Thin Solid Films 517 (2009) 3345–3349

Contents lists available at ScienceDirect

Thin Solid Films

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

First principles study on the properties of *p*-type conducting In:SnO_2

Guoqiang Qin, Dongchun Li, Zhijun Feng, Shimin Liu *

State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, 066004 Qinhuangdao, China

ARTICLE INFO

Article history:
Received 26 March 2008
Received in revised form 3 December 2008
Accepted 11 December 2008
Available online 24 December 2008

Keywords:
Transparent conducting oxide
Electronic properties
Optical properties
First principles calculations

ABSTRACT

Detailed theoretical investigations on the structural, electronic and optical properties of *p*-type conducting In:SnO_2 have been conducted by first principle calculations. Analysis on the thermal stability via standard enthalpy of formation calculations shows that In:SnO_2 remains stable at very high In concentration, although the lattice constant expands in a distorted rutile structure with the increase of indium content. This can be attributed to the larger ionic radii and the one less 5*p* electron of In^{3+}. Due to the differences in thermal stabilities of the structures with the same indium concentration, the preferred In^{3+} distribution is to occupy the Sn sites in different (110) slabs, followed by occupying the location in the same (110) slab with a maximized distance between indium ions. Indium element in SnO_2 introduces a band in the low energy region originated from the In 4*d* orbitals and an acceptor energy level slightly above the Fermi energy. While the large effective mass of the electron holes in the valence band results in the small *p*-type conductivity of In:SnO_2. The tiny changes in the conduction band and band gap lead to the invariability of the optical spectra in the ultraviolet-visible region. On the contrary, the dramatic enhancement of dielectric function, reflectivity and absorption in infrared region can be interpreted by the transition from the occupied states to the empty bands near E_f as well as the exciton effect. These features make In:SnO_2 a good candidate for applications such as transparent conducting materials, infrared reflecting materials and gas sensors.

1. Introduction

Tin-doped indium oxide (In_2O_3:Sn) or ITO, as a typical transparent conducting oxide (TCO), has received extensive studies for its use in applications such as flat panel displays and solar cells [1–3]. In preparing TCOs, In_2O_3 is always treated as a substrate material, while Sn is considered an adjusting element to obtain low resistivity (<200 μΩ cm) and high transmittance (>90%) in the visible light range of the spectrum [4,5]. On the other hand, transparent conducting materials, such as Sb doped SnO_2, have also received much attention for their excellent electronic and optical properties [6,7]. In fact, these two kinds of materials are extraordinarily similar, not only in their electronic and optical behaviors, but also in their fabrication processes and the selecting principle for doping elements, i.e., to get *n*-type electron conductivity. In contrast, *p*-type In_2O_3 or SnO_2 based transparent conducting materials are not so popular, especially for In:SnO_2, although they have a range of important applications, for example, acting as a "functional" window to transmit visible light yet generate electricity in response to the absorption of ultraviolet photons [8]. Recently, Ji et al. prepared *p*-type In:SnO_2 by both sol–gel dip-coating [9] and spray pyrolysis methods [10], where the structures and conduction modes relied greatly on the indium content, while their optical properties seem to be independent of the indium level. Meanwhile, it is found that indium-doped SnO_2 thin films are sensitive to both reducing and oxidizing gases with high operating temperature and extremely short response time (20 s for 900 ppm H_2, [11]), indicating the feasibility of In:SnO_2 as potential gas sensor [12,13]. However, to date no theoretical investigations on In:SnO_2 has been reported yet to reveal the origin of its outstanding properties caused by the doping effect of indium. Therefore, in this study we focus on the doping effect of indium on the structural, electronic and optical properties of In:SnO_2 to obtain some interpretations and even guidelines for future experimental work.

2. Calculation method

CASTEP code [14] was employed to calculate the structural, electronic, optical properties by first principle calculations based on a plane wave basis set with periodic boundary condition. The electron–electron exchange and correlation effects were described by Perdew–Burke–Eruzerhof in generalized gradient approximations (GGA) [15] within the density functional theory (DFT). Ultrasoft pseudo-potentials [16], known for their high efficiency in calculating the structural and electronic properties, were used for the electron-ion interactions. Norm-conserving pseudo-potentials [17] were adopted to obtain optical properties for its higher reliability in optical property description. In order to confirm the convergence of the calculation, the cutoff energy required in the calculations of the solid state with respect to the scheme of Lin et al. [18] was 340 eV, which corresponds to a criterion of convergence of 0.1×10^{-5} eV/atom. The states Sn 5 $s^2$5p^2, O 2 $s^2$2p^4 and In 4d^{10}5 $s^2$5p^1 were treated as valence

* Corresponding author. Tel.: +86 3358074726; fax: +86 3358074545.
E-mail address: lsm@ysu.edu.cn (S. Liu).

0040-6090/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2008.12.030

states. To model the In doped SnO_2 the supercell technology was employed, where a 2×2×1 supercell containing 8 SnO_2 formular units and a larger supercell (2×2×2) containing 16 SnO_2 formular units were built up. The Brillouin Zone integration has been performed over a 3×3×8 K and a 3×3×4 K points set for these two supercells respectively. However, it was found that the differences in the energies/atom as well as the electronic and optical properties obtained by these two supercells were negligible.

Indium element was introduced by replacing tin atoms with the least concentrations for two the supercells as 12.5% and 6.25%, respectively. These values are very high in the sense of traditional doping conception and could be more accurately regarded as mixed oxides or oxide solid solutions. However, in experimental studies, to evaluate the effect of In concentration, the In/Sn ratio was usually set as high as 0.1 [19] (and, in some cases, the number could reach 0.4) [9]. Hence, to some extent, the In concentration in the employed supercell is comparable to the experimental value, although we recognized that the larger supercell is capable to deliver more detailed and comprehensive information. In the following parts of this paper, in order to get consistency with the experimental reports, we still call it "doped" or "doping" for In:SnO_2 sometimes, but one should keep in mind that it exceeds the traditional doping circumscription and extends to the mixed oxides or oxide solid solutions.

3. Results and discussion

Tin dioxide, also called cassiterite, crystallizes in the rutile structure at ambient pressure which has a tetragonal symmetry with the phase (face centred cubic), space group $P4_2/mn$ m. The unit cell of SnO_2 is characterized by the two lattice parameters a, c and the internal parameter u: the positions of the four oxygens are $\pm(u,u,0)$ and $\pm(\frac{1}{2}+u,\frac{1}{2}-u,\frac{1}{2})$. In the present study, a, c and u of the equilibrium structures obtained by performing geometry optimization with fully ionic positions relaxation are 4.737 Å, 3.186 Å and 0.307 respectively, coinciding perfectly with the experiments (4.737 Å, 3.186 Å, 0.307) [20,21]. After replacement of indium atoms for Sn atoms, the lattice parameters a, c and the cell volume V increase, causing the structure distorted a little from the primitive tetragonal structure. This structural behavior is easily understood by taking the larger ionic radii (0.8 Å 0.69 Å for the 6-fold coordinated In^{3+} and Sn^{4+}, respectively, from Ref. [22]) and one less 5p electron of In atom into account. The X-ray Diffraction (XRD) curves of In doped SnO_2 support this structural behavior, where the diffraction peaks shifted towards smaller diffraction angles [9]. On the other hand, the structural distortion caused by In doping will further decrease the stability of In:

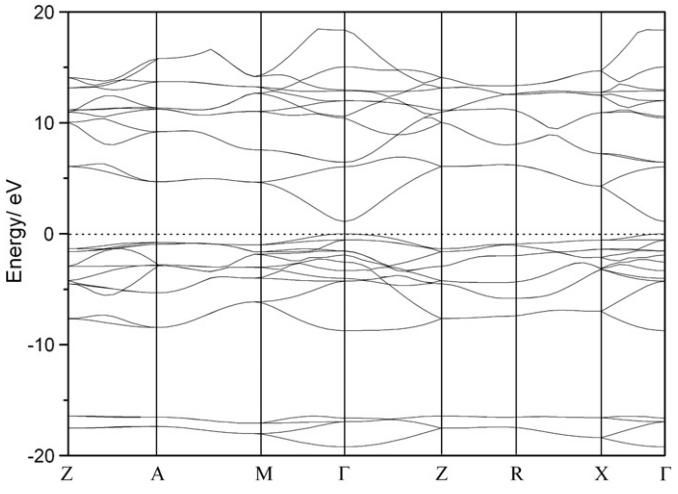

Fig. 1. Energy band structure of SnO_2. The short dashed line represents the Fermi levels set to zero.

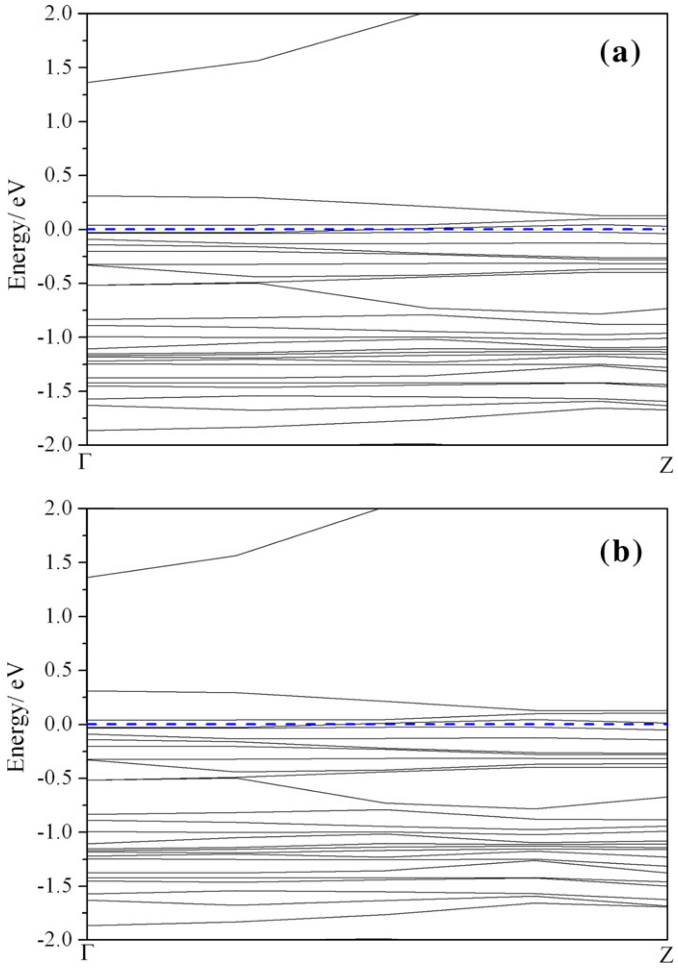

Fig. 2. Band structures near the top of valence band of indium doped SnO_2 for (a) $InSn_7O_{16}$, (b) $In_2Sn_6O_{16}$ in which the short dashed lines represent the Fermi levels set to zero.

SnO_2 which can be revealed by the standard enthalpy of formation (ΔH_f) defined as the enthalpy change associated with the formation of a compound from its constituent elements with all substances in their standard states. The bigger ΔH_f indicates the more stable crystal structure. Using the similar method in Ref. [23], ΔH_f is determined as: $\Delta H_f(In_xSn_{1-x}O_2) = x\,\mu_{In} + (1-x)\mu_{Sn} + 2\mu_O$, where the chemical potentials μ_O, μ_{Sn} and μ_{In} are referred as to the calculated total energies of O in O_2 molecules [1/2 $E_{tot}(O_2)$], Sn in α-Sn [$E_{tot}(Sn^0)$] and Indium in a distorted face-centered-cubic structure just like α-Sn [$E_{tot}(In^0)$]. The calculated ΔH_f for SnO_2 is −6.35 eV, close to the experimental value of −5.98 eV [24]. The error in our calculation is 6.19%, larger than the result by GGA+U (0.84%), but smaller than the error obtained with other GGA calculation reported in Ref [23] (12.88%).

With the introduction of In, ΔH_f is reduced, where the value of In:SnO_2 with In/Sn ratio of 1:3 is −5.28 eV. The decrease in thermal stability is demonstrated by the weakened XRD peaks or even phase separation of in heavily In doped SnO_2 to form another In–Sn–O ternary phase, the bixbyite phase, i.e. tin doped In_2O_3 (ITO) [4]. This structural change induces the transition of the conducting mode from p-type to n-type [9]. It is also remarkable that, however, the structure remains energetically stable even for rutile-type InO_2 (the calculated ΔH_f is −3.17 eV, while at ambient temperature, it is in the vicinity of 26 meV. This may explain the truth that the In:SnO_2 phase with high In content can exist at room temperature, although the rutile-type InO_2 has not been observed experimentally.

Besides the concentration, the distribution of In is also essential because the homogeneity or the inverse atom disorder can impose