Chemical Physics Letters 614 (2014) 15–20

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Study of the effect of Cu heavy doping on band gap and absorption spectrum of ZnO

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ARTICLE INFO

Article history:
Received 13 June 2014
In final form 3 September 2014
Available online 10 September 2014

ABSTRACT

Contradictory experimental absorption spectra blue shift and red shift results have been reported in the literatures. To solve this problem, this study investigates the electronic structure and absorption spectra of $Zn_{1-x}Cu_xO$ ($x = 0$, 0.0313 and 0.0625, respectively) and $Zn_{32}CuO_{32}$ supercells employing first-principles calculations with GGA+U method. By increasing the Cu substitutional doping concentration from 3.13% to 6.25%, the following results are obtained: increased magnetic properties, narrower band gaps, and a significant red shift in the absorption spectrum. These findings are in good agreement with the experimental results. The changes of band gap and absorption spectrum for interstitial doping and substitutional doping are opposite.

1. Introduction

Zinc oxide is an important II–VI type semiconductor that possesses a direct wide band gap of 3.37 eV [1] and a high exciton binding energy of 60 meV [2] at room temperature. ZnO also has low dielectric constant, large electric-coupling ratio, high chemical stability, as well as excellent piezoelectric and photoelectric properties. This type of semiconductor has potential applications in short-wavelength optoelectronic devices, such as laser and light-emitting diodes. In experimental and theoretical studies, the structure of ZnO can be changed easily by effective alloying with a dopant, which involves ZnO material energy band engineering. In addition, by regulating the ZnO band gap, the performance of ZnO-based optoelectronic devices can be improved. Therefore, doped ZnO has vast applications in the production of solar cells [3], liquid crystal displays [4], gas sensors [5], UV laser diodes [6], transparent conductive films [7], and diluted magnetic semiconductors [8].

Extensive works on photoelectrical properties of doped ZnO have been carried out. Kulyk et al. [9] prepared Cu-doped ZnO by radio-frequency magnetron sputtering; their results showed that the grain size and band gap decreased, and the absorption band edge shifted to low levels with increased Cu concentration. Wu et al. [10] prepared singly doped Co and Cu as well as co-doped ZnO thin films using the sol–gel process. They also investigated the influence of Co and Cu doping on the surface morphologies of ZnO films, and found blue double peaks at all ZnO thin film samples caused by transition of electrons from conduction band minimum (CBM) to zinc vacancy or from Zn interstitial to valence band maximum (VBM). However, the green peak is highly relevant to the oxygen slip formed by doping. Ma et al. [11] prepared Cu-doped ZnO films by radio-frequency reactive magnetron sputtering and studied the microstructures and optical properties of doped systems. The results indicated that ZnO films exhibited a strong orientation toward the *c*-axis and a uniform grain size after Cu-doping. Furthermore, the intensities of blue (~485 nm) and green (~527 nm) peaks showed significant increase after annealing. Fu et al. [12] investigated the photocatalytic performance of Cu-doped ZnO nanoparticles prepared using the sol–gel process.

Theoretical calculations have also been performed to determine the photoelectrical properties of doped ZnO. For instance, Kong and Gong [13] calculated the band gap of Be substitutional and interstitial doping ZnO using the GGA method, and found that substitution of Zn atoms by Be could enhance the band gap of ZnBeO phases, while interstitial Be atoms would decrease the band gap. Ye et al. [14] calculated ferromagnetism of Cu-doped ZnO by the local density approximation (LDA) (Hedin-Lunquist form) and generalized gradient approximation (GGA) (Perdew–Burke–Ernzerhof form). Li et al. [15] investigated the magnetic and optical properties of doped ZnO nanosheets using the GGA+U method. Their results revealed that the replacement of two Cu atoms by two Zn atoms enhanced the magnetic properties of the doped

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http://dx.doi.org/10.1016/j.cplett.2014.09.005
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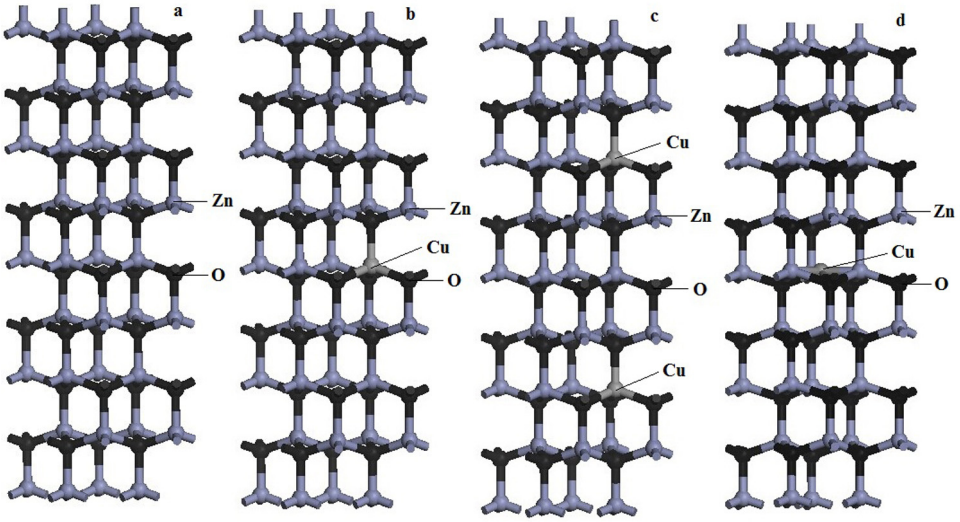

Figure 1. The $2 \times 2 \times 4$ supercells for (a) undoped ZnO, (b) $Zn_{0.9687}Cu_{0.0313}O$, (C) $Zn_{0.9375}Cu_{0.0625}O$, and (d) $Zn_{32}CuO_{32}$.

system. Moreover, the absorption spectrum exhibited a noticeable red shift with increased doping concentration. Kang et al. [16] analyzed the variations in the ferromagnetism of carrier doping in $Zn_{1-x}Cu_xO_{1-y}X_y$ (X = N and F; x, $y = 0.0277–0.0833$) by the full-potential linear muffin-tin orbital (FP-LMTO) method. Their experimental results showed that Cu magnetic moments at low Cu concentrations increased and decreased by N and F doping, respectively. Meanwhile, Liu et al. [17] calculated the band gap variations and absorption spectrum of wurtzite $Zn_{1-x}Co_xO$ using the GGA method, and found that the band gaps broadened and the optical absorption edge exhibited a significant blue shift given an atomic fraction of Co. Duan et al. [18] investigated the electronic structure and optical properties of ZnO doped with transition metals and N. Their calculations indicated that the co-doping of transition metals (Mn, Fe, Co, and Cu) and N favored the formation of p-type ZnO.

Although good results on the effects of Cu doping on the optoelectronic properties of ZnO have been theoretically and experimentally achieved, speculations remain upon comparing the band gaps and absorption spectra of undoped and Cu-doped ZnO. Increased Cu substitutional doping from 3.13% to 6.25% widened the band gap and caused a blue shift on the absorption spectrum [19], which contradicted the findings of Ref. [20]. From crystal periodicity, we can obtain useful results by performing first-principles calculations of the band structure, band gap, and the absorption spectrum of Cu-doped ZnO, with a doping concentration range similar to that presented in previous works [19,20]. We believe that the results can contribute to better design and improved preparation of short-wavelength optoelectronic devices from Cu-doped ZnO.

2. Theoretical model and computational method

2.1. Theoretical model

ZnO has a hexagonal wurtzite crystal structure that belongs to the space group $P6_3mc$ and C_{6v}^4 symmetry. The unit cell comprises two hexagonal close packed lattices along the c axis and sleeve; the lattice parameters are $a = 0.3249$ nm and $c = 0.5205$ nm. The $2 \times 2 \times 4$ supercells for undoped ZnO, $Zn_{0.9687}Cu_{0.0313}O$, $Zn_{0.9375}Cu_{0.0625}O$ and $Zn_{32}CuO_{32}$ were applied to calculate the process of geometric optimization and energy. Three substitutional doping levels of 0%, 3.13%, and 6.25% with zero, one and two Zn atoms replaced by Cu atom, respectively, were examined.

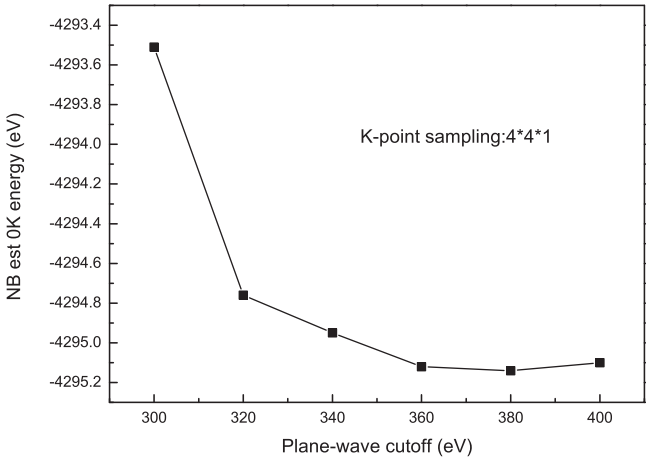

Figure 2. The test of energy convergence as the cut-off varied for undoping ZnO.

$Zn_{32}CuO_{32}$ is a system of one Cu atom interstitial doping. The atomic positions of Cu dopants are displayed in Figure 1.

2.2. Computational method

Calculations were performed by CASTEP package [21–23] as implemented in the Materials Studio software. The software is based on the density functional theory (DFT) using the plane-wave ultrasoft pseudopotential method [24–26]. Perdew Burke Ernzerhof (PBE) scheme in the generalized gradient approximation (GGA) was used to treat the exchange-correlation energy. We first optimized the structure of undoped ZnO, $Zn_{0.9687}Cu_{0.0313}O$, $Zn_{0.9375}Cu_{0.0625}O$ and $Zn_{32}CuO_{32}$ and then calculate the electronic and optical properties.

During optimization, Brillouin zone integrations were first performed with the special k-point method over a $4 \times 4 \times 1$ Monkhorst-Pack mesh. Energy convergence during cut-off variation for undoping ZnO supercells was also tested (Figure 2). The total energy of the system begins to converge at the cut-off energy of 320 eV and presents good convergence at the cutoff energy of 380 eV. Therefore, cutoff energy at 380 eV is the most ideal for all calculation models. Second, the plane wave energy was set at 1.0×10^{-5} eV/atom, and the maximum tolerances of force, stress, and displacement were set at 0.3 eV/nm, 0.05 GPa and