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First Principle calculation of Indium doped ZnO using LDA and GGA approximation

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ABSTRACT

ZnO semiconductor is a potential candidate for the information processing, energy storage, communication and optoelectronic devices. Various physical properties of the ZnO have been demonstrated both experimentally and theoretically. We reported the different characteristics of undoped and Indium doped ZnO using first principle calculations under the framework of density functional theory. Both wurtzite and zincblende phases of the ZnO are examined using local density approximations (LDA) and generalized gradient approximation (GGA) with different exchange correlation potential within DFT for band structure calculations. Results reveal that the pure ZnO is a direct band gap semiconductor which can be employed for wide range of optoelectronics devices. The accuracy of the results are also checked with reported experimental data which are in consistent. We investigated Indium metal doped ZnO, in order to explore the influence of the doping on structural and optical properties. The band structure and total density of states for various percentages of Indium (x = 0, 0.25, 0.50 and 0.75) in ZnO are calculated with the help of density function theory. Calculations revealed the shifting of Fermi level in the conduction band with increasing indium concentrations. The conductivity are also examined with different percentages of Indium. The results also compared with the previous reported data, which is consistent with the results obtained here.

1. INTRODUCTION

Currently, Scientists are paying more interest in optoelectronic devices because they are trying to find the way of minimizing the energy losses among all other optoelectronic materials. Zinc oxide (ZnO) is an inexpensive, with a band gap of 3.3 eV, having Wurtzite, Zincblende and rock salt structures (Fan et al. 2008). ZnO also used as a dilute magnetic semiconductor as reported by Yi et al. (2010). Pearton et al. (2007) has systematically investigated the ferromagnetic behavior of transition metal doped ZnO. Due to its high

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transparency in visible region and also due to its high electrical conductivity, it is used as window layers and anti-reflecting coating in solar cells as reported by Wang et al. (2013). Furthermore, due to its remarkable optical and electrical properties, it is used in Gas sensors and transparent electrodes as reported by Mahmoud et al. (2009). ZnO has its economical advantages over all other transparent conductive oxides (TCO), because it has excellent electrical and optical properties with very low cost. ZnO also has its application in the field of liquid crystal displays, in Piezoelectric devices (Sohn et al. 2014) and moreover in Surface acoustic wave devices as reported by Du et al. (2007).

To obtain the photoelectric properties with stability of ZnO thin film, the doping techniques is very important and has been focused in last decade. Much attention has been focused for Indium doped ZnO using different experimental procedures and theoretical analysis using density functional theory Wang et al. (2012), Hu et al. (2011),Severiano et al. (2014), Ramo et al. (2014) . The electrical properties are also change by doping in ZnO as Hsin-Chiang You* investigated that the oxygen vacancies increases when the Indium concentration increases, which results in releasing electron and increasing the channel carrier concentration You, (2013). The first principle calculation based on the density functional theory has been performed using CASTEP code. They studied the effect of high indium concentration on the electrical conductivity, effective mass and electron mobility. The results obtained in this report have shown the discrepancy with the results obtained by Qing-Yu et al. (2013). Recently, the electronic properties of IIIA group (Ga, Al, and In) has been presented using Wien2k code. The study was based on the deep understanding on the intrinsic defects on the ZnO based nanosheets, which is a building block for the future of nano devices. Furthermore, the half metallicity was obtained when Indium is doped in ZnO, leading to a high spin polarization. The strong coupling between the In-p orbital and impurity level above the valence band suggested that hole doping mediated the magnetic moments in Indium doped ZnOs Feng et al. (2013). Optical properties have been reported of In-doped wurtzite ZnO based on first principle (Xie et al. 2011). Transparent conducting oxide based on In doped ZnO has been presented using the local density approximation with Hubbard model using the first principle calculations (Zhou et al. 2008). Based on the first principle calculations, band gap variation in In doped ZnO has been studies by (Kim and Park, 2001). Furthermore, N mono doped Ga-N, Al-N and In-N based ZnO has been studies in details and authors also calculated the effective mass and structure (Ping et al. 2010). In this paper, we have investigated the effect of high concentration of indium as (25%, 50% and 75%) on the structural and electrical properties using density functional theory. We have also focused on the interaction between the states of Zn, O and In that would be helpful to control the optical properties In based ZnO compounds.

2. COMPUTATIONAL DETAILS

We have used the Amsterdam density functional package (ADF:Band) to carry out the band structure and density of states calculations using the Kohn-Sham equation by employing the density functional theory (DFT). This program basically provides the calculations self consistently within the framework of DFT. This program also provides the various k-space within the Brillouin zone using the method of tetrahedron. Here, we used KSPACE = 3 for the study of structural and optical properties of all Indium based ZnO compounds. We also employed the double zeta basis (DZ), showing no spin polarization is involved throughout the simulation. Relativistic effect is not included in this simulation work. General accuracy parameter considered which is equal to 3.5. The Localized density approximation (LDA) and generalized gradient approximation (GGA) was employed. In GGA, different exchange correlation was employed to explore the better understanding about the analysis of geometry and density of states. We found that GGA:PBE has shown the accurate calculation of the band diagram and also the induced of states. The structures were fully optimized with convergence energy of 10^{-4} eV. In case of indium placement by Zn atom, relaxation in structure was observed with changing of bond and kinetic energy. Ionic radii for Zn, O and In are set to be 0.74, 1.4 and 0.8 Å, respectively. The valence electron was considered for (Zn: $3d^{10}$, $4s^2$) (O: $2s^2$, $2p^4$) and (In: $4d^{10}$, $5s^2$, $5p^1$). For static and energy calculations as well as the geometry optimization, the Brillouin zone is set by 5 x 5 x 5 k-point Monkhorst–Pack mesh.

3. STRUCTURE

The structures were designed for both Zincblende and wurtizite indium doped ZnO. The super cell of (211) unit cell was considered for Zincblende structure containing 8 atoms with cell parameter of a = 4.51 Å. In order to obtain the desired concentration of Indium in unit cell, one zinc atom is replaced by In atom to obtain 25% concentration of Indium. Similarly, two and three atoms of Zinc atom are replaced by Indium atom to obtain the concentration of 50 and 75 %, respectively. Fig. 1 indicates the optimized structures of Indium doped Zinc oxide for Zincblende and wurtizite with different values of x including (x = 0.25, 0.50 and 0.75). Similar case was employed to obtain for wurtzite structure of ZnO with super cell of (211) which also contain 8 atoms. The structure consists of total 8 atoms in which one atom of Zinc is replaced with one atom of Indium to obtain 25% of doping. Similarly 2 and 3 atoms are replaced with Zinc atom to obtain the 50 and 75% of doping. The unit cell dimension for wurtzite was selected such as a = b = 3.246 Å and c = 5.200 Å.

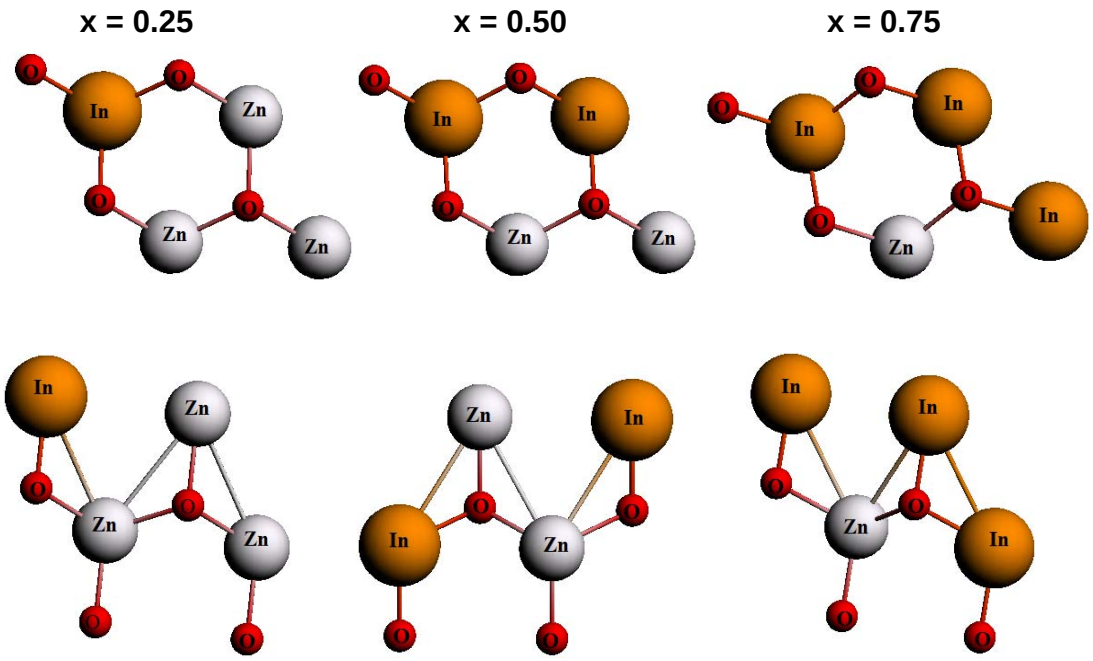

Fig. 1 Structure diagram of Indium doped ZnO for both zinblende and wurtzite with various indium concentration of 25, 50 and 75%.

4. RESULTS AND DISCUSSION

It is clearly seen from Fig. 2 that as the concentration of In increases the Fermi level shift into the conduction band indicates the n-type degenerate semiconductor. The shifting of Fermi level clearly indicates the number of electrons moves into the conduction band with increasing the In concentration. Let n1, n2 and n3 are the relative number of electrons shifting into the conduction band in case of x = 0.25, 0.50 and 0.75, respectively. We have calculated the n1, n2 and n3 using the area under the curve using density of states and energy, between the top of the valence band and Fermi energy. The values of n1, n2 and n3 are calculated by integrating based on the OriginPro. Fig. 3 shows the graph between the In concentration and relative number of electrons showing that conductivity increases with increasing the concentration of Indium. It is clear from figures that the Fermi level shifts into the conduction band. The result obtained in our simulation case has shown the good consistency with the results obtained by Qing-Yu et al. (2013). In Fig. 2 (a), the Fermi level shifts from 2.5 to 5 eV when Indium concentration increases from 25 to 75 %. While In wurtzite case as shown Fig. 2 (d), the Fermi level shifts from -2 to 2 eV same doping range mentioned above.

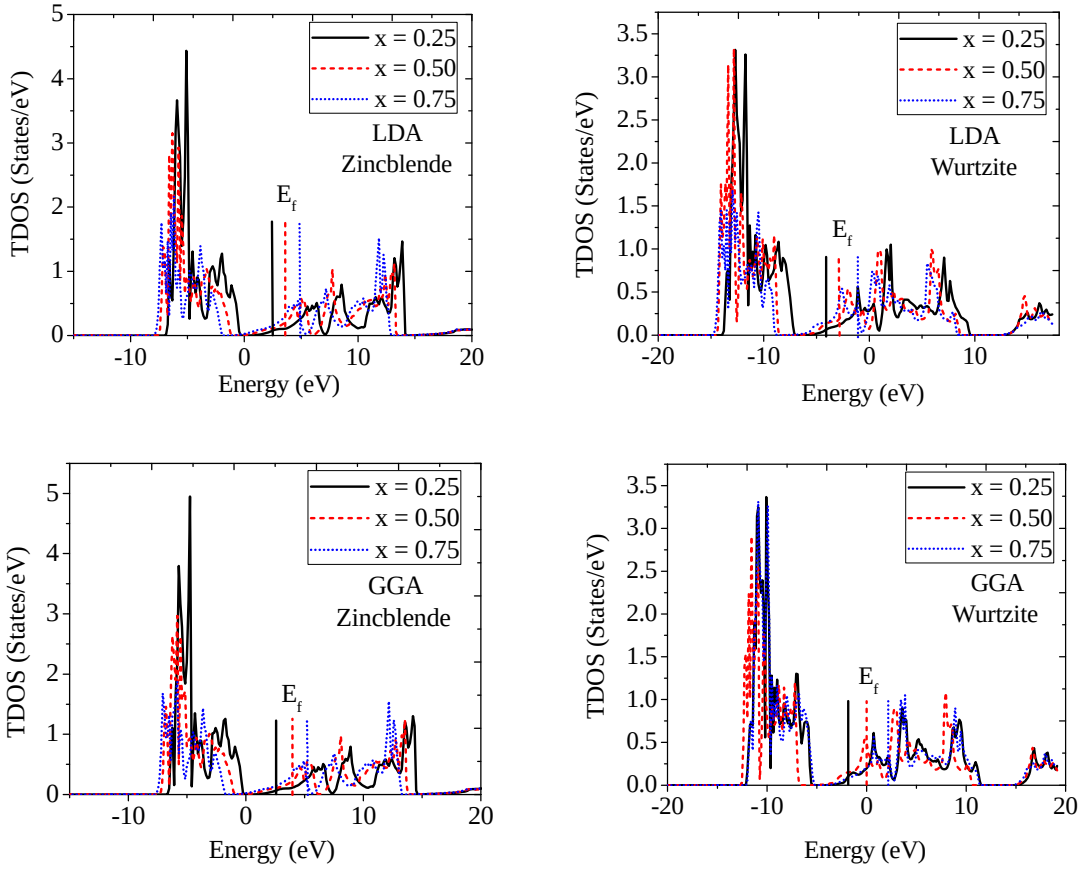

Fig. 2 Total density of states for zincblende and wurtzite structure using LDA and GGA under various In concentration from 25 to 75 %.

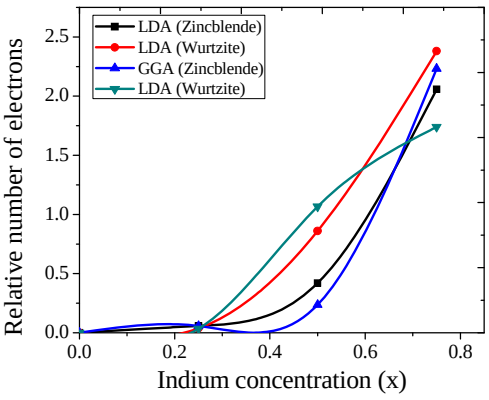

Fig. 3 Indium concentration dependent relative number of electrons for zincblende and wurtzite structure.

After discussion of electrical conductivity with introducing Indium doping, we calculated the comparison of partial density of states with total density of states to find the coupling between the states. Fig. 4 (a) represents the total density of states of wurtzite structure using LDA analysis. Fig. 4 (b) shows the partial density of states of O, Zn and Al. It can be seen from Fig. 4 (c) that there are three states are more dominant that creates the valence and conduction band. We observed that bottom of the valence band is formed by the O-2s states, while O-2p and Zn-3d are very important in high energy region. Here, we consider In-5s and O-2p states to determine the coupling between them. It is noted that the Fermi level lies at the energy of -4 V in the valence band as shown by the doted lines. The density of states from energy -16 V to -10 V represents the O-2p and Zn-3d states. Further, the states lies over the Fermi level are due to the O-2p and In-5s states. These states are showing the strong hybridization between them. The covalent bond is formed between them instead of ionic bond. There is no hybridization was observed between the O-2p and Zn-3d states. The results are obtained here have good consistency with those results obtained by Feng et al. (2013).

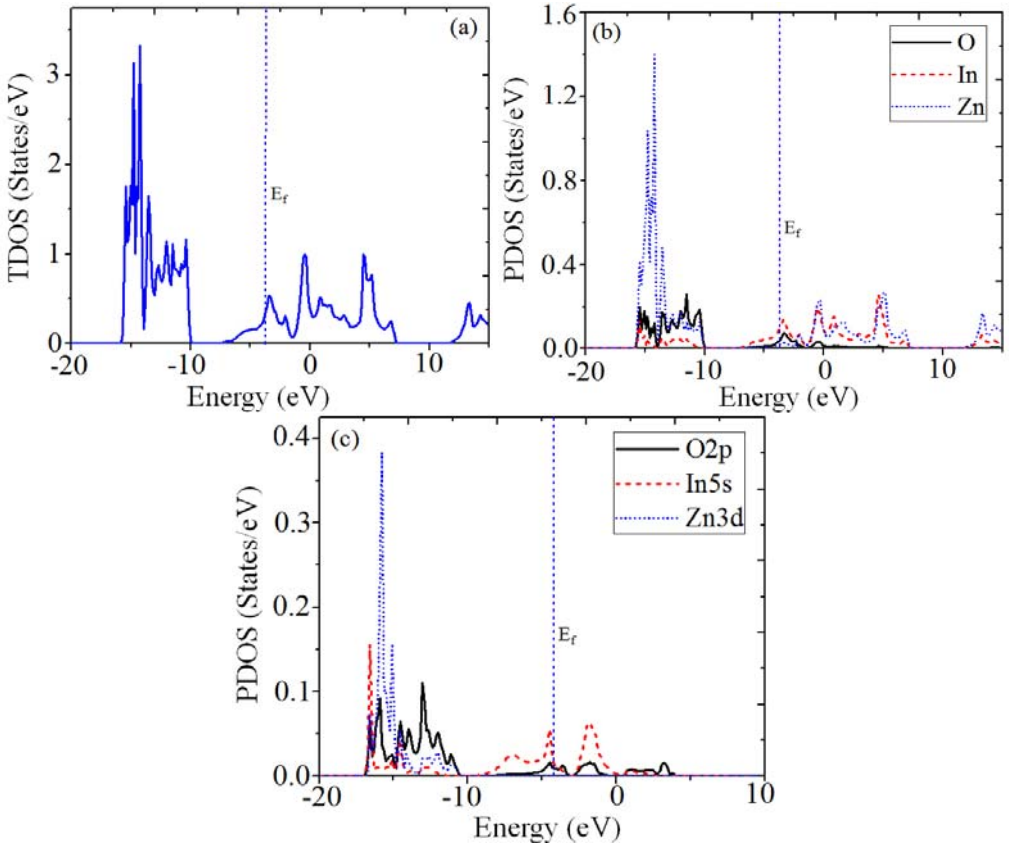

Fig. 4 Calculated (a) TDOS (b) PDOS (Zn, O, and In) and (c) PDOS (O2p, In5s and Zn3d) of Indium doped ZnO. Fermi level is set to be -4 eV.

5. Conclusion

The density functional theory of indium doped ZnO has been performed using the ADF-Band tools. The convergence was achieved with indium doping showing the stability of structure. The structure has shown the degenerate type semiconductor due the shifting of Fermi level into the conduction band when Indium doping increases. The calculations of relative number of electrons revealed that, when Indium concentration increases from 25 to 75%, the number of electrons shifted into the conduction band. The effect of was also analyzed which revealed the strong hybridization occurs between the O-2p and In-5s at the Fermi level. These coupling level predominantly provide the concepts to control the optical properties of Indium doped ZnO.

References

Du, X.Y., Fu, Y.Q., Tan, S.C., Luo, J.K., Flewitt, A.J., Maeng, S., Kim, S.H., Choi, Y.J., Lee, D.S., Park, N. M., Park, J. and Milne, W.I. (2007), "ZnO film for application in surface acoustic wave device," *J. Phys., Conference Series,* **76**, 012035.

Fan, C., Wang, Q., Li, L., Zhang, S., Zhu, Y., Zhang, X., Ma, M., Liu, R. and Wang, W. (2008), "Bulk moduli of wurtzite, zinc-blende, and rocksalt phases of ZnO from chemical bond method and density functional theory," *Appl. Phys. Letts.,* **92**, 101917.

Feng, X.-Y., Wang, Z., Zhang, C.-W. and Wang, P.-J. (2013), "Electronic structure and energy band of IIIA doped group ZnO nanosheets," *J. Nanomaterials,* **2013**, 181979.

Hu, Z., Jiao, B., Zhang, J., Zhang, X. and Zhao, Y. (2011), "Indium-Doped zinc oxide thin films as effective anodes of organic photovoltaic devices," *Inter. J. Photoenergy,* **2011**,158065.

Kim K. J., and Park Y. R. (2001). "Large and abrupt optical band gap variation in In-doped ZnO," *Appl. Phys. Letts.,* **78**, 475-477.

Mahmoud, F. A., Kiriakidis, G., (2009), "Nanocrystalline ZnO thin film for gas sensor application," *J. Ovonic Research,* **5**, 15 – 20.

Pearton, S. J., Norton, D. P., Ivill, M. P., Hebard, A. F. Zavada, J. M., Chen, W. M. and Buyanova, I. A. (2007), "ZnO doped with transition metal ions," *IEEE Trans. Electron Dev.,* **54**, 1040-1048.

Ping, L., Sheng-Hua, D., Li, Z., Jiang-Ying, Y. and Guo-Hong L. (2010), "Comparisons of ZnO codoped by group IIIA elements (Al, Ga, In) and N: a First-principle study," *Chin. Phys. B,* **19**, 117102.

Qing-Yu, H., Ji-Jun, L., Chun, Y., Chun-Wang, Z., Er-Jun, Z. and Yue, Z. (2013), "First-principles study on the effect of high In doping on the conductivity of ZnO," *Chin. Phys. B,* **22**, 077103.

Ramo, D. M., Chroneos, A., Rushtonb, M. J. D. and Bristowe P. D. (2014), "Effect of trivalent dopants on local coordination and electronic structure in crystalline and amorphous ZnO," *Thin Solid Films,* **555**, 117–121.

Severiano, F., Garcia, G., Castaneda, L., Gracia-Jimenez, J. M., Gomez-Pozos, H. and Luna-Lopez, J. A. (2014), "Electroluminescent devices based on junctions of indium doped zinc oxide and porous silicon," *J. Nanomaterials,* **2014**, 409493.

Sohn, J. I., Hong, W.-K., Choi, S. S., Coles, H. J., Welland, M. E., Cha S. N. and Kim, J. M. (2014), "Emerging applications of liquid crystals based on nanotechnology," *Materials,* **7**, 2044-2061.

Wang, Y.-C, Lin, B.-Y., Liu, P.-T. and Shieh, H.-P. D., (2013), "Photovoltaic electrical properties of aqueous grown ZnO antireflective nanostructure on Cu(In,Ga)Se2 thin film solar cells," *Optic Exp.,* **22**, A13.

Wang, J.-C., Cheng, F.-C., Liang, Y.-T., Chen, H.-I., Tsai, C.-Y., Fang C.-H. and Nee, T.-E. (2012), "Anomalous luminescence phenomena of indium-doped ZnO nanostructures grown on Si substrates by the hydrothermal method," *Nanoscale Research Letts.*, 2012, **7**, 270.

Xie, F. W., Li, P., Zhang, L. Q., Wang, X. L., Wang, H. and Song, X. F. (2011), "Optical properties of in-doped wurtzite ZnO based on first-principle," *Adv. Mater. Research,* **335–336**, 32-35

Yi, J. B., Lim, C. C., Xing, G. Z., Fan, H.M., Van, L.H., Huang, S. L., Yang, K. S. Huang, X. L., Qin, X.B., Wang, B.Y., Wu, T., Wang, L., Zhang, H. T., Gao, X.Y., Liu, T., Wee, A. T. S., Feng, Y. P. and Ding J. (2010), "Ferromagnetism in dilute magnetic semiconductors through defect engineering: Li-doped ZnO," *Phy. Rev. Letts.,* **104**, 137201.

You, H.-C. (2013), "Indium doping concentration effects in the fabrication of zinc-oxide thin-film transistors," *Int. J. Electrochem. Sci.,* **8**, 9773 – 9784.

Zhou, X. H., Hu, Q.-H. and Fuc, Y. (2008), "First-principles LDA+U studies of the In-doped ZnO transparent conductive oxide", *J. Appl. Phys.,***104**, 063703.