Optik - International Journal for Light and Electron Optics 175 (2018) 268–274

Contents lists available at ScienceDirect

Optik

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

Original research article

Theoretical and experimental studies of La- substituted In_2O_3 nanolayer via the modified Becke-Johnson (mBJ) potential

H.A. Rahnamaye Aliabad

Department of Physics, Hakim Sabzevari University, 96179-76487, Sabzevar, Iran

ARTICLE INFO

PACS:
68.35.bg
78.20.Ci
71.15.Mb
71.20.Be

Keywords:
DFT
Optoelectronic properties
Spray pyrolysis
Indium oxide nanolayers

ABSTRACT

Optoelectronic properties of nanolayer of pure indium oxide (In_2O_3) and substituted with La are investigated by the both density functional theory (DFT) method and the experimental spray pyrolysis technique. The reported experimental results are X-ray diffraction (XRD) and absorption coefficient spectra and the theoretical results are band structure, density of states (DOS), dielectric functions, refractive index and absorption coefficient. Obtained results show that, substituting In atom by La decreases the value of the band gap mainly due to the number of states originating from La- d states in the bottom of the conduction band. It is found that the refractive index of indium oxide nanolayers increases with the substitution of In with La. The experimentally obtained results confirm the calculated theoretical results.

1. Introduction

Transparent metallic oxides such as indium oxide (In_2O_3) belong to a wide band gap semiconductor family have attracted great attention in the optoelectronic, gas sensor and photocatalytic devises [1–3]. The doped indium oxide could effectively improve the sensitivity of sensor performance. Anand and co-workers have observed that in indium oxide compound, 10% Dy^{3+} doping increases the lattice constants and sensor response value [4] and 3% Mn doping increases photoluminescence intensity [5]. Also, they have found that 5% Tb^{3+}-doped indium oxide sensor had the best ethanol -sensing performance at 300 °C [6]. Recent experimental results show that the Ag-doped In_2O_3 based sensor has high responses to formaldehyde (HCHO) [7] and Zr-doping increases NO_2 gas sensing performance [8]. Obtained results by Yamada *et al.* show that a thin film of Mo-doped In_2O_3 (IMO) has high transmittance above 70% in a wide wavelength range of 0.3–2.5 μm [9] and shin *et al.* results show that the transmittance of IMO layers reach to 84.86% in conventional indium tin oxide (ITO) electrodes at 600 °C [10].

The nanocomposites based on Au/In_2O_3 have high response values about 53.08 [11] and 37 [12] and it is suitable for detection of CO gas [13]. Au-ZnO/In_2O_3 -based gas sensors also have fast response speed to C_2H_2 gas [14]. The nanostructure based on Pb/In_2O_3 has a response of 32.57–100 ppm to ethanol [15]. La^{3+}-doped In_2O_3 sensor is also more sensitive to H_2S [16]. On the other hand, Er^{3+} ions doped In_2O_3 is used in fiber amplifiers [17]. The doping of rare earth elements such as La, Er and Yb improved the responses of In_2O_3 sensors to the alcohol [18] and In_2O_3 doped with rare-earth element yttrium showed improved optoelectronic efficiency [19]. The optical band gap of In_2O_3 decreases from 3.61 eV to 3.27 eV with Eu^{3+} doping [20]. It is also observed that, the band gap of indium oxide increases with Sn doping [21]. The partial density of states analyses showed that a Sn atom substituted for an indium one formed three impurity bands with s-like symmetry [22]. The experimental and the first principles calculations results also show that Fe, Co and Ni/In_2O_3 compounds have ferromagnetic ordering [23]. For the other transparent metallic oxides such as ZnO, it is shown that ZnO doped by La is a nonmagnetic system, while for Ce, Pr, Pm, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb

E-mail addresses: Rahnama@hsu.ac.ir, Rahnamaye@gmail.com.

https://doi.org/10.1016/j.ijleo.2018.09.024
Received 27 April 2018; Received in revised form 4 September 2018; Accepted 7 September 2018

dopants a large enhancement of magnetic moment in ZnO is observed [24]. The ZnO: Eu system, has carrier-mediated ferromagnetism property while the ZnO:Pd system possesses no ferromagnetism property [25].

In the present study, I have investigated the optoelectronic properties of pure and substituted In_2O_3 with La by the expermental spray pyrolysis techniqe and the density functional theory (DFT) approache (mBJ approximation). Lanthanum- substituted indium oxide thin films aredeposited on glass substrates by spray pyrolysis techniqe. Indium oxide is crystallized in three different space groups: $R\bar{3}c$, $I2_13$ and $Ia\bar{3}$. The $R\bar{3}c$ space group with the rhombohedral crystal structure is used for first principle calculations [26].

2. Experimental procedure

La- substituted In_2O_3 thin films with the different La concentration have been deposited on glass substrates by spray pyrolysis technique. The spray pyrolysis technique is the most useful methodfor preparation of the doped transparent oxides thin films. For fabrication of undoped In_2O_3 thin films, intial solution is composed of $In(NO_3).4H_2O$(0.08 wt%), H_2O(0.44 wt%), HNO_3(0.04 wt%) and CH_3CH_2OH(0.44 wt%) (wt% stands for weight percentage in solution). La- substituted In_2O_3thin filmshave been fabricated by adding of $N_3O_9La.6H_2O$ (5 wt%, 10 wt%, 15 wt%, 20 wt% and 33 wt%) to the initial solution. In the next steps, for the preparation of the thin films, the glass substrates were cleaned and then kept on a hot plate (500 °C). Deposition parameters are including: The carrier gas (O_2) pressure is 1.6 atm, flow rate is 17 ml min^{-1} and distasnce between substrate and nozzle is 40 cm A 250 nm layer thickness was produced by spray pyrolysis technique. In this work,obtained results are very broad, therfore I have presented La-substituted In_2O_3thin films with 15 wt% La concentration.

3. Computational methods

The full potential linearized augmented plane waves (FP-LAPWs) method as implemented in the WIEN2k package [27] is used to calculate the structural, electronic and optical properties of pure and La- substituted In_2O_3. The modified Becke-Johnson (mBJ) and the Spin- Polarized Generalized Gradient Approximation (SPGGA) are used for calculation of the exchange-correlation interactions. The mBJ potential performs the calculation of band gaps with accuracy similar to the computationally expensive GW calculations [3]. This method provides band gaps almost equal to the experimental values. In solving the Kohn–Sham equations, the relativistic effects have been taken into consideration. In the present calculations, the selected parameter that determines the size of the secular matrix is $R_{MT} \times Kmax = 7$, where the R_{MT} is muffin-tin sphere radii and Kmax is the cut-off wave vector in the first Brillion zone (B.Z). The selected muffin-tin radii for In, La and O are 2.4, 2.5 and 1.6 (in atomic unit) respectively. The iteration process was stopped after the calculated total energy was converged to less than 0.0001 Ry.

In the first principle calculations, the lattice optimization is performed in order to find the relaxed lattice constants for the pure and La- substituted In_2O_3. The final calculations are performed with the relaxed lattice constants. Most of the more complicated crystal structures have free internal structural parameters, which can optimized using the calculated forces on the nuclei. In this work, for geometry optimization with Force tolerance, the geometry optimization calculations are converged when all forces are below 2.0 mRy/bohr.

4. Results and discussion

4.1. Experimental results

X-ray diffraction (XRD) patterns of the nano layers are obtained by the Philips diffractometer using CuKα radiation with λ = 1.542 Å. As mentioned in the section 2, I have just presented the XRD pattern of In_2O_3: La (15 wt %). Fig. 1 shows that the (222) plan of the In_2O_3 crystal grew more predominantly than any other plans. This reveals that the (222) peak of the nano thin film

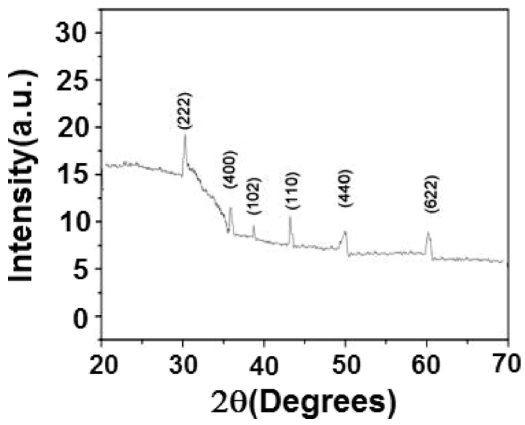

Fig. 1. Obtained XRD spectra substituted In_2O_3 with La concentration 15 wt%.