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Role of point defects on conductivity, magnetism and optical properties in In_2O_3

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ABSTRACT

In order to assess the effects of point defects including transition metal doping on its electronic structure, the self-consistent band structure of the transparent oxide In_2O_3 (in the Ia_3 structure) has been calculated with oxygen vacancies, oxygen and indium interstitial atoms and several transition metal dopants using density functional theory based first principles calculations. An oxygen vacancy alone does not act as a strong native donor but when combined with interstitial indium and (substitutional) transition metal doping, shallow donor levels close to the conduction band are formed. Spin polarized calculations show measurable magnetism in some of the transition metal doped systems while the dielectric functions indicate whether such systems remain transparent among other things.

1. Introduction

The growing interest in Magnetic Semiconductors (MSs) in recent years has captured the attention of many experimental and theoretical research groups. Many researchers have found such magnetic semiconductors by doping transition metals (TMs) into semiconductors such as SnO_2, In_2O_3, TiO_2, ZnO [1–4]. In fact, MSs are used in the construction of negative index metamaterials (NIMs), that is an optical system which posses a negative refraction index. Also the interest in Diluted MSs, which have a significant connection to spintronics, is another reason for such studies. Recent experimental work [1,2] has reported the presence of magnetic phases in undoped TiO_2 and In_2O_3. However, there are various controversies related to the theoretical and experimental studies in these compounds. Agostan et al. [5] have recently carried out an extensive study on geometry and electronic structure with point defects in In_2O_3 and we are in agreement with their results for the most part. A previous study [6] had suggested that oxygen vacancies and indium interstitials cannot act as intrinsic donors, claiming that no intrinsic defects can produce high electron densities seen in this material. However, here we show that substitutional TM doping and other point defects, such as oxygen vacancies, have a significant effect on the electronic properties of In_2O_3. While there is a fair number of theoretical studies of the pure compound, optical and magnetic properties related to defects have not been examined in detail and our theoretical study is an attempt to systematically examine these effects due to certain selected point defects in In_2O_3 and look for any possible trends that can be clearly identified at this level.

2. Structural information and computational details

In_2O_3 exists in three different space group symmetries $I2_13$, Ia_3 and R_3. Among these three structures, In_2O_3–Ia_3 with a band gap of about $E_g = 3.7$ eV has been extensively studied both theoretically and experimentally [7–9]. In_2O_3–Ia_3 crystallizes in a cubic-bixbyite-type structure which has 80-atoms in its unit cell (Fig. 1). It has two types of Indium atoms and one type of Oxygen atom at Wyckoff positions 8b, 24d and 48e, respectively.

In this study, we investigate several defect structures such as interstitial atoms and vacancies. Since In_2O_3 (Ia_3 – Space-Group No. 206) unit cell has thirty two Indium atoms and forty eight oxygen atoms, unique labels, following Ref. [10], are assigned to each In and O atom (In: 1–32, O: 1–48). The oxygen vacancies are created by removing oxygen atoms from the 80-atom unit cell and allowing it to relax. We have concentrated only on a single oxygen vacancy (V_O) position (Wyckoff y, $-z + 1/2$, $x + 1/2$ where $x = 0.3905$, $y = 0.1529$ and $z = 0.3832$ in Cartesian units [7,10,11]) in all oxygen vacancy related calculations throughout this Letter. This oxygen vacancy was created by removing the above oxygen atom (O_{22}) as shown in Fig. 1. Interstitial indium (In_i) and interstitial oxygen (O_i) calculations are done by placing an In or O atom at (empty) a-site and c-site positions in the cubic bixbyite structure. The c-site (Wyckoff 16c) is the vacant anion site which provides enough space to accommodate excess oxygen or indium as interstitial atoms. This 16c site is a special position in the Ia_3 space group with Wyckoff coordinates (x, x, x) where $x = 0.116$ in reduced

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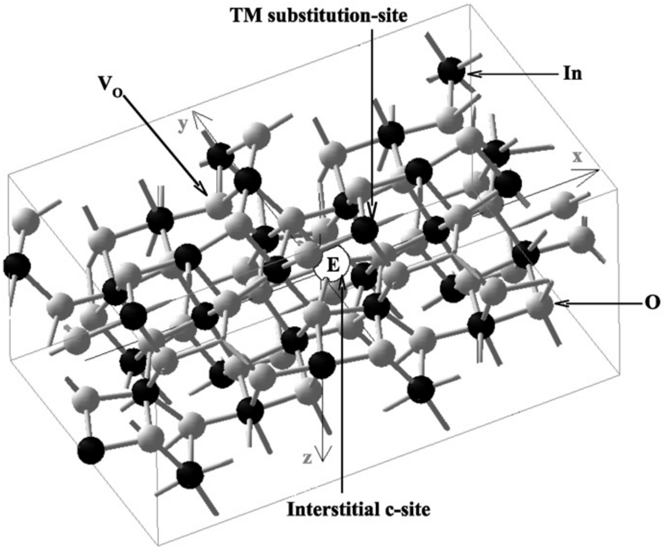

Fig. 1. Bixbyite-type structure of In_2O_3–Ia_3, gray spheres denote oxygen and dark spheres denote indium atoms. There are two nonequivalent indium atom sites with each indium atom surrounded by six oxygen atoms. Interstitial atom position at c-site is noted by E and a-site is at the center of the structure $(0, 0, 0)$. V_O denotes the oxygen site that was used to create an oxygen vacancy.

units [12]; and is tetrahedrally coordinated by four cations. The a-site (Wyckoff coordinates $(0, 0, 0)$) depicts an octahedral position in the sublattice of six d-site indium atoms. Transition metal (substitutional) doping is done at a 8b-site, replacing an indium atom. We have used the experimental lattice parameter $a_0 = 10.117$ Å [11] of the crystal unit cell of In_2O_3–Ia_3 structure.

This investigation of the electronic structure of In_2O_3, with and without point defects, has been carried out using first principles calculations. The calculations are based on the density functional theory (DFT) [13,14] within the local density approximation (LDA) and its spin-polarized version, as implemented in the VASP package [15–17]. The interaction between electrons and atomic cores is described by PAW pseudopotentials implemented in the VASP package. The use of PAW pseudopotentials allows us to construct all-electron-like wave functions for In and O valence electrons and hence address the problem of inadequate wave function sampling of the core region. The wave functions are expanded using plane waves with a cut off energy of 300 eV. Brillouin Zone integrations are carried out with a Monkhorst–Pack [18] grid of k-points and the lowest energy structure was determined using Broyden–Fletcher–Goldfarb–Shanno (BFGS) [19] based algorithms. For all of the following results, optimization is carried out until typical forces on the atoms are around 0.01 eV/Å.

3. Results and discussion

3.1. Band gaps and defect concentration

It is well known that the LDA has difficulties in predicting band gaps and band placements in semiconductors; However, various corrections, such as LDA + SIC, LDA + U and GW, are found to rectify these errors to some degree [20]. Here we use the LDA calculations primarily to obtain energetics and observe certain trends in the band structure when defects are included. We believe that these trends are not severely affected by the flaws in the LDA. Calculated LDA band structure of the undoped In_2O_3–Ia_3 (Fig. 2(b)) is in good agreement with previous studies, such as the one reported in Ref. [7]. The direct band gap, E_g^{dir} is identified as the energy difference between the lowest unoccupied band state and the highest occupied band state at the Γ point. Here $E_g^{dir} = 1.26$ eV which compares well with previous calculations [7,21–23]. The second band gap, (E_g^s) is identified as the minimum energy difference between the two lowest conduction bands (CB) which is found to be 2.0 eV. Detailed band structures of Sn and Mo doped In_2O_3 in Fig. 4(c) and (e) are also in good agreement with previous calculations [24].

Since we are limited to an 80-atom unit cell due to limitations in computer memory, the minimum concentration of defects that can be studied is higher than the threshold values mentioned in the literature [25]. However, from the present set of calculations, we can still draw several interesting conclusions.

3.2. Total energy

Trends in total energy, calculated using the variational principle such as in the present DFT + LDA scheme, are much more reliable than the calculated spectroscopic properties and can be used to identify stable structures. Our goal here, as stated earlier, is to examine a few selected defects and their effects on magnetic and optical properties and not a comprehensive study of the energetics of possible defect structures as in Ref. [5]. We have used total energy calculations to identify the most stable vacancy as well as interstitial positions from the selected combinations. However, we note that the formation energies calculated in the above reference for related systems, such as oxygen vacancies and indium interstitials, identify our selected defects as stable and responsible for shallow donor levels.

Using fully relaxed configurations, we have confirmed (see Refs. [12,26]) that the interstitial c-site with tetrahedral coordination is the (energetically) most favorable (stable) site for having either In or O as an interstitial (as shown in Fig. 2). This result points to the fact that in the total energy hypersurface, there are (at least several) shallow wells (in energy) with minima corresponding to the above interstitials. Depending on the method of sample preparation and ambient conditions, oxygen or indium atoms can occupy these sites. For example, at high oxygen partial pressure, it is possible for an oxygen atom to occupy this interstitial site. The above implication leads to an interesting conclusion with regard to the conductivity and magnetism of In_2O_3 at high oxygen partial pressure (see Section 3.4).

3.3. Interstitial indium (In_i) and oxygen vacancy defects

In Fig. 3, we set valence band maximum (VBM) of the defect-free system to be zero and this is a widely applied practice in defect analysis. However, the calculated eigenvalues in the small defect-containing supercell may deviate from the actual values of the infinite solid and corrective methods have been suggested in Ref. [27]. From Figs. 3(a), (b), (e) and (f), it is apparent that new defect induced states appear in the gap region of the defect-free (pure) compound where an In interstitial is combined with an oxygen vacancy. Therefore the present calculations show that the interstitial indium coexisting with an oxygen vacancy might be a good candidate to create donor levels near the gap region of the defect-free system that can contribute to the nearly free electron density and hence conductivity. An interstitial indium at a-site (In_{i-a}) or an interstitial indium at c-site (In_{i-c}) is also observed to form shallow donor levels below the conduction band. However, as seen in Fig. 3, such an interstitial indium alone is not as relevant but still can act as a shallow donor level.

While the indium interstitial provides extra valence/conduction electrons to the system, the creation of an oxygen vacancy leads to unsaturated or dangling bonds in the vicinity of the vacancy, replacing the strong covalent bonds that gave rise to the semiconducting behavior. This is the primary reason for the reorganization of the band structure and hence the DOS when compared with