Solid State Communications 204 (2015) 47–50

Contents lists available at ScienceDirect

Solid State Communications

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

First-principle study on Ag-2N heavy codoped of *p*-type graphene-like ZnO nanosheet

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ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form
12 December 2014
Accepted 13 December 2014
Communicated by Y.E. Lozovik
Available online 19 December 2014

Keywords:
ZnO nanosheet
p-type conductivity
First-principles

ABSTRACT

In this article, two different Ag-2N heavy codoped of graphene-like ZnO nanosheets have been investigated based on first-principles density-functional theory. The geometric optimization, Density of States (DOS) and Band structure (BS) for all models are calculated, respectively. The results indicate that Ag substituted on the cation site (Ag_{Zn}) exhibit a strong attractive interaction with a nitrogen acceptor located at the nearest-neighbor oxygen site, forming passive Ag-N complex. This study can be a theoretical guidance to improve the electrical conductivity of *p*-type graphene-like ZnO nanosheet by heavy codoping.

1. Introduction

Zinc oxide is a promising optoelectronic material, which can be utilized for blue and ultraviolet light emitting diodes, laser diodes, and solar cells due to its wide band gap of 3.2 eV [1,2]. It has been suggested that undoped ZnO is *n* type due to a large number of intrinsic defects such as oxygen vacancies (V_O) and Zn interstitials (Zn_i) [3]. *p*-type doping of ZnO has attracted great attention, both theoretically and experimentally, because of its potential application for next-generation short-wavelength optoelectronic devices [4–9]. The obstacle that prevents full utilization of ZnO as a novel optoelectronic material is the inability of obtaining *p*-type conductivity with high hole concentration and low resistively. Therefore, many efforts have been made to achieve *p*-type ZnO, with using many techniques and dopants [10].

At the nanoscale, ZnO brings us more sweet surprises [4–11]. The versatile chemical bonding of ZnO leads to probably the richest family of nanostructures among all materials, which have been successfully synthesized through a variety of experimental techniques. Compared with the bulk crystalline ZnO, these low-dimensional structures have demonstrated extraordinary electrical and optical performances and are promising candidates for many novel applications in transparent electronics, gas sensors, transducers, solar cells, and biomedical devices [12]. Particularly, two-dimensional (2D) systems show peculiar properties, which are different from their counterparts bulk phases. The formation of planar nanosheets of ZnO have been predicted to occur as the number of ZnO layers are reduced [13], and one monolayer of ZnO has been shown to be stable [14]. ZnO in nanoscale may have even more interesting properties [15–19]. It has been experimentally observed that planar ZnO nanosheets are stable and the transition to wurtzite structure occurs in the 3–4 monolayers for ZnO on Ag substrates through surface X-ray diffraction and scanning tunneling microscopy, which provided a direct evidence for the presence of planar ZnO nanosheets [20].

Because the interaction of Ag and N codoped of graphene-like ZnO (Gr-ZnO) is of great technological interest, what properties distinguishable from unsaturated bare nanosheets? Yet a theoretical understanding of electronic properties of these functionalized ZnO nanosheets remains unclear. In this article, Density functional theory (DFT) computations are performed to systematically investigate the structural, electronic and magnetic properties of a low dimensional system composed by a flat monolayer of ZnO atoms with a graphene-like structure. Two different graphene-like Ag, N codoped Gr-ZnO nanosheet models, which the proportion of Ag:N equals to 1:2, have been constructed. Meanwhile, Density of States (DOS), Band structure (BS), atom Mulliken charges and the populations analysis are performed to determine changes of atomic and electronic structures of doped Gr-ZnO nanosheet. These studies provide us a deep understanding of the novel properties of doped ZnO nanosheets, which is essential to employ them as building blocks for future nanodevices.

2. Computational methods

The simulation is calculated by first-principles DFT, which is provided by DMOL^3 [21–23]. The generalized gradient

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http://dx.doi.org/10.1016/j.ssc.2014.12.014
0038-1098/

approximation (GGA) of Perdew and Wang (GGA-PW91) is employed to optimize geometrical structures and calculate properties [24]. The all-electron relativistic Kohn-Sham wave functions are expanded in the local atomic orbital basis set for DMOL^3 [21]. The valence-electron configurations are: Zn-3d^{10}4s^2, O-2s^{2}2p^4, N-2s^{2}2p^3, Ag-4d^{10}5s^1. Similar functional have been successfully used to study the structural and electronic properties of water, Si and Cu nanowires [25,26]. The nearest distance between nanosheets in neighboring cells is greater than 15 Å to ensure no interactions. For geometry optimization, both the cell and the atomic positions are allowed to fully relax. The k-point is set to $6\times6\times1$ for all structures, which brings out the convergence tolerance of energy of 1.0×10^{-5} Ha (1 Ha=27.2114 eV), maximum force of 0.002 Ha/Å, and maximum displacement of 0.005 Å. The electronic distributions of Gr-ZnO are carried out by Mulliken charge analysis, which is performed using a projection of a Linear Combination of Atomic Orbitals (LCAO) basis and to specify quantities such as atomic charge, bond population, charge transfer etc. LCAO supplies better information regarding the localization of the electrons in different atomic layers than a plane wave basis set does [27]. The obtained relative values of the charge e, but not the absolute magnitude, display a high degree of sensitivity to the atomic basis set and a relative distribution of charge[10,28,29].

The structure of Gr-ZnO nanosheet is originally constructed from ZnO wurtzite crystal, in which all atoms are in sp^3 hybridization with each Zn (O) atom surrounded by four neighboring O (Zn) atoms at the corners of a tetrahedron. The Zn-O bond length in ZnO nanosheet is calculated to be 1.876 Å. Moreover, the bond angle within the newly formed planar layer increases from the wurtzite tetrahedral, 108.044° to plane trigonal, 120.017°. Similar to the hexagonal wurtzite ZnO, the Gr-ZnO is also a semiconductor with a direct band gap of 1.649 eV. Based on the unit cell, a $4\times4\times1$ supercell of Gr-ZnO containing 32 atoms is constructed.

The formation energies (E_f) of a defect (N_O or Ag_{Zn}) are defined as follows: [30]

$$E_f(D)=E_{tot}(D)-E_{tot}(ZnO)-\sum_i n_i\mu_i \quad (1)$$

where E_{tot} (D) is the total energy of the supercell containing the defect and E_{tot}(ZnO) is the total energy of the equivalent supercell containing only Gr-ZnO. n_i and μ_i are the number and the chemical potential of the atoms added to (positive n_i), or taken from (negative n_i) the reference supercell in order to create the defect, respectively.

The chemical potentials of O and N are measured according to the energy of an oxygen atom in an oxygen molecule and a N atom in a nitrogen molecule. The chemical potentials of Zn and Ag are taken as the energy per atom of bulk metallic Zn and Ag, respectively.

To determine whether it is energetically preferred that two dopants bind, for example, Ag_{Zn} and N_O, in the neutral charge state, we calculate the binding energy which is defined as:

$$E_b(ZnO:Ag-2N)=E_{tot}(ZnO:Ag-2N)+E_{tot}(ZnO)-E_{tot}(ZnO:N)-E_{tot}(ZnO:Ag) \quad (2)$$

where E_{tot}(ZnO:Ag-2N), E_{tot}(ZnO:N), and E_{tot}(ZnO:Ag) are the total energies for supercells containing defects $Ag_{Zn}N_O$, N_O, and Ag_{Zn}, respectively. A negative value of E_b corresponds to a metastable or a stable dopant pair when both are present in the system. According the equation, in the above case, the system energy is the lowest, and the structure is the most stable [30].

3. Results and discussion

For substitutional N on the O site forming the defect N_O, and substitutional Ag on a Zn site forming the defect Ag_{Zn}, when a second N atom is added to the defect (Ag_{Zn}-N_O), there are two possible locations: the defects (Ag_{Zn}-N_O) and N_O in the near and far apart arrangements, respectively. The co-doping concentration of two different heavy codoped Gr-ZnO are both 9.375at%. The corresponding structures are shown in Fig. 1. In addition, considering the symmetry, stability, and computing speed, the substitution location is as close as possible to the center position. According to Eq. (1), we find the total energies of the configurations in the near arrangement is 41 meV lower than the energy of the complex defect (Ag_{Zn}-N_O) and N_O far apart. Thus, the second N atom slightly prefers to occupy nearest-neighbor sites of Ag to form the complex defect (Ag_{Zn} -2N_O).

The bond distance of undoped and doped Gr-ZnO are shown in Table 1. N^1, N^2 mean that N atom is in the far away site and nearest-neighbor site, respectively. As for the (Ag_{Zn}-2N_O) complex defect system, the distance between Ag and the N atom is 1.976 Å. The bond length of O-Ag is 2.053 Å on average, and the average distance between N and Zn atom is 1.854 Å. While for the (Ag_{Zn}-N_O+N_O) defect system, the distance between Ag and the N atoms is 2.036 Å. The bond length of O-Ag is 2.013 Å on average, and the average distance between N and Zn atom is 1.851∼1.854 Å. In order to clarify the impurity mechanism of p-type doping of Gr-ZnO, the populations analysis and atom Mulliken charge transfers

Table 1
The populations analysis and bond distance of doped Gr-ZnO. N^1, N^2 mean that N atom is in the far away site and nearest-neighbor site, respectively.

Structure	Bond type	Population	Bond length (Å)
Undoped-ZnO	O-Zn	0.48	1.876
(Ag_{Zn}-2N_O) in ZnO	N-Zn	0.70	1.854
	N-Ag	0.33	1.976
	O-Ag	0.32	2.053
(Ag_{Zn}-N_O+N_O) in ZnO	N^1-Zn	0.60	1.854
	N^2-Zn	0.75	1.851
	N-Ag	0.26	2.036
	O-Ag	0.28	2.013

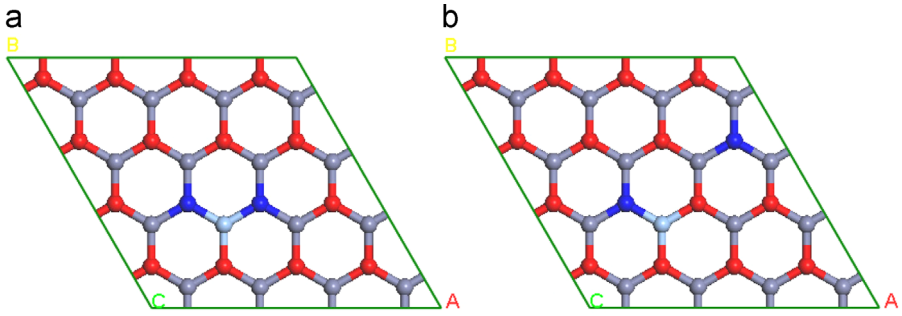

Fig. 1. Schematic illustration of $4\times4\times1$ supercell Gr-ZnO nanosheet with defects (Ag_{Zn}-N_O) and N_O in the near (a) and far (b) arrangements, where larger (gray) balls, small (red) balls, blue balls and light blue balls stand for Zn, O, dopant N and Ag, respectively.