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FIRST PRINCIPLE STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF TIN-DOPED INDIUM OXIDE ARMCHAIR NANORIBBON

O.P.Verma*, M.R. Meshram, A.K. Mishra

* Deptt. of Electronics & Telecommunication Engg. Bhilai Institute Technology, Durg,(C.G) INDIA
Deptt.Of Electronics & Telecommunication, Govt Engineering College, Jagdalpur(C.G) INDIA.
Deptt.Of Electrical and Electronics Engg, Bhilai Institute Technology, Durg (C.G) INDIA.

ABSTRACT

Using first principles using density functional theory (DFT), DFT calculations with a local exchange-correlation (XC) functional give the relaxed atomic coordinates of the stable state. we investigate the structural and electronic properties of tin doped armchair nanoribbon Indium Oxide (ITOANR). The study includes optimization of ITO nanoribbon using SIESTA computational program followed by Density of states (DOS) and Partial density of States (PDOS) analysis. Finally the charge density was plot which were helpful in explaining the different aspects of the electronic interaction in ITO. Interconduction band transitions are identified as possible origin of conflicting, claiming a much larger difference between the direct and indirect gap and band positions. The study finds possible application of ITO in optoelectronic and Light Emitting Devices application and help one to understand the orbital behavior of Tin (Sn), Oxygen (O) and Indium (In) atoms which may promote further studies in the concerned material. Our results show that the shift in position of tin doping with respect to the ribbon edge causes change in the structural geometry and electronic structure of ITOANR. Finally, we report a study of the surface properties and the peculiar electronic structure of indium oxide (In2O3) for the application of solid-state lighting devices.

KEYWORDS: Density functional theory (DFT), Indium Oxide (In2O3), Nanoribbon, Tin doped armchair nanoribbon Indium Oxide (ITOANR), Density of states (DOS) and Partial density of States (PDOS), Exchange-Correlation (XC)..

INTRODUCTION

Indium tin oxide (ITO, or tin-doped indium oxide) is a solid solution of indium(III) oxide (In2O3) and tin(IV) oxide (SnO2), typically 90% In2O3, 10% SnO2 by weight. It is transparent and colorless in thin layers while in bulk form it is yellowish to grey [1,2]. In the infrared region of the spectrum it acts as a metal-like mirror. Indium tin oxide is one of the most widely used transparent conducting oxides because of its two chief properties, its electrical conductivity and optical transparency [4,9], as well as the ease with which it can be deposited as a thin film [3]. As with all transparent conducting films, a compromise must be made between conductivity and transparency, since increasing the thickness and increasing the concentration of charge carriers will increase the material's conductivity, but decrease its transparency [5,8]. Transparent conducting oxides (TCOs) have attracted extensive attention for decades due to their remarkable applications in photovoltaic, solid-state lighting devices and optoelectronic devices [7,28]. The development of functional nanostructure TCOs with unique properties, and an expansion of their functionalities are therefore research directions of significant current interest. Among TCOs, In2O3 is widely applied because of its high charge carrier concentration and mobility [8]. The important role of surfaces in tuning properties in materials shows the importance of studying nanostructures materials with high surface areas. Here the synthesis of phase-controlled In2O3 nanocrystals (NCs) is examined and the effect of doping and composition on the materials properties is showed through SIESTA [29]. Owing to the relevance of size, structure and composition for manipulating properties of nanomaterials, synthesis of well-defined nanocrystals of pure and doped In2O3 has been of considerable interest for fundamental studies as well as for technological applications of Lighting era[24,26].

COMPUTATIONAL DETAILS

In our calculations, the armchair nanoribbon of ITO is simulated within the supercell approach with 100 atoms in the unit cell. The simulation is performed based on the quantum mechanical many-electron problem using density

functional based approach. The calculations are performed using the SIESTA (Spanish Initiative for Electronic Simulation with Thousands of Atoms) code based on the density functional theory (DFT) [19,33]. The exchange and correlation energies are treated within the local density approximation (LDA) according to the Ceperley Alder (CA) parametrization along with double-zeta basis set with polarization functions (DZP) [22]. We adopt a rectangular supercell where the nanoribbon and its periodic images are separated by a vacuum distance. A grid cut-off of 250 Ry is used and the Brilouin zone was sampled by using Monkhorst-Pack scheme with a (1×1×5) k-point sampling.

The first step while starting a simulation is getting a physical coordinates of the structure which we have obtained windows based structure optimization tool. The optimization is carried out in four steps viz mesh cutoff, k-point, lattice optimization and final optimization. The cut-off for ITO-ANR is obtained to be 250 Ry while the value of k-point is found to be in the grid of 1x1x5. All the atomic positions were fully relaxed until the magnitude of the force on each atom are smaller than 0:01 eV/À.

The system is at the minimum energy in a box having lattice constant of 23.3 Aº. Finally the structure is optimized with several conjugate gradient steps which yielded a fully optimized structure with 100 atoms which includes In, O and Sn. The optimized structure is then used to calculate different properties viz DOS, PDOS and Charge Density.

RESULT AND DISCUSSION

(a) Structural properties: The optimized structure of ITO-ANR is shown in figure 1. The brown balls represent In-atom while a red and green ball shows O and Sn-atoms respectively. The average bond lengths of In-O and Sn-O are found to be 1.81 and 1.78 Aº respectively which is consistent with the earlier reported values 1.80 Aº and 1.79 Aº [17, 29].

The structure is stable for higher number of atoms as SIESTA simulates the structure for more number of atoms than is visible in the structure.

The bonds between the atoms are well optimized and show a symmetrical structure useful for the study of the crystal structures and optical applications.

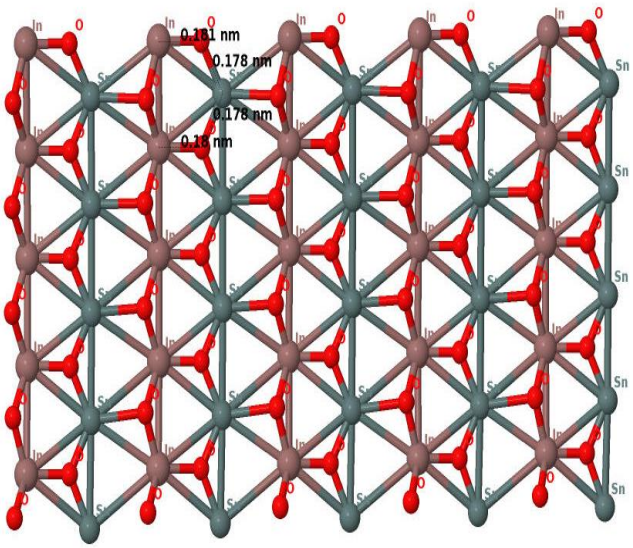

Figure 1: Structure of armchair nanoribbon of ITO

(b) Electronic properties: Figure 2 shows the DOS/PDOS of ITO-ANR. First part of the graph represents the DOS and elemental PDOS while second and third part shows the orbital energy states. The Fermi level is set to zero energy for proper analysis. It is clearly visible from the first part that highest energy contribution is obtained from In atom due to its electropositive nature [26]. The contribution of other atoms can be seen on comparing the DOS and PDOS. 5p1-orbital of In atom contributes in the lower energies of the valence band while 2p2-orbital of oxygen contributes in the near Fermi level. Also 5p1 orbitals of In atoms are responsible for energy states in the conduction band. The

contribution of Sn 5p2 orbitals have higher excitation value as is visible from the 3rd part of the graph. The orbital contribution points towards the possible application of the material in luminescence field for opto-electronic application. The electronic band structure of all the considered silicon doping sites in present study have been calculated along the Γ- X direction of the Brillouin zone.

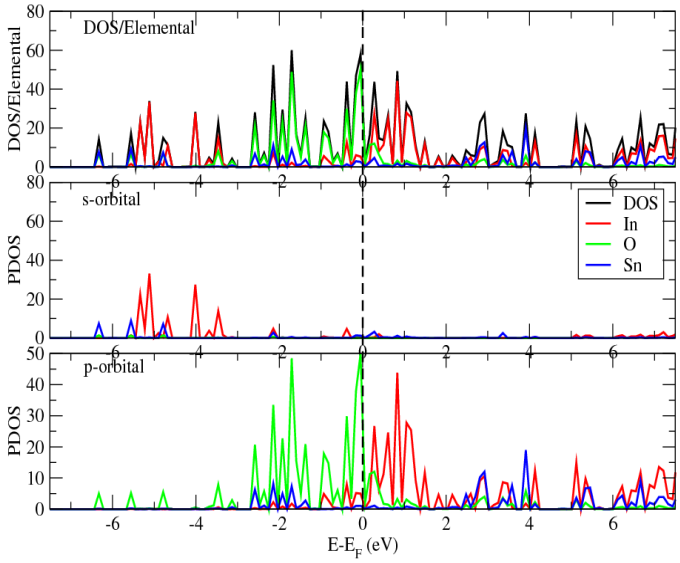

Figure 2: DOS/PDOS of ITO-ANR

On analyzing the electronic band structure, we observed that the relative positions of valence band and conduction band vary with doping positions [30]. The band structure corresponding to tin doping position is found almost similar. Similarly, band structures for doping positions are found almost identical. we also plotted density of states (DOS) graph and corresponding partial density of state (PDOS) profiles. The DOS of pristine ITOANR, depicted in Fig. 3(a), displays that all spin up and down states possess mirror like symmetry which justices the spin degeneracy of electronic states as observed in the band structure.

The corresponding PDOS plot shown in Fig. 3(b) for all the orbitals in the unit cell is dumped sequentially into a file, which represents equal availability of states for up and down spin electrons and hence supports the band structure and DOS profile. Further, from PDOS profile, notice that the major contribution for occupied and vacant states arises from edge atoms. We find two peaks near the Fermi level, first for up spin electrons in valence band and other for down spin electrons in the conduction band. The narrow gap between these two peaks suggests that tin doping (either single or double atom) at right sites makes semi-metallic rather than half-metallic.

(c) Charge density analysis: For qualitative characterization of the bonding interaction between constituents, charge-density and electron localization function (ELF) analysis have been performed for Sn doped In2O3. Charge density analysis is an important tool for optical property studies. Analysis of the charge distribution shows that the highest charge density is residing in the immediate vicinity of the atomic sites, reflecting the dominant ionic-type bonding. If the bonding interaction between In and O is purely ionic, one could expect negligible charge-density distribution between these ions, for a complete understanding of electronic states and individual contribution of atomic orbital's, Figure 3 shows the charge density plot of the ITO, (a) shows the contour lines of In atoms while (b) and (c) shows the plot for Sn and O respectively. The ionic nature of Sn can be assumed for the charge distribution shown in figure (b) While the lower energies can be seen in figure (a) for In-atoms. The plot signifies possible flow of energies in discreet levels which is an important property for opto-electronic application.

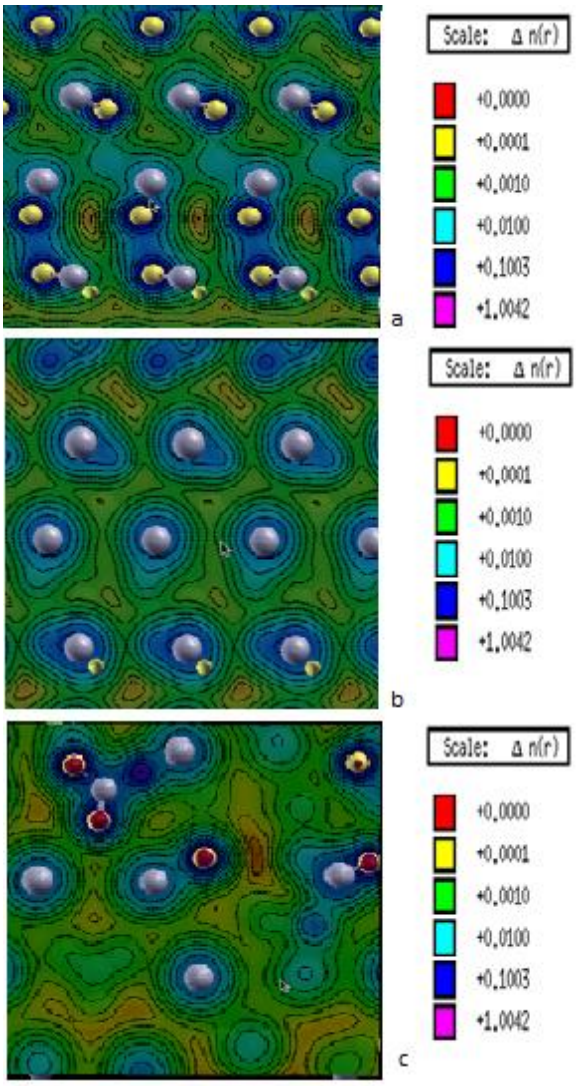

Figure 3: Charge Density of ITO (a) In- atoms (b) Sn- atoms (c) O-atoms

CONCLUSIONS

In summary, the effects of Sn doping on the structural and electronic properties of ITOANR have been investigated systemically by using first principles spin-polarized calculation. The electronic band structures have quite different behavior with doping positions and sensitive to doping sites. We notice that silicon doping in ITOANR reduces its band gap. More importantly, the band gap becomes zero when two Sn atoms are doped at Oxygen sites. From the orbital decomposition analysis and orbital as well as site-projected density of states, the characters of the valence and conduction bands have been analyzed.

Interestingly, for two Sn atom doping at O and In sites, ITOANR remains symmetric. These results suggest the way to control the electronic properties of ITOANR by adjusting Sn doping sites.

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