

Analysis on O₃ sensing and conducting property of Sn doped In₂O₃ using hydrothermal preparation method

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Abstract

The In₂O₃ nano material is prepared by hydrothermal method and is doped with Sn by 5, 10, 15 and 20 mol. concentration. The elevated property is studied keenly. All doped samples are characterized using proportionate technical tools. The distortion of fundamental lattice pattern of In₂O₃ due to the Sn doping is identified. The lattice pattern is slowly changed from simple cubic to tetragonal form. The modified property of the compound at 20 mol. of Sn is elaborately studied. The O₃ sensing characteristic mechanism is explored which is very high at 20 mol. of Sn doping.

Keywords: In₂O₃, SnO₂, XRD, SEM, XPS, O₃, Gas sensing

1. Introduction

Tin doped Nano indium oxide is a multi phase conducting and transparent oxide material which is extensively used in various optoelectronic devices by virtue of its high stability, reproducibility, fascinating optical and conducting ability [1-3]. In last decade, the nano SnO₂ materials have much attention in fabrication of flat panel display, Light emitting diodes, solar cells and sensors as transparent electrode since it has potential applications in nano electronic industry. Apart from that, even though, it has infinite platform in optoelectronic devices and electrodes [4-5], it has been extensively studied so far because of its most applications in gas sensors [6-7]. The physical properties of In₂O₃ nanostructures can be altered by impurity adding, coating with surfactants and annealing temperatures [8]. The physical and chemical properties of final product is depends on the concentration of doping materials and compositional pattern. Usually, the nano In₂O₃ material has received the Sn atoms in its regular lattice sites and the basic lattice pattern is altered on par with the doping material [9]. Thus, the new property of the In₂O₃ material is born and it is used for the new applications. After viewing the literature, it is found that, some of the earlier works[10] related to In₂O₃ for optical and conducting purpose, particularly few works have been made for studying the gas sensing property[3,11-12]. In this work, the nano In₂O₃ material is prepared and is doped with Sn at 10, 15 and 15 mol. percentage using hydrothermal method. The prepared material is characterized by XRD, SEM, PL, Conductivity and XPS tools. Further, the gas sensing property and conducting sensitivity have been studied.

2. Experimental methods

2.1. Preparation

A certain amount of In(NO₃)₃ .H₂O mixed with Sn(Cl₂)₂ 2H₂O (5%,10%,15% & 20%), 1,4 -butadiol and deionized water was stirred. The solution is dripped slowly in 30ml ammonia, a milk white precipitate is appeared. By dripping ammonia, the pH value is maintained as the solution was changed to alkaline, thus it was completely precipitated. The white colloidal gel was kept in a constant temperature bath at 60°C for 20 hours and it was further slowly heated until a light brown solution. The solution was again dried at 60°C. In order to study the effect of annealing temperature on the structural, optical, and morphological properties, the prepared In₂O₃ powder were annealed at 300°C calcined for 3hours, and pale yellow In₂O₃ nano powder was obtained. The Phase identification and crystallite size determination were carried out using PAN alytical X' Pert X-ray diffractometer (CuK α radiation, $\lambda = 1.5406 \text{ \AA}$). XRD data were collected in the 2 θ range of 20–70° using step scan mode with step width of 0.02° and step time 2.40 s. The surface morphology of the samples was investigated by scanning electron microscopy (SEM Hitachi S-3400N). The optical properties of the prepared thin films deposited on glass substrate which includes the transmittance spectra are studied over the wavelength range (300- 1600 nm) using UV/Visible spectrometer (Anthoslabtec, Krefeld, Germany). X-ray photoelectron spectroscopy (XPS) analysis was carried out by using Multilab-2000 (Thermo-scientific UK) spectrometer using a monochromatic MgK α X-ray source (1256 eV) with analyzer pass energy of 10 eV.

3. Results and discussion

3.1. XRD analysis

The XRD pattern as prepared Sn doped In_2O_3 with different concentration is as shown in Figure 1. The XRD data has been taken at 300°C , is optimized temperature in which the favorable characteristics of the materials have been exposed and it is validated by the previous works [13]. The XRD peaks are observed at 10 and 15 mol. percentage of Sn doping and all the results obtained at 300°C . At 10 and 15 mol. percentage, the peaks are found at 32° , 40° and 52° from (222), (400), (431), (440) and (622) planes. All peaks of two samples are representing simple cubic lattice which is strongly emphasized by consistent placement of the peaks. But, at 20 mol. of Sn doping, the above observed peaks have little shifted by nearly 5° at (222) and (400) planes. This peculiar observation illustrated that, the simple cubic structure is rather deformed and converted in to tetrahedral form. This is mainly due to the rigorous occupation of Sn atoms in the place of In. The basic lattice formation of In_2O_3 is somewhat disturbed by the exhaustive insertion of Sn atoms which leads the change of mechanical force constant of bonds between the In and O.

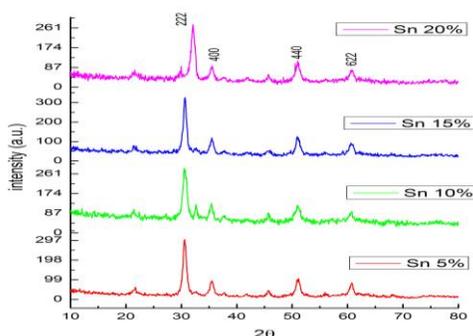


Fig 1. XRD pattern of Sn doped In_2O_3 at different concentrations

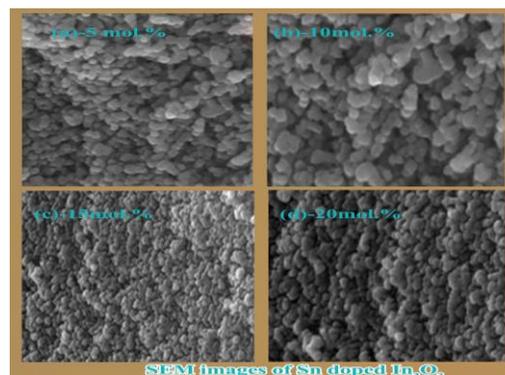


Fig 2. SEM images of Sn doped In_2O_3

3.2 SEM analysis

The SEM images of the ITO powders at different Sn concentrations are shown in Figure 2 (a-d). All the substrates are fully covered by ITO particles in the nano scale level, where the size increased with increasing of doping concentration of Sn. This is in good agreement with XRD results. In addition to that, the surface micrographs of ITO powder exhibit nano crystalline and continuous dense microstructure (no pores can be observed) were appeared which is due to the composition of nanoparticles. In figure 2a, it can be seen that, the nano particles were coagulated and grains were not seen clearly. In figure from 2b to 2c, it is able to see the growing of nano particles. In figure 2d, the nano particles can be distinguished clearly and the grain boundaries could be viewed perceptibly. From the SEM images, it is inferred that, the nano particles were shaped and the crystallites structure was completed at 20 mol. %.

3.2. EDAX examination

The characteristic EDAX spectrum of the ITO powder at 20 mol. is shown in Figure 3. From the figure, it can be seen that, the deflected signals corresponding to Sn, In and O are appeared with maximum intensity which represent the composition of the present compound. Form the result it is inferred that, the complete nano crystal is formed with adequate doping concentration. This result is in accordance with the uniformity criteria given for ITO in the earlier report [14].

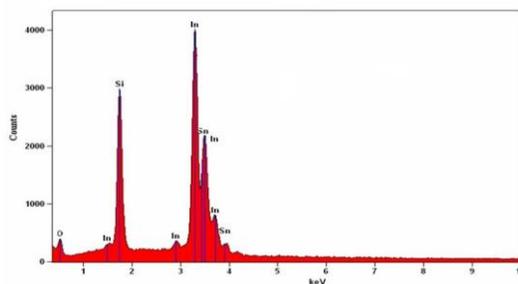


Fig 3. EDAX spectra for ITO powder with Sn concentration.

3.4. XPS data analysis

The Figure 4 shows the recorded spectra of X-ray photoelectron spectroscopy (XPS) at 20 mol.% Sn doped indium oxide nano powder which displayed the Photoelectron peaks for In, Sn and O. In the spectra, the binding energy range is confined to be 430-460 eV for In- $d_{3/2}$ and In- $d_{5/2}$. The binding energy of the O by 1s peak is ranging from 530-526 eV. The binding energy for Sn- $d_{3/2}$ and Sn- $d_{5/2}$ peak is ranging from 480-500 eV. Hence, no other peaks related to the surface contamination, are not found. The XPS spectra for In 3d, Sn 3d doublets and O 1s peak are shown in Figure 4 (a-c), respectively. These peaks showed the evidence of the binding state of In and Sn since there is no other sign of broadening or splitting of the peaks. In addition to that, the peaks in the spectra designated that, the oxygen atom is able to bond with both the indium and tin and thus ITO is formed as in the earlier report [15]. The binding energy of In 3d $_{5/2}$ is found to be 444 and 452eV which was attributed by the In³⁺ bonding state from In₂O₃ which was similar to the previous studies [16-17]. The binding energy of Sn 3d $_{3/2}$ & d $_{5/2}$ is found to be 486 and 495 eV respectively and corresponds to the Sn⁴⁺ bonding state from SnO₂ [18].

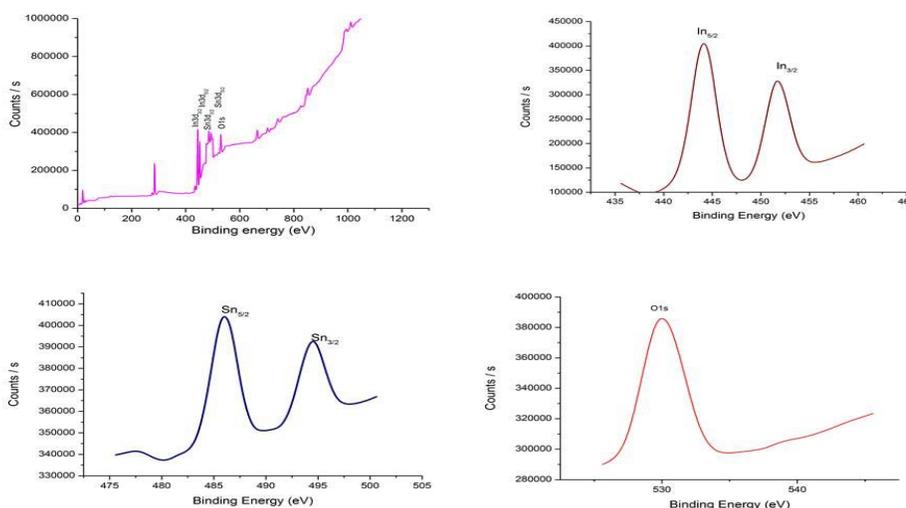


Fig 4. XPS spectra of 20% Sn doped ITO powder.

3.5. Optical studies

The Figure 5 (a-d) showed the optical transmittance as a function of wavelength in the range of 300-1600 nm with different doping ratios (5, 10, 15 and 20 mol. %). From the Figures (a-d), it is observed that, the optical transmittance is maximum and higher than 80%. From this result, it is concluded that, the threshold optical activity of the samples is found with minimum doping concentration. But in the maximum concentration (20 mol.%), the optical activity of the samples is elevated as in the earlier report[19].

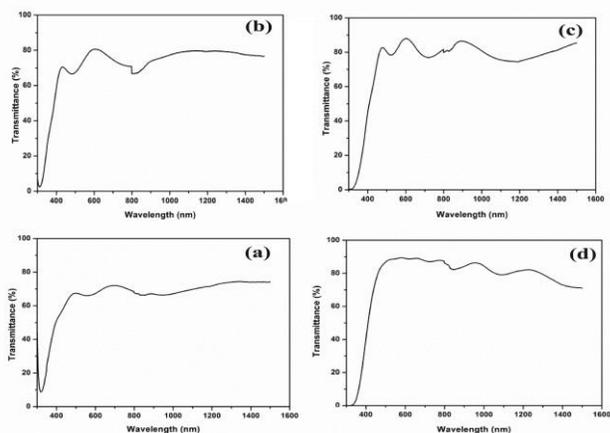


Fig 5. Transmittance spectra of Sn doped ITO powder.

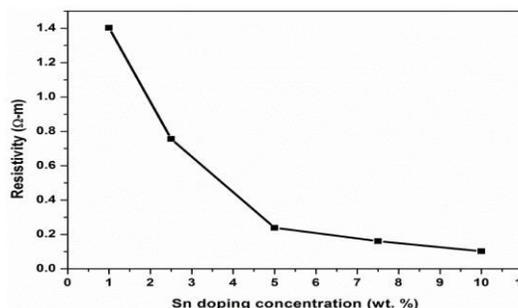


Fig 6. Resistivity of different doping concentration.

3.6. Resistivity analysis

Figure 6 showed the effect of Sn doping concentrations on the resistivity of ITO nano particles. The resistivity of the particles decreases as the Sn concentration increases. As the present compound was basically metal oxide, the compound has an amount of resistivity naturally. When it was doped with Sn with minimum amount, its resistivity decreased. When the doping concentration was increased further and at 20 mol., the material resistivity is found to be decreased much. Thus, the resistivity of the material could be tuned by the doping concentration. The similar result was observed in the earlier work [20]. In this case, the resistivity is decreased from 1.5 Ω to 0.09 Ω when the doping concentration is increased from 5 mol.% to 20 mol.%. Fig. 7 shows the variation of sensitivity and response time with annealing temperature. The response time reaches a maximum at 2 min, and then recovers within 4 min. The sensitivity is higher for the powder with smaller particle size, and the response time increases with larger particle size. Given that In_2O_3 :Sn nanoparticles are n-type semiconductors with oxygen vacancies that generally provide donor states, the conductivity of the In_2O_3 :Sn nanoparticles is directed by the steady concentration of adsorbed oxygen ions and determined by chemical dynamics, including oxidation and diffusion.

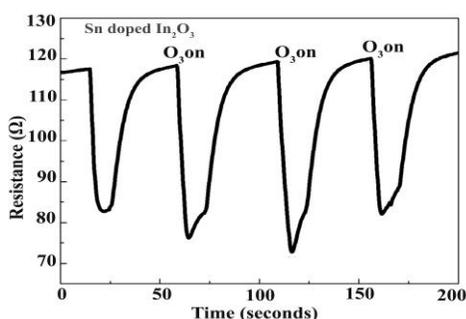


Fig 7. Time response curve of Sn doped ITO powder.

4. Conclusion

In this work, the Sn nano atoms doped with In_2O_3 nano material in different mol. concentration. All the samples are characterized and the optimized sample is found at 20mol. concentration of Sn. The basic lattice pattern of In_2O_3 is somewhat distorted and it is evidenced from the XRD peak shift. The SEM analysis explored the particle amalgamation of sample at 20 mol. Sn. The binding energy of the compositions of the doped material found from the XPS data. The resistivity test is carried out from its result; it is observed that, the sudden fall of resistivity taking place at 20 mol. of Sn in In_2O_3 . From the optical studies, it has been observed that, the optical activity of 20 mol. of Sn is elevated up to 80%. The In_2O_3 material gained by nano fusing exposed exceptional structural properties for gas sensors. The structure of the material is readily accessible to ozone gas molecules. The morphology of the sensor can be varied significantly and even-ordered nano materials can be easily fabricated using the technique used in this work.

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