

Study on the synthesis of Indium Tin oxide (ITO) nanomaterial using sol gel process and its potential for CO gas detection

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Abstract. This paper described the synthesis of doped and undoped nanomaterial Indium Tin oxide (ITO) using sol-gel process with the base materials from Indium Nitride ($\text{In}(\text{NO}_3)_3$) and Tin Chloride (SnCl_4). Doping was done using Palladium Chloride (PdCl_2), with the molar ratio of 90:10 and 70:30, respectively. Physical characteristics of the nanocrystallites were examined using SEM, EDS, XRD, and FTIR, whereas its resistivity was tested against CO gas. The result showed that the ITO powders have a crystal size smaller than 100 nm, with a cubic crystal structure (byxite type), and having strong molecular bonds for In-O-In and Sn-O-Sn. The response to CO gases showed a decreasing resistivity with increasing CO gas concentration, showing its potential for gas sensor application.

1. Introduction

Indium Tin oxide (ITO) is a semiconducting material that has been widely used in the field of optoelectronics. Many devices such as CCD (Charged Coupled Device), LCD (Liquid Crystal Display), solar cells, LED (Light Emitting Diode), Photo Diode, Photo Transistor, and Laser, have used layers of ITO because of its optical transparency and high reflectivity in ultraviolet range [1]. In the field of sensor, ITO has been used as an active material to detect gases such as NO_2 [2], methanol [3], H_2 [4], and CO [5]. This widespread application has made ITO an interesting topic to be studied more intensively, especially its synthesis process and characteristics. The process of forming layers of ITO can be conducted using many different techniques, such as sputtering [6], CVD (Chemical Vapor Deposition) [7], thermalevaporation [8], and spray pyrolysis [9], and the resulting layer characteristics are very dependent on the process parameters used during deposition [10]. A simple and thus very popular method in synthesising an ITO material is by sol-gel process. Compared with the other techniques, sol-gel process has the advantages in terms of homogeneity, purity, low processing temperature, simplicity in adding dopant elements, and compatibility with microfabrication processes. Previous works in the application of sol-gel process to synthesise ITO nanomaterials have been demonstrated by Li and Ren [11], Hjiri *et al* [12], Silva *et al* [13], and Ibrahim and Moghdad [14]. Therefore this research was conducted to synthesise ITO nanomaterial using sol-gel process. Characterisation was conducted to study the physical characteristics of the resulting ITO powders using SEM, EDS, XRD, and FTIR, and the electrical characteristic was studied using four-point probe in response to CO gas.

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2. Experimental

Indium Nitride ($\text{In}(\text{NO}_3)_3$) and Tin Chloride (SnCl_4) have been chosen as the base materials, and PdCl_2 was used as the dopant material. Four samples have been prepared in this experiment with each molar composition as seen in Tabel 1. Sample A and B were for the undoped ITO, and sample C and D were for the doped ITO.

Tabel 1. Molar composition of all samples

Sample	$\text{In}(\text{NO}_3)_3$	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	PdCl_2	% Molar Ratio
A	10 g	1.1 g	-	90 : 10
B	10 g	4.28 g	-	70 : 30
C	10 g	1.1 g	0.28 g	90 : 10
D	10 g	4.28 g	0.36 g	70 : 30

Initially, 10 g of $\text{In}(\text{NO}_3)_3$ was dissolved in 10 ml H_2O . All materials were then mixed for each sample, and added with 15 ml Diethylene Glycol. The resulting mixture was stirred using magnetic stirrer for 2 hours, while maintaining its temperature at 60°C and $\text{pH} = 1$. A clear solution (sol) was then resulted. The next step was to increase the pH of the sol solution by adding 10 ml of ammonium (NH_3) solution. This has resulted in pH value of the solution = 9. Stirring was then repeated for 2 hours using magnetic stirrer, while maintaining its temperature at 60°C , and a white gel was formed. The resulting white gel was then filtered and rinsed with DI water, and dried for 24 hours. The final step was to dry the white powder in an oven at 60°C for 3 hours, followed by calcination at 400°C for 2 hours.

3. Results and discussion

The ITO powders resulted after calcination process at 400°C have a dark brown color for sample A and B (undoped), and light brown color for sample C and D (doped). It appeared that the addition of PdCl_2 has caused the difference in the resulting ITO powders.

3.1. Morphology

Initial observation showed that the grain size of the resulting ITO powder for sample A was much below 100 nm. As can be seen from the SEM results in Figure 1a, the majority of the grain size measured around 50 nm. For sample B, the average particle size was even smaller than sample A, as seen from Figure 1b. This is in consequence with the increase in Tin (Sn) components of the ITO composition. The atomic radius for ion In^{3+} is 0.81 Angstrom, whereas that of Sn^{4+} is 0.71 Angstrom. In sample B, with the composition of Sn : In = 70 : 30, there are more Sn^{4+} ions replacing the In^{3+} ion position in their lattice structure than in sample A.

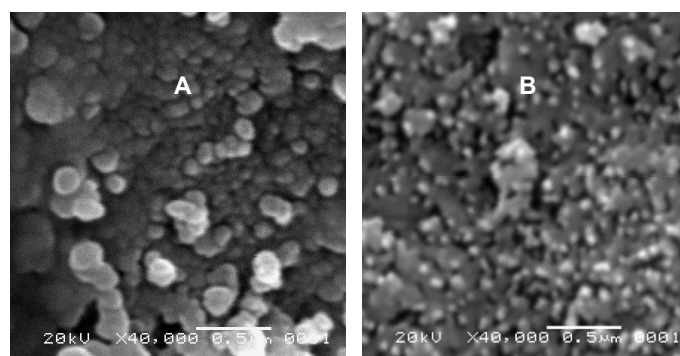


Figure 1. SEM view of: (a). sample A, and (b). Sample B

As can be seen in Figure 2, the addition of Palladium dopant did not have a significant effect to the average particle size of the ITO powder. Although Pd^{2+} ion has an atomic radius of 86 Angstrom, its composition of only 2% from the total ITO composition did not have enough strength to alter the ITO particle size.

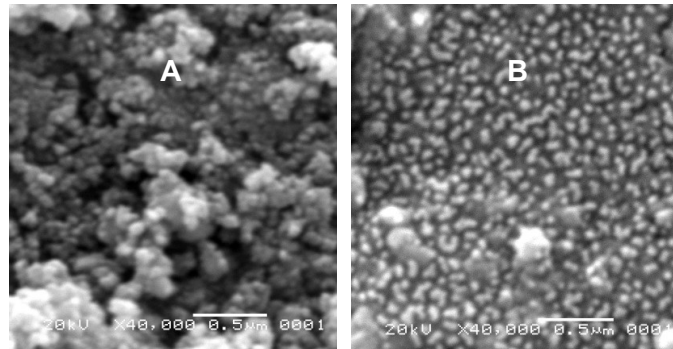


Figure 2. SEM view of: (a). sample C, and (b). Sample D

3.2. Composition

To study the elemental composition of the resulting ITO powders, the EDS spectrum of each sample has been taken. ITO consists of three elements, In, Sn, and O, which are formed by substitution of Sn atom into In^{3+} in In_2O_3 compound (through doping substitution mechanism). Therefore the chemical structure of ITO can be expressed in the form of $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-2x}$.

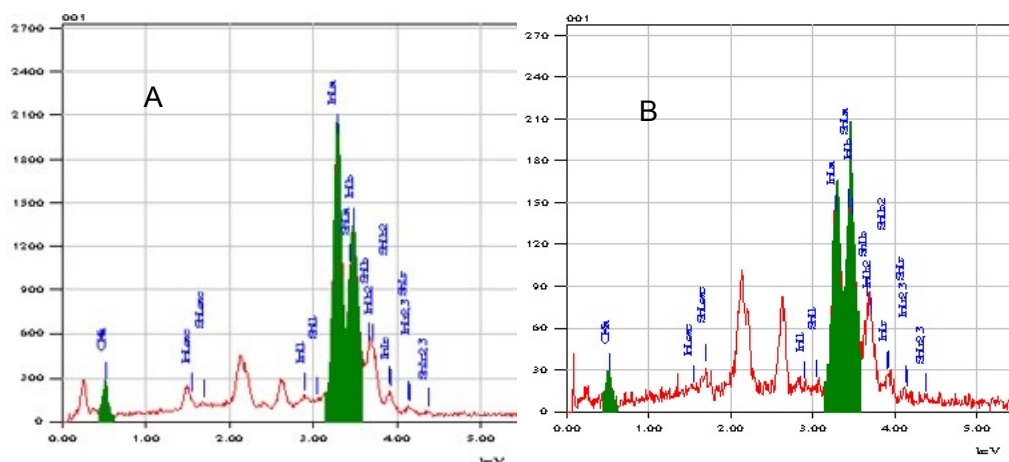


Figure 3. EDS spectra of the ITO powder: (a). sample A, and (b). Sample C

Tabel 2. The content of O, In, and Sn in the ITO compound extracted from the EDS spectra, and the corresponding x value from the chemical formula $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-2x}$.

Sampe	% O (8)	% In (49)	% Sn (50)	X value
A	18.87	49.57	31.56	0.75
B	19.67	32.77	47.55	1.27
C	18.47	57.90	23.63	0.53
D	19.07	45.35	35.58	0.90

From the EDS spectra as shown in Figure 3, it was obtained that the percent composition of O, In, and Sn for sample A was 18.87%, 49.57%, and 31.56%, respectively. Since the atomic weight of O, In,

and Sn is 8, 49, and 50, therefore the value of X in the chemical formula of ITO was approximately 0.75. By the same technique of calculation, the value of X for sample B, C, and D was obtained, and the results are as seen in Table 2.

3.3. Crystal structure

The XRD results for all samples showed that the ITO compound (In_2SnO_5) has been formed, along with Indium Oxide (In_2O_3). In ITO compound, each Sn^{4+} atom replaces In^{3+} producing one free electron, therefore ITO material will retain its bixbyte type cubic structure from In_2O_3 . This can be seen in Figure 4 where the highest peaks of both compounds are located close to one another. For sample A, the highest peak of plane <222> occurs at (2θ angle) 30.44 for In_2O_3 , and 32.64 for In_2SnO_5 , whereas reflection of planes <400> and <440> occurs at 45.295 and 50.190 (for ITO).

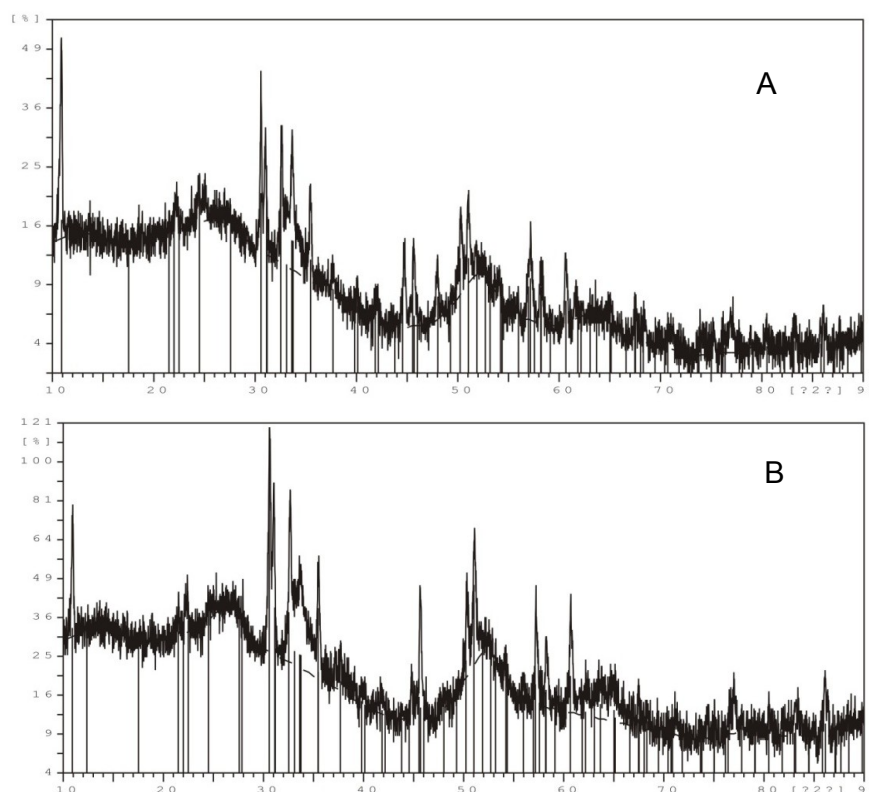


Figure 4. XRD spectra of the ITO powder: (a). sample B, and (b). Sample D

The addition of Pd as dopant material did not shift the location of the spectrum peaks. However, the peak intensity increased even for the same molar concentration. The peak intensity for sample A at 32.64 increased from 151 to 256 (in sample C). This increase showed that the addition of Pd dopant material had a positif effect on the crystal structure of the ITO nanomaterials. In sample B and D, InOCl compound was formed caused by the increase in molar percentage (from 10% to 30% of the SnCl_4).

3.4. Molecular bonds

The molecular bonds of the ITO nanomaterial have been analysed using FTIR spectra. Since ITO is composed of In, Sn, and O, therefore the FTIR spectra should provide information on the molecular bond between In-O-In, Sn-O, and Sn-O-Sn. From the spectrum of all samples, it was found that the peaks are located at the the wavelength between $\sim 400\text{ cm}^{-1}$ sampai $\sim 700\text{ cm}^{-1}$, in which the bonds were dominated by metal and oxygen bonds. Figure 5 shows the FTIR spectra of the ITO powder for all

samples, and the wave numbers corresponding to the peaks of the molecular bonds are listed on Tabel 2.

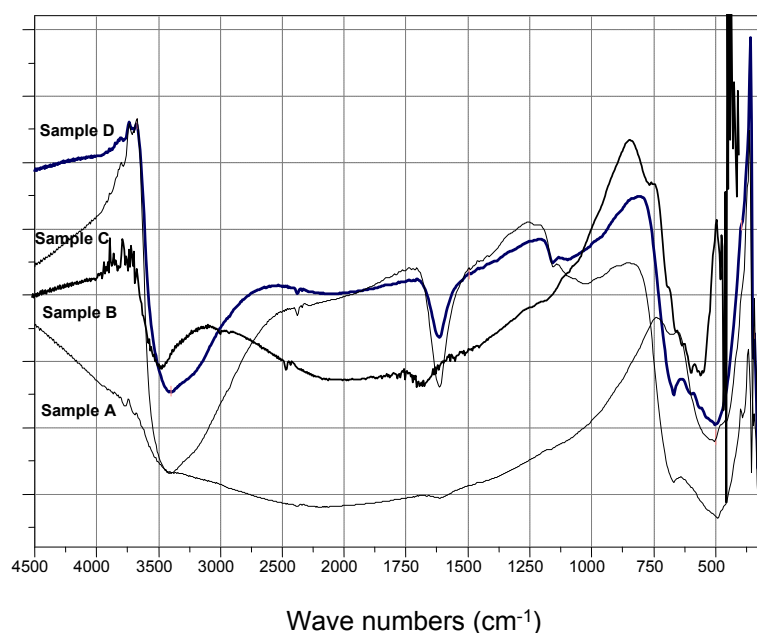


Figure 5. FTIR spectra of the ITO powders for all samples

Tabel 2. Wave numbers (cm^{-1}) for molecular bonds obtained from ITO spectra for all samples

Sample	In-O-In	Sn-O	Sn-O-Sn
A	453.27	503.42	671.23
B	389.62	489.92	667.37
C	443.63	493.78	669.30
D	325.97	499.56	669.30

3.5. Resistivity of the ITO nanomaterials

The study of electrical characteristics of the ITO nanomaterial was aimed to identify its resistivity changes in the presence of CO gas. The measurement of resistivity of the ITO powder was done using four-point-probe. As such, 0.3 g of ITO from each sample was pressed and then put inside a measurement chamber. The ITO sample was then exposed to the CO gas for 5 min, and the amount of CO was determined by the flow rate of the gas (1 ml/s and 5 ml/5). As shown in Figure 6, the results of the measurement showed that for all samples, the resistivity dropped as the amount of CO gas was increased. This is as expected since CO is one of reducing gases for metal oxide materials. In response to increase in molar Sn content, the resistivity decreased for the undoped samples (sample A to B), and increased for the doped samples (sample C to D). The addition of Pd content to the ITO has caused a lower drop in the measured resistivity as the amount of CO was increased.

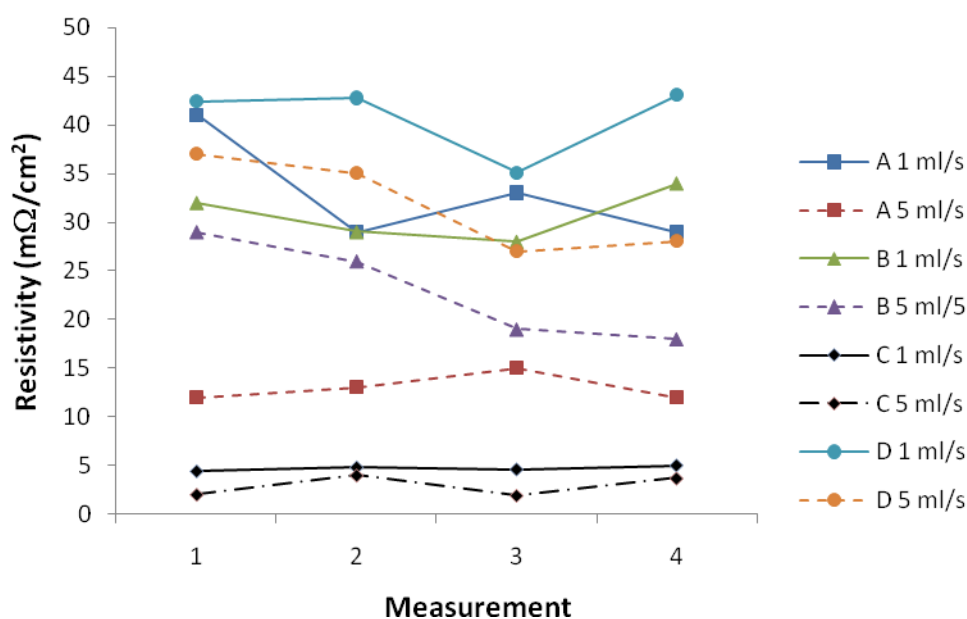


Figure 6. Resistivity of the ITO powders in response to CO gas

4. Conclusion

The synthesis of doped and undoped nanomaterial Indium Tin oxide (ITO) using sol-gel process has been described in this paper. Both physical and electrical characteristics of the resulting ITO powders have been studied. The morphology of the ITO powder showed nanometer grain size and smaller as the Sn content increased. The chemical structure of ITO can be expressed in the form of $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-2x}$, with the value of x as obtained by EDS spectra increased with increasing Sn content. The crystal structure of the ITO nanomaterial as obtained from the XRD peaks is the same as that of In_2O_3 . The molecular bonds constituting the ITO are between In-O-In, Sn-O, and Sn-O-Sn. From the FTIR spectra of all samples, it was found that the peaks were located at the wavelength between $\sim 400\text{ cm}^{-1}$ sampai $\sim 700\text{ cm}^{-1}$. The response to CO gases showed a decreasing resistivity with increasing CO gas concentration, showing its potential for gas sensor application.

Acknowledgments

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