First Principles Calculations of Electronic Band Structure of Nb-Doped ZnO

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Abstract. Based upon the density functional theory (DFT) in this paper, the first-principles approach is used to study the electronic band structure of Nb-doped wurtzite ZnO with different concentration. Three doped structures were considered: A Nb atom replaced by a Zn atom and two Nb atoms replaced by two Zn atoms in different positions. For the pure ZnO, the Fermi level is in the valence band maximum, but in the Nb-Doped ZnO supercell, Fermi level shifts to the conduction band and exhibits similar metallic properties.

Introduction

ZnO is an oxide semiconductor and a promising material for electronic, it has become interested topic due to its direct wide bandgap (Eg≈3.3 eV)[1]. Compared with MgO and other optoelectronic materials, ZnO has a low dielectric constant, big photoelectric coupling rate and excellent piezoelectric. And the exciton binding energies of ZnO is up to 60 meV, it is a Blu-ray emission in the ultraviolet and promising areas of new optoelectronic materials. So it has a wide range of applications in gas sensors[2], ultraviolet lasers[3] and transparent conductive films[4].

In recent years, people in addition to extensive research ZnO films, also studied the doped ZnO films of different metals. Doped Al[5], Be[1] In[6] and other elements can be get an ideal electrical properties of n-ZnO thin films, significantly improved the conductivity of ZnO thin films[7]. However, concerning the theoretical calculation and analysis of the influence of the structure of Nb-doped ZnO were seldom reported.

In this paper, first-principles density functional theory[8] is used to calculate the electronic band structure of Nb-doped ZnO. Four different models are used to study the role of Nb-doped ZnO (concentration of Nb are 0, 6.25% and 12.5%), and to study band structure and density of states (DOS) of Nb-doped ZnO.

Models and calculation method

The ideal ZnO has a hexagonal wurtzite structure. A 2 × 2 × 2 supercell of the wurtzite ZnO is shown in Fig. 1. Each unit cell contains 2 Zn atoms and 2 O atoms, and there are 32 atoms in all. When one of Zn atom was replaced by Nb atom, it is called Nb-doped ZnO. Changed the number of Nb atoms in the supercell, we can get different concentrations of Nb(x=6.25%, 12.5%). For the concentrations is x=6.25%, one model is obtained by replacing 1 Zn atom with 1 Nb atom. Two different positions of Nb atoms are considered following the research work of Jia et al.[9-10], which concentration is x=12.5%: the “near” configuration, in which the Nb atoms in the same unit cell are separated by a single O, and the “far” configuration, in which they are connected via -O-Zn-O- bond. Then we considered for the effect of doping concentration on the electronic structure of Nb-doped ZnO.

The calculations are carried out by using the CASTEP package provided by the Material Studios 5.0 by Accelrys. The package is an ab initio quantum mechanics codes based on density functional theory[11]. In the package, the ionic potential is substituted by a pseudo-potential, the electronic wave function is expanded by the plane wave, and the exchange and correlative potential of electronic-electronic interactions are improved by the generalized gradient approximation (GGA)[12]. In our calculation, a 4 × 4 × 2 k-point mesh in the Brillouin zone is used, the cutoff

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energy of the plane wave is 370 eV, and the calculation precision is set to be 2.0×10−5 eV/atom. The test calculations with higher cutoff energies and denser k-point grids are also performed, and the overall results remain unchanged. Then the electronic structures are calculated on the basis of the optimized supercell.

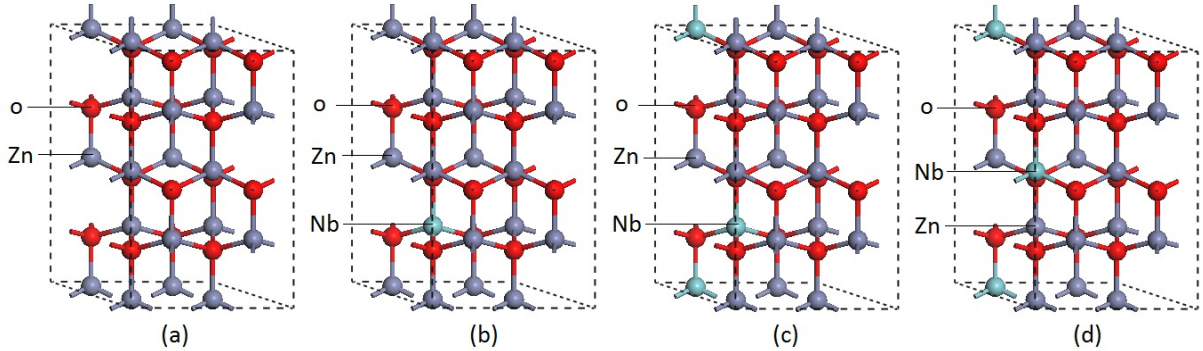

Fig. 1. (a) pure ZnO, (b) 1 Zn atom replaced 1 Nb atom, Nb-doped ZnO in the (c) separated by a single O and (d) separated by -O-Zn-O- bond.

Results and Discussion

First, the structure of pure ZnO wurtzite unit cell is optimized in the calculation. The lattice constants are a =3.283 Å and c =5.311 Å. Deviation with the experimental value (a =3.253 Å, c =5.213 Å[13]) is only about 1%, meaning that our calculation is reasonable.

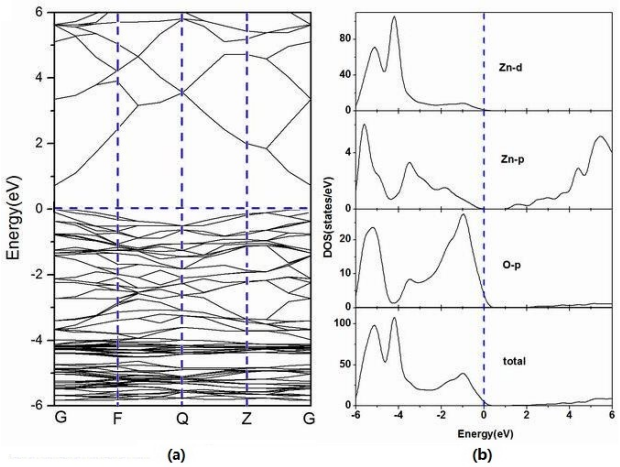

Fig. 2. (a) Band structure and (b) DOS of pure ZnO.

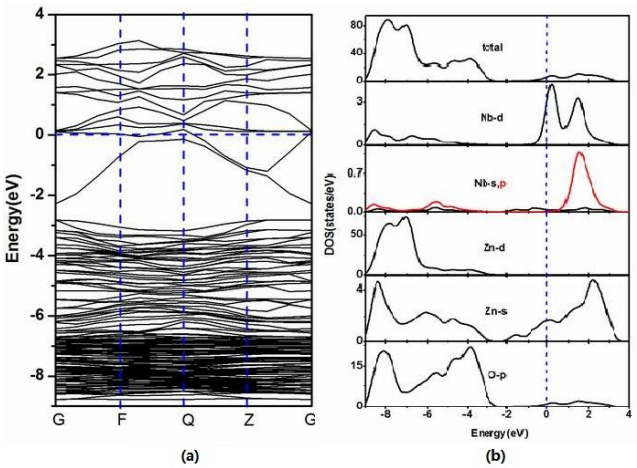

Fig. 3. (a) Band structure and (b) DOS of Nb-doped ZnO with x=6.25%.

According to the optimized crystal structure, we calculated the band structure, DOS and partial DOS (PDOS)[14] near the Fermi energy of pure ZnO in Fig. 2. From Fig. 2(a), it can be seen that valence band maximum and conduction band minimum are both in the G-point, meaning that pure ZnO is a semiconductor material with wide direct band gap. Here, the band gap is 0.73 eV, which is in agreement with the theoretical results of other researchers[15], but much smaller than the experimental results (3.3 eV). This difference originates from the GGA approximation adopted in the calculation process. From the DOS in Fig. 2(b), we found that the valence band of ZnO by the O 2s states occupied the bottom. In the high energy region is mainly composed of electrons of O 2p states and electrons of Zn 3d states hybrid. The O 2p states are the most dominant in the energy range between -4 and 0 eV, and the Zn 3d states locate mainly in the energy range between -5.8 and -4 eV. Therefore, the width of the band gap ZnO mainly decided by O 2p states and Zn 4s states.

Next, in order to investigate the Nb-doped effect of the electronic structures, we calculated the band structure and DOS of Nb-doped ZnO with x=6.25% in Fig. 3(a,b). Compared with the pure

ZnO, the remarkable feature of the band structure of Nb-doped ZnO is that the forbidden band gap narrowing, which indicates that the material is n-type metal. The upper valence band from -7 to -3 eV originates mainly from the O 2p states, and the lower valence band from -9 to -6.4 eV is derived from the Zn 3d states. The impurity bands of Nb 3d states lie just across the Fermi energy, which is partially occupied with a bandwidth of 2.5 eV. On the other hand, the energy difference between valence band maximum and the Fermi level is about 2.8 eV, which is much larger than the band gap of pure ZnO (0.73 eV here). As a result, the transition of an electron from valence band to unoccupied states will need more energy in Nb-doped ZnO.

Fig. 4(a, b) shows the DOS of replacing two Zn atoms with Nb atoms in the separated by a single O and separated by -O-Zn-O- bond. From Fig. 4(a), it can be seen that the impurity energy band becomes wider. Meanwhile, along with the concentration of Nb increased, the band gap became narrower. It determined the width of the band gap energy increased VBM (Valence Band Maximum) and CBM (Conduction Band Minimum) is declining. The energy difference between the valence band maximum and the Fermi level is increased to 2.86 eV. Comparing with the results presented in Fig. 4(a, b), the separated by -O-Zn-O- bond makes the Nb 3d states more localized and strong, and the energy difference between the valence band maximum and the Fermi level becomes larger than the separated by a single O, which proves that different doped structure will affect the physical properties of the system, although the configurations are same.

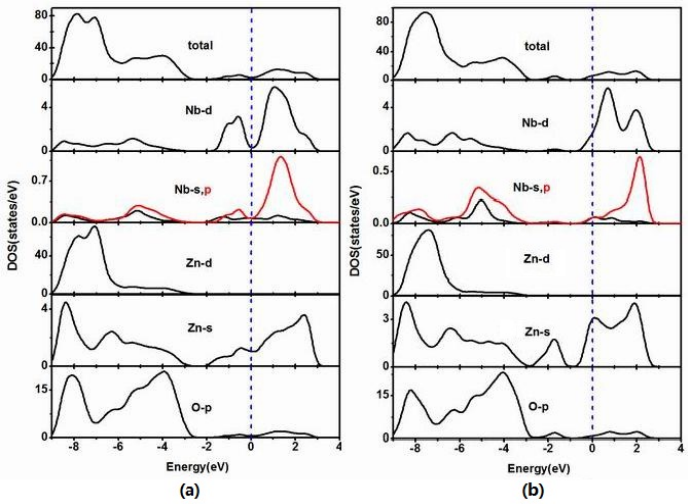

Fig. 4. DOS of two Nb-doped ZnO in the (a) separated by a single O and (b) separated by -O-Zn-O- bond.

Conclusion

In this paper, electronic band structure of Nb-doped ZnO with different situations is studied by using the first-principles with the generalized-gradient approximation. The results showed: Nb-doped ZnO display n-type semiconductor characteristics. For the pure ZnO, the Fermi level in the valence band maximum. For Nb-doped ZnO, the Fermi level move into conduction band, and to show similar characteristics with the metal.

Acknowledgments

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