Bandgap control in ZnO with Na and Cl adatom: DFT Calculations

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Abstract. The Zinc oxide is well known as a direct wide bandgap semiconductor material with many promising properties for blue/UV optoelectronics, transparent electronics, spintronic devices and sensor applications. Controllable bandgap tuning is important to widen its possible applications. In the present work, we applied density functional theory to study bandgap tuning of ZnO by introducing Na atom and Cl atom. Sodium acts as p-type doping, while chlorine acts as n-type doping for ZnO. The effect of Na and Cl doping in the study was calculated using the Density Functional Theory (DFT) method. The results indicate that ZnO, which is a natural n-type semiconductor when doped with p type, has an increase in bandgap, on the contrary, doping with n type decreased its bandgap.

1. Introduction

Zinc oxide (ZnO) materials have been used in many scientific and industrials areas such as piezoelectric transducers, optical waveguides, acoustic media, conductive gas sensors, transparent conductive electrodes, varistors. Today, ZnO materials have emerged as a complement or alternative to GaN in optoelectronics owing to a direct wide bandgap of pure ZnO (Eg 3.3 eV) at 300 K. They also have the same structure, Wurtzite structure with a very similar lattice constant. However, ZnO is in several ways superior to GaN, among others, because it can form large single crystals and the binding energy of exciton which is also large (60meV). From the technological side, it is also simpler because crystal growth is easier to occur. This causes the price to be cheap.[1], [2].

Zinc oxide is naturally a n-type semiconductor with very high electron densities. By substituion Zn sites with group-I elements (Li, Na, and K) and O sites with group-V elements (N, P, and As) p-type doping in ZnO can be realized[3].

2. Methods

All the calculations were carried out using the periodic supercell model under the framework of density functional theory (DFT). The structure optimization and electronic structure calculations were carried out by using ABINIT Package[4]. The exchange-correlation potential is treated in the level of the GGA using Perdew-Burke-Ernzerhof (GGA-PBE)[5] and the plane wave basis set in the calculation, and the Brillouin-zone integration is performed with a Mokhorst-Pack k-point grid.

Na/Cl atoms were placed on ZnO unit cell by substitution Zn or O atoms as represented at Figure 1.
Figure 1. supercel 2x2 ZnO system with: a) nothing b) one Na atom and one Cl atom c) one Na atom d) two Na atoms e) three Na atoms f) one Cl atom g) two Cl atoms h) three Cl atoms

3. Results and Discussions

The calculation results of the bandgap value of pure ZnO, Na-doped ZnO, Cl-doped ZnO, and Na-Cl doped ZnO doping Na-Cl are listed in the table:
Table 1. Fermi Energy and Band gap of ZnO systems

| ZnO systems               | Band gap (eV) |
|---------------------------|---------------|
| Pure ZnO                  | 0.6           |
| ZnO + 1 Na atom           | 0.8           |
| ZnO + 2 Na atoms          | 1.1           |
| ZnO+ 3 Na atoms           | 1.4           |
| ZnO+ 1 Cl atom            | 0.6           |
| ZnO + 2 Cl atoms          | 0.4           |
| ZnO+ 3 Cl atoms           | 0.05          |
| ZnO+1 Na atom + 1 Cl atom | 0.3           |

Density of State of pure ZnO shows that the conduction band of ZnO mainly derived from orbital the O-2p state, while the valence band is mainly composed of the Zn-3d state and the O-2p state.

Figure 2. Density of State of pure ZnO

Considering the electronic configuration the Na atom which has one valence electron replaces the Zn atom which has two valence electrons, the Na atom in Na-doped ZnO should be a p-type dopant. However, from Table 1, it can be seen that the addition of Na atoms widened the bandgap this agree well with previous first principle studies[6]. It suggested that the impurity state induced by Na atom is located at the valence band such that broadens the bandgap.
The density of state feature of Na-doped ZnO with one, two, and three Na atoms are very similar so that we here only show the Density of state of ZnO doped with three Na atoms (Figure 3). The Density of state indicates that the 2p orbitals of Na atom contribute to the valence and conduction bands of the p orbitals.

In Cl-doped ZnO, one Cl atom, with five valence electrons, replaces O atom which has four electrons. Pure ZnO is believed as a N-type semiconductor. One Cl atom acts as a N-type dopant giving extra electron. In several cases, electron carrier concentration exceeds the conduction band edge density of states known as Moss-Burstein effect[7]. In this work, Moss Burstein effect does not occur, it seems that extra electrons of Cl induce an impurity state below the conduction band so that narrow the band gap of ZnO [8].
4. Conclusion

This first principle density functional theory calculations have shown the effects of Na and Cl atoms on the electronic structure of ZnO. Doping Na atoms enhance the band gap of ZnO, while doping Cl atoms narrow the band gap of ZnO. Influence of Cl atom is relatively more that that of Na atom so that Codoping Na-Cl narrow the band gap of ZnO.
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