

The electronic and optical properties of indium doped zinc oxide nanosheets



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HIGHLIGHTS

- The half-metallic properties of the In doped ZnONS is found.
- The energy band of the In doped ZnONS moves to lower energy range.
- The absorption coefficient, refractive index $n(\omega)$ and reflectivity $R(\omega)$ of the In doped ZnONS induced red-shift.

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ABSTRACT

Electronic and optical properties of the pure ZnO crystal and In doped ZnO nanosheets (ZnONS) are systematically explored by using an accurate density functional method. The half-metallic properties are induced by the doping of Indium in ZnO nanosheets from the spin dependent density of states and band structure analysis. The optical properties of the In doped ZnONS, such as the absorption, refraction and reflectivity, show a red-shift corresponding to the dielectric function compared to that of the pure ZnONS. The new transition peaks near the Fermi levels are observed due to the In doping, which were deduced from the direct transitions of electrons from the impurity indium atom.

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1. Introduction

ZnO has received considerable interest, due to its larger bandgap of 3.37 eV [1] and higher exciton binding energy of 60 meV [2] at room temperature, for its practical application in gas sensors, liquid crystals display and ferroelectric transparent thin-film transistors. In comparison to other optoelectronic materials, such as GaN [3], ZnO has a lot of advantages such as low static dielectric constant [4], large optical coupling coefficient [5], high chemical stability [6], excellent piezoelectric and photoelectric properties [7,8].

Metal oxide nanostructures have been recently investigated from both experimental and theoretical standpoints due to their potential applications in the fabrication of the novel electronic devices. Recently, the experimental and theoretical studies about the magnetic and electronic properties of the doped ZnO semiconductor have been reported [9,10]. Hu [11] et al. achieved two-dimensional ZnO thin nanosheets on a large scale, in which Zn thin nanosheets were first grown via a thermal decomposition and reduction of the starting ZnS powder, and then converted to the ZnO nanosheets via a simple oxidation process. Umar [12] et al. had prepared the two-dimensional

ZnO nanosheets using ZnCl_2 and O_2 as source materials for Zn and oxygen. Especially, doping ZnO with IIIA elements is one of the most popularly used approaches to tune the performance of ZnO material. Nanoscale semiconductor materials doped with IIIA ions can present magnetic properties which are potential for future magnetic device applications, as well as to understand the fundamental physics of magnetism in semiconductors [13]. Particularly, two-dimensional (2D) systems show peculiar properties which are different from their counterpart bulk phases [14].

Though some studies on In-doped ZnO have been already reported [15], the theoretical studies focusing on the optical properties for the ZnO nanosheets have been rarely involved. In the present work, we performed first-principle spin polarized calculation for In-doped ZnO nanosheets to study their electronic and optical properties, with the purpose to understand optical transition mechanism.

2. Computational details

The first-principles full-potential linearized augmented plane wave (FLAPW) method based on the generalized gradient approximation (GGA) [16] is used for the exchange-correlation potential within the framework of the density-functional theory to perform the computations, as implemented in the WIEN2K simulation

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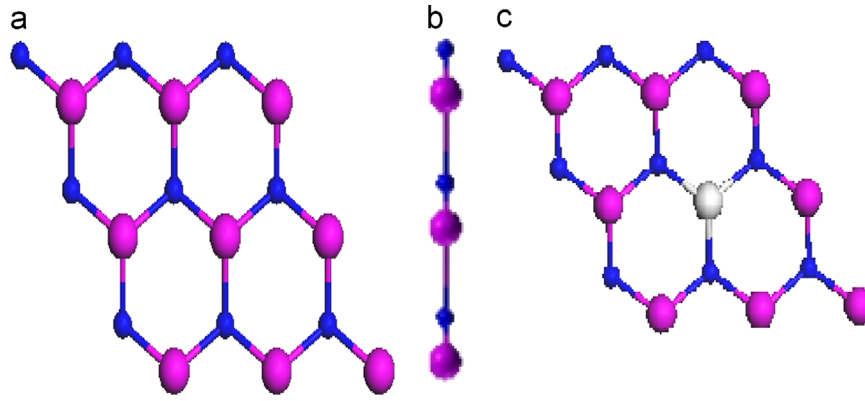


Fig. 1. Structure of ZnO nanosheet, the pink ball stands for Zn atom, the blue ball is O atom and the white ball is In atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

package, in order to investigate the electronic and magnetic properties of 2D ZnO. All calculations are based on the model of (2×2) supercell cut from initial bulk ZnO(0001) plane, which contains 9 Zn and 9 O atoms, as shown in Fig. 1.

A generalized gradient approximation is used to treat the exchange correlation potential. The relativistic effects are taken into account. The valence electrons for the Zn and O atoms are 12 (Zn: $3d^{10}4s^2$) and 6 (O: $2s^22p^4$), and atomic sphere radii of Zn and O atoms are set to 1.9 and 1.6 a.u., respectively. An energy cutoff of -8.0 Ry is employed for the LAPW basis to describe the wave functions in the interstitial region.

The Brillouin zone (BZ) is represented by the set of $6 \times 6 \times 1$ k -points for the geometry optimizations and for the static total energy calculations. The structural relaxation is done until the forces on each atom are smaller than 10^{-2} eV/Å.

3. Results and discussion

3.1. Electronic structures

The geometric structures of the pristine are shown in Fig. 1. After full optimization, the pristine ZnO transform from the initial wurtzite configuration to a flat graphitic structures, in which the optimized Zn–O bond lengths are 1.8 Å.

Total and partial DOS of In doped ZnONS are presented in Fig. 2. It is notable that both the O 2p and In 5s states are located in the Fermi energy level. It indicates that there exists strong hybridization between the In 5s and O 2p states and the In–O bond is quite covalent instead of purely ionic. The local density of state that locates in -7.1 eV is derived largely from the O 2p, Zn 3d and In 5s states. The valance band with an energy range from -6.8 to -5.6 eV shows a strong d character and comes mostly from the Zn-3d states [17]. The DOS from -5.3 to -1.3 eV are derived largely from O 2p and slightly from In 5p states. The broad conduction bands between 0 and 7.5 eV are mainly composed of O 2p and In 5s states.

In doped ZnONS shows a property with the unequally occupied of the spin-up and spin-down branches. It is important to note that the Fermi level (E_F) is largely crossed by spin-down states, while in spin-up states, E_F located in the energy gap, which indicates that the system belongs to half-metallic properties [18]. In the spin-up states, the impurity bands introduced by In occupy the energy level above the valance band maximum (VBM), which shows that In-doped can lead ZnO to a n -type semiconductor.

We first consider a 3D wurtzite bulk ZnO structure in which all atoms are fourfold coordinated through hexagonal directed sp^3 orbital. The direct bandgap structure of the bulk ZnO is shown in Fig. 3(a). The calculated bandgap at the Γ point is 0.81 eV, which is

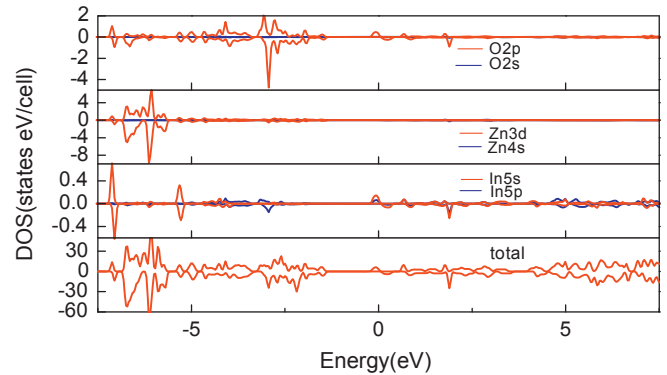


Fig. 2. Partial and total DOS of In-doped ZnO sheet.

smaller than the experimental value. This underestimation is due to the GGA approximation, which does not consider the non-continuity of the exchange-correlation, which does not affect our theoretical analysis [2]. The band structure of the In-doped ZnONS structure is shown in Fig. 3(b). We can see that the spin-down channel has a bandgap whereas the spin-up channel has partially filled bands showing half-metallic properties, which are the ideal case for spin injection applications due to the 100% spin-polarized carriers. The bandgap of the In-doped ZnONS is 1.2 eV, which is larger than that of pristine ZnO. At the same time, the bandgap moves into valence band, in other words, it shifts to the lower energy side.

3.2. Optical properties

3.2.1. Imaginary part of dielectric function

All the optical properties' polarization is xx in this paper. As well known that in the linear response range, the solid macroscopic optical response function can usually be described by the frequency dependent dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ [19], which is mainly connected with the electronic structures. The real part $\epsilon_1(\omega)$ is derived from the imaginary part $\epsilon_2(\omega)$ by the Kramers–Kronig transformation. All other optical constants, such as the absorption coefficient, reflectivity, and energy loss spectrum, are derived from $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$. The change curve of imaginary part $\epsilon_2(\omega)$ can be given by calculating [20]. The calculated imaginary part of dielectric function of pure ZnO, pristine ZnONS and In-doped ZnONS are shown in Fig. 4.

For the pure ZnO crystal, as seen from Fig. 4(a), the imaginary part of the dielectric function has four main peaks (9.86, 12.92, 14.87, and 19.06 eV) in the xx direction. The first peak corresponds to the electron transition between O-2p and Zn-4s states, the second and third peaks come from the electron transition between

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