-up and spin-down of the total distribution. It exhibits asymmetry. In the Fermi level (Figure 4) vertical dashed line occupying less state, we can know that spin-up number of points are larger than that of spin-down electrons after the electronic density of states, thus the net magnetic moment exhibits ferromagnetism.

4. Conclusion
In this paper, the first-principles study has been performed to evaluate the structural properties of the pure and Pd-doped BN, such as the band structure and the density of states. The calculations reveal that Pd-doped BN is a half-metallic ferromagnet with 100% carrier spin polarization, and the ferromagnetism arise from the strong hybridization between the Pd4d and N2p state. At BN doped with 3.125% Pd concentration, the different energy calculations show that the ground state is FM state. These results suggest that it is possible to fabricate BN based on DMS by doping with Pd. This DOS of BN compared with conventional dilute magnetic semiconductors, its doping concentration is smaller. And Pd doped BN is paramagnetic. Thus, Pd doped BN might be a kind of promising diluted magnetic semiconductors. Compared with conventional dilute magnetic semiconductors, doping concentration is much smaller. There is no doubt that you can find the ideal semiconductor. Thus, Pd doped BN might be a very promising diluted magnetic semiconductor. Pd-Cu codoped shows doped
BN group having two elements with BN group may be implemented, which is based on the latest proposed BN group.

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