

Effect of Different Doping Concentrations and Its Characterizations of Nanocrystalline ITO Nano Particles

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Abstract

Nanocrystalline ITO particles are prepared by Combustion Synthesis. Similarly, the structural and morphological properties for as prepared different ratio of powders to be 9:1 and 5:5 were found. Thermogravimetry analysis shows the liberation of O, H, N and metal particles with respective temperatures and loss of weight in mg. The structural, optical grain boundary and electrical studies due to variation of theoretical mobility's with SEM analysis were discussed. The lattice constants were found to be 10.09 and 10.16 Å for different composition of powders. Here we present the preparation, Thermo gravimetric (TGA) analysis, structural studies, and morphological properties of ITO synthesized by decomposition of ITO by Sol-gel method.

Keywords: In₂O₃; SnO₂; Combustion and Thermo gravimetric analysis

Introduction

Transparent conducting oxide (TCO) nanoparticles of tin, indium and zinc oxides (doped and undoped) have been extensively studied due to their high optical transmittance and electrical conductivity. These particles are useful in photovoltaic and photo thermal applications [1]. Unlike the more commonly used indium tin oxide, zinc oxide is a non-toxic, inexpensive and abundant material. It is chemically and thermally stable in hydrogen plasma processes which are commonly used for the production of solar cells. They are conducive to heat loss through convection, resulting in rapid reduction of product temperature. In other words, there would be a continual increase in the available active nano particle area. In addition to the energy regulation, visible color changes may be exploited architecturally, i.e. so called 'fancy windows'. ITO has been extensively studied due to its wide applications in industry as coating material for energy saving of Lamp, transparent electrode for watch, LCD and indication element for office equipment and automobile measuring instrument, and coating material for screen panel, and is expected to use as selectively permeable membrane and transparent conductive for solar cell.

In oxide materials properties particularly indium oxide and tin oxide its resulting agents, such as hydrogen, carbon monoxide, ammonia and hydrocarbon gases will react with chemi-adsorbed oxygen. The synthesis of nanostructured In₂O₃:SnO₂ by combustion technique. The method is fast, and yields nanopowders with a fairly narrow particle size distribution. Recently, gel combustion routes using a variety of organic fuels like urea, hydrazine, citric acid and others have been reported to be promising methods to prepare a variety of oxides including nanocrystalline In₂O₃:SnO₂. In a sense, indium doped with tin oxide powder can generate a lot of gases when burned. If such application is utilized in the synthesis of oxide powders, a great deal of gases can be released via the combusting reactants. This process will reinject the carrier and increase the sensor conductance. It is well known that the electrical conductivity in indium oxide is due to non-stoichiometric composition as a result of oxygen deficiency [2].

The Synthesis and characterization of nanostructured n-TCOs is a

very important and well established field in nanotechnology and is still growing in stature. Therefore, the formation of nanocrystalline P-type counterpart may open up an extremely important and interesting field of research for the fabrication of all transparent nano active devices. This will not only give a new dimension in the field of 'Transparent Electronics' but new avenues may open up in the nanoparticles research keeping an eye on its tremendous applications in optoelectronics technology.

In₂O₃ is one of the most promising candidate's for such tasks. It is a well known semi conducting oxide already used practically worldwide. When In₂O₃ is doped with Sn, a so called (ITO) is formed. High conductivity of ITO is attributed to the high carrier concentration which is caused by incorporation of Sn ions into In₂O₃ host lattice and oxygen nonstoichiometry. ITO has a cubic bixbyite structure with the lattice parameter a=10.118 Å. Electrical conductivity (σ) for best quality ITO samples was found to be 10⁴ S/cm². The as prepared powder exhibited SnO₂ as secondary phase whereas different temperature powdered particle showed single phase In₂O₃:SnO₂ with high conductivity [3].

The optical properties of nanocrystalline semiconductors have been studied extensively in recent years. If the particle size of a semiconductor becomes comparable to the Bohr radius of the exciton, the ratio of surface atoms to those in the interior increases remarkably leading to the surface properties playing an important role in the properties of the material. Semiconducting nanoparticles also exhibit a change in their electronic properties relative to that of the bulk counterpart as the

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size of the solid becomes smaller, the band gap becomes larger. These quantum size effects have stimulated great interest in both basic and applied research [4].

Experimental Section

In₂O₃-SnO₂ powder were prepared with indium In (NO₃)₂.2H₂O, ingots (>99.9%, Sisco research laboratory) and Sn(NO₃)₂.3H₂O (98% Loba Chemie) as source material. A stock solution of indium In (NO₃)₂.2H₂O, ingots (>99.9%, Sisco research laboratory) and Sn(NO₃)₂.3H₂O (98% Loba Chemie). Solution was made by using this material so as to obtain a concentration of 0.5 M In³⁺. For the preparation of 90/10 and 50/50 In/Sn oxide powders, a calculated quantity of In (NO₃)₂.2H₂O and Sn(NO₃)₂.3H₂O was dissolved in the required amount of water. The volume ratio of the mixed salt solution/ organic solvent was 9:1 and 5:5. The doping concentration (0.05) M of Sn(NO₃)₂ obtained by stirring the In (NO₃)₂.2H₂O with concentrated HNO₃. The mixture was diluted with water and the resultant solution was stirred magnetically for 2 h. Urea was added to the above mixture till a gel of hydrated indium tin oxide appeared. It was stirred for additional 30 min at an ambient temperature. This gel form mixture is analyzed by thermal decomposition by TGA analysis and it was found confirmed that some hydrous salts are present on that mixture. This mode is characterized by slow and flameless reaction. Solution Combustion Synthesis used all over the world to prepare oxide materials for a variety of application. An oxide material prepared by rapidly heating aqueous solutions containing stoichiometric amounts of respective metal nitrate (oxidize) and fuels like urea [5].

In order to obtain one mole of tin nitrate 2 moles of Indium nitrate ψ moles of fuel are then added.

$$\psi = \frac{\text{Total valences of elements in the fuel}}{\text{Total valences of elements in nitrates}}$$

$$\text{In} (-15) + \text{Sn} (-8) + \psi (+6) = 0$$

$$9 (-15) + 1 (-8) + (6) \psi = 0$$

Adiabatic flame temperature T_f of the combustion reaction is:

$$T_f = 298 + \frac{\sum_{\text{Reactants}} (\gamma_i x \Delta H_{f,i}) - \sum_{\text{Products}} (\gamma_j x \Delta H_{f,j})}{\sum_{\text{Products}} \gamma_j x C_p} \text{ in } K$$

ΔH_f=Enthalpy of formation of the products or the reactants respectively.

C_p=Heat capacity of the products at constant pressure and at 298 K

γ=Molar number. The flame temperature was calculated as 855 K.

This formula shows that the flame temperature not only depends on the nature of the fuel but also on the fuel to nitrate ratio (depending on the value of ψ) [6].

Physical characterization of the powders

Thermal characteristics of the precursor material were studied on a Netzsch TG/DTA (409°C) unit at a heating rate of 10°C/min. The nanoparticles confirmation were carried out by powder X-ray

diffraction (XRD) X-ray diffractometer (XRD) with monochromation CuK_α target (1.5406°) at a scan rate of 2°/min. Scanning electron microscope (SEM) work on the calcined powders were performed under Scanning Electron Microscope Cambridge 53400N, and the chemical composition was examined using EDAX attachment (Norton system six, Thermo electron corporation instrument, Super DRY 11, USA) with the SEM unit.

Results and Discussion

The full width half maximum of each peak is the width (in degrees) at half the maximum peak intensity. The FWHM of a peak can be related to the average crystallite size. An estimate of the average crystallite size, of the particle is made by Debye Scherer equation and FWHM of the XRD peaks for different orientations. The estimate excludes the effects of the peak broadening due to the instrument used and any effect of residual stresses in the ITO particle. The more predominant orientations are 222, 400, 440 and 622 in the ITO crystal. These estimated values are compared with the standard values given for the lattice constants of In₂O₃ (89-4598). A characteristic shift towards lower angle compared to reflexes of ideal crystal is always observed for all peaks. This indicates a systematic lattice expansion. This phenomenon has also been reported by many other authors and some of them have been summarized. Particles in the peripheral position exhibit generally broader peaks, indicating larger micro strain or smaller crystallite size and less pronounced 440 and 622 reflexes the values were tabulated in Table 1.

The results are similar to a previous investigation on the effect of sputter geometry on ITO films [5]. The analysis of crystal structure revealed that the detected peak of the nano particle was corresponding with that of crystallized ITO are shown in Figure 1. That is, very intense peak was found at the three most important peaks of In₂O₃ namely 222, 400, and 440 reflections. The peaks do not deviate from the PDF intensities, implying random non oriented arrangement of the ITO

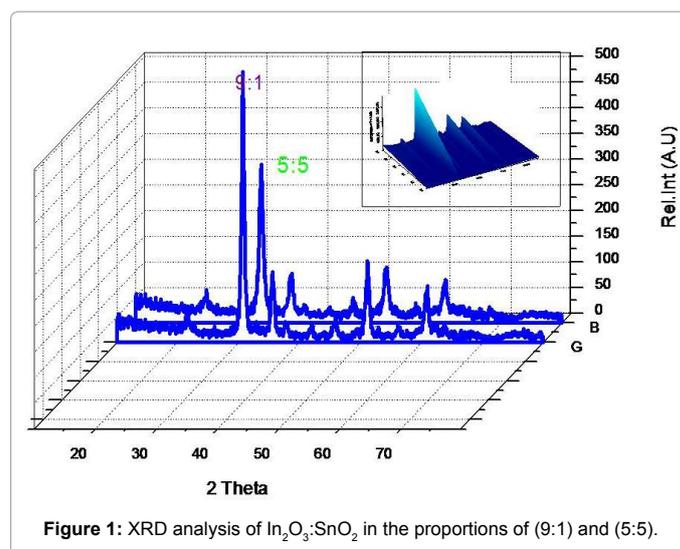


Figure 1: XRD analysis of In₂O₃:SnO₂ in the proportions of (9:1) and (5:5).

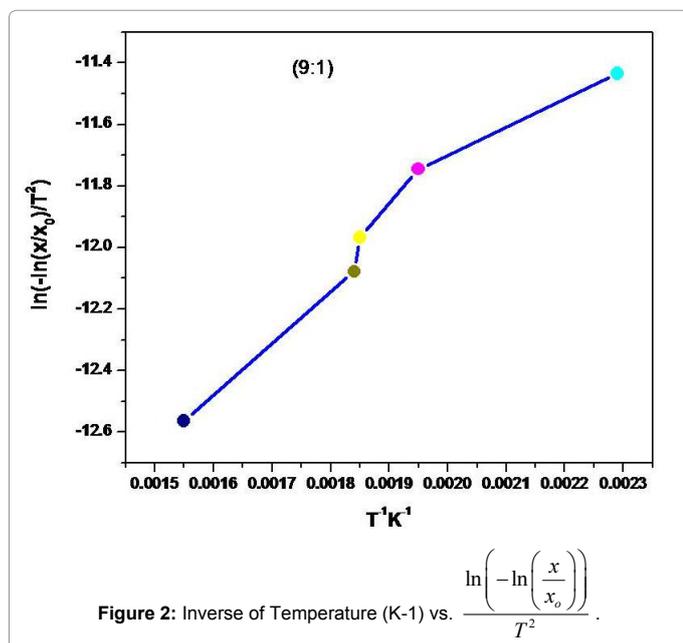
Sample	Residual Stress δ= $\frac{0.94\lambda}{(FWHM)Cos\theta}$	Lattice constant (Å)	Grain Size= (nm) $\frac{0.94\lambda}{\beta Cos\theta}$	No.of Unit cell $n = \frac{4}{3} (3.14) \left(\frac{D}{2}\right)^3 \frac{1}{V}$	Porosity P = $\left(1 - \frac{\rho}{\rho\tau}\right) \times 100$
In ₂ O ₃ 50% SnO ₂ 50%	1.666	10.147	9.5486	436.07	50
In ₂ O ₃ 90% SnO ₂ 10%	1.521	10.124	8.716	333.94	50.679

Table 1: XRD results of as prepared samples for (9:1) and (5:5) of structural studies.

particles. The crystal size and its values were tabulated shown in Table 1. The major peaks due to SnO₂ at 26.8° and SnO at 32° 2 theta were absent in the observed pattern, indicating complete miscibility of In and Sn in the proposed composition [6]. It is known that in ITO material, Sn is tetravalent each Sn⁴⁺ replacing In³⁺ substitutionally, thereby donating a free electron for the conductivity in the process shown in Table 2. So the ITO materials retain the cubic In₂O₃ structure up to the solid solubility limit of the SnO₂ in In₂O₃ [7-9]. Porosity of the samples is nearly equal to one another and TGA analysis was carried out for the proportion of (9:1).

TGA-DSC analysis

Thermo gravimetric analysis (TGA) and Difference Thermo



gravimetric Analysis (DTA) were simultaneously applied to the dried powder of the nanoparticle 2-3 mg with a computer controlled Instrument-SDT Q600 V8.3 Build 101. The thermal evolutions of the ITO powder particles were followed by Thermogravimetry (TG) and Different Thermal Analysis (DTA). TG measurements were carried out by taking 2.5430 mg of as-prepared In₂O₃:SnO₂ (ITO) in a quartz pan to minimize bed effects during decomposition of the sample. The heating program was 30-1100°C and the heating rate was 20°C/min per min in air, and the purge gas employed was nitrogen, at a flow of 45 ml/min. The decomposition behavior of the sample is shown in Figure 2. It is observed that only 6.88% weight loss is noticed in the entire decomposition programme and the weight loss is due to chemidesorption of adsorbed water molecules during exposure of the sample to the atmosphere. The DSC analyses were carried out using a Shimadzu DSC-50 differential Scanning Calorimeter Thermal Analyzer. About 3 mg of ITO powdered particle was weighed very accurately in the aluminum DSC pan and placed in the DSC cell. It was heated from 0°C to 1000°C at a rate of 20°C/min under air atmosphere shown in Figure 2 and listed in Table 3 [10-13]. In support of TGA, simultaneous DTA was recorded in the same temperature range to confirm the decomposition steps. A chemidesorption of adsorbed species or a chemical decomposition is an endothermic process. It occurs by absorbing heat to raise the enthalpy of the system to a critical limit of its thermodynamic stability before it dissociates.

SEM analysis

Figure 3a and 3b shows the surface morphology of ITO powdered particles prepared at two different proportions of 9:1 and 5:5 at room temperature for 0.5 Molar solution concentrations observed. From these images it can be seen that the grain sizes of the powdered particles are not uniform. Therefore average grain sizes were estimated from different grains within the powder and to be about 0.8 μm to 2.5 μm. It is also seen that the edge texture of the particles become sharper and the grain boundaries become clearer by increasing the Sn content. It exhibits spherically shaped secondary particles consisting of primary nano spheres of approximately 0.8 μm to 2.5 μm [14]. The elemental

Sample	$\varepsilon = \frac{\Delta d}{d_0} = \frac{\Delta d}{d_{hkl}}$	$\tau = \frac{I_{m(hkl)}}{I_{0(hkl)}} = \frac{1}{n} \sum_{i=1}^n \left(\frac{I_{m(hkl)}}{I_{0(hkl)}} \right)$	$\sigma = \sqrt{\frac{\sum(\tau-1)^2}{n}}$	$\frac{I_{ITO}}{I_{ITO} + I_{IO} + I_{TO}} \times 100$	$\frac{1}{D^2} \times 10^{18}$ lines/m ²
In ₂ O ₃ 50% SnO ₂ 50%	0.00342	0.06213	0.5415	73.94	0.01097
In ₂ O ₃ 90% SnO ₂ 10%	0.00205	10852	0.0492	73.38	0.01316

Table 2: XRD results of as-prepared samples of (9:1) and (5:5) of structural studies.

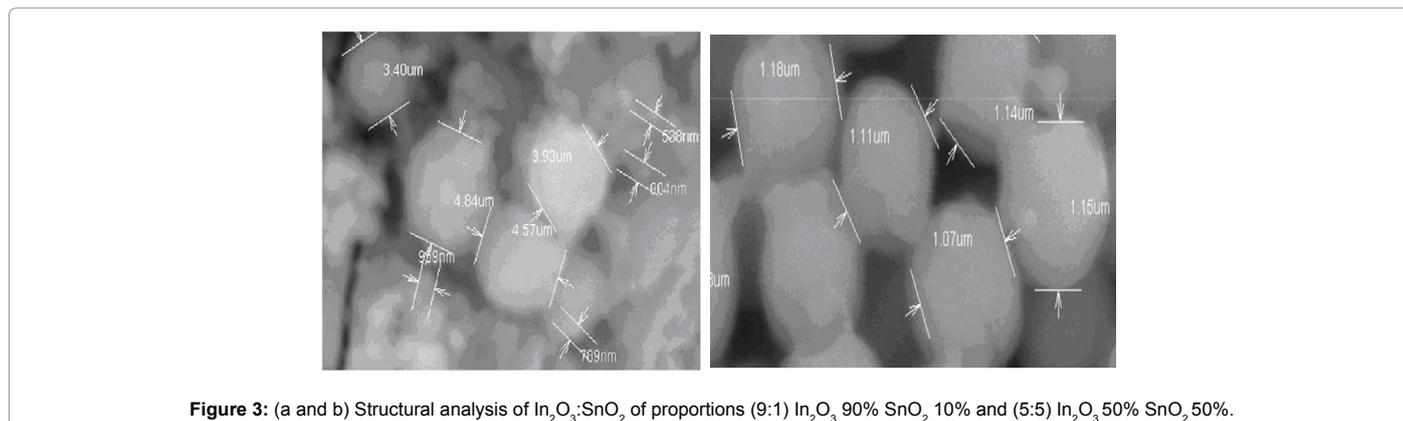


Figure 3: (a and b) Structural analysis of In₂O₃:SnO₂ of proportions (9:1) and (5:5) In₂O₃ 90% SnO₂ 10% and (5:5) In₂O₃ 50% SnO₂ 50%.

T^{-1}	$\frac{\ln\left(-\ln\left(\frac{x}{x_0}\right)\right)}{T^2}$
0.00229	-11.435
0.00211	-11.406
0.00194	-11.745
0.00195	-11.993
0.00184	-11.9677
0.00185	-12.079
0.00155	-12.565

Table 3: Temperature in Kelvin Vs $\frac{\ln\left(-\ln\left(\frac{x}{x_0}\right)\right)}{T^2}$ of the sample (9:1).

analysis results were tabulated in Table 3, the two proportions of ITO 9:1 and 5:5 [15].

Conclusion

The size of the nano particle and the crystal size of the two different proportions were observed and its size lies in the very small range of 8-10 nm. The crystal size of 5:5 NPs are slightly smaller than the proportions of 9:1. The weight loss ratio of these proportions was entirely different and its value of 5:5 increased than 9:1. In our case the lattice parameter and dislocation densities were under the confinement regimes. This is due to the small crystal size of the prepared particles. Due to its agglomeration the particle size becomes larger in μm shown in its morphological studies of Scanning Electron Microscopy. The Elemental results analysis well matched with the calculated prepared molar ratio of the source materials.

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