

Synthesis of Indium Oxide (In_2O_3) Nano Particles Using Sol Gel Method as Active Material on Gas Sensor

Slamet Widodo

*Research Center for Electronics and Telecommunications
Indonesian Institute of Sciences
PPET-LIPI, Kampus LIPI Jl. Sangkuriang Bandung 40135
Email : slametwido50@gmail.com, slametwi_dodo@yahoo.co.id*

Nanang Sudrajad

*Research Center for Electronics and Telecommunications
Indonesian Institute of Sciences
PPET-LIPI, Kampus LIPI Jl. Sangkuriang Bandung 40135
Telp. : (022) 2504660, 2504661; Fax : (022) 2504659*

Abstract

Synthesizing of indium oxide (In_2O_3) nano particles using sol-gel process as an active sensing material of gas sensor has been carried out. As starting material, indium acetate/ $\text{In}(\text{CH}_3\text{COO})_3$ was dissolved in diethylene glycol and heated up at 130°C until homogeneity is achieved. Nitric acid (HNO_3) was added under vigorous stirring where the resulting mixture was heated at 180°C for 5 hours. After drying at 400°C for 2 hours and annealing at 500°C for 1 hour, a yellow fine powder was obtained, which was identified by using XRD and SEM. From the observation it has been found that the materials are in nano size range.

Keywords: Active material, Indium Oxide (In_2O_3), nano particles, sol gel, gas sensor.

1. Introduction

The air can be said to have been contaminated, when the composition of the gases in it has exceeded the threshold concentration is acceptable.

To determine the air pollution that occurs, the necessary tools that can detect the gas concentration of a gas in the air which in this case is a gas sensor. So the gas sensor is a useful tool for detecting a quantity, in this case is the concentration of the gas and turn it into an electrical quantities that can be measured.¹⁻³. Sensors should basically have the advantage, among others, the cost is not expensive, the workmanship is simple and mobility characteristics to detect⁴⁻⁶. For the purpose of detecting this, several metal oxides have been studied and can be used as a gas sensor material is indium oxide (In_2O_3). Indium oxide as the active ingredient which is very sensitive to pollutant gases, one of which is NO_2 ⁷⁻⁸.

To increase the sensitive nature of the metal oxide, the metal oxide is made with nanometer size, thus increasing its surface area. One reliable method to synthesize nanometer-sized metal oxides is the sol-gel process.

2. Metal Oxide

The Metal oxide is an oxide compound with covalent character of the structure. A wide variety of metal oxides, such as tin dioxide, SnO_2 ⁹, tungsten trioxide (WO_3)¹⁰, zinc oxide, ZnO ¹¹, Indium Tin Oxide, ITO¹², indium oxide (In_2O_3)¹³, Ferric Oxide¹⁴, Titan Oxide¹⁵ and others. As a result of covalent structure, called a ceramic oxide material. In the form of thin layers (thin film) is a metal oxide transparent to light. Especially for zinc oxide and tin oxide, have semiconductive properties, so it can be applied to transparent conducting oxide (TCO) layer LCD, LED, electrichromic windows.

Usually the metal oxide structure is needed is shaped crystals (crystalline). The structure is repeated in a certain period and in three dimensions. To determine the quality of the material, can be used X-ray diffraktometer (XRD) and SEM.

3. Methods

3.1. Sol-Gel Process

The development of sol-gel process began in the 1880s. Various types of microfiltration membranes have been known so far, which is based on metal or carbon, but its application is limited to the size of the pores. The sol-gel process consists of several steps, among others: hydrolysis, condensation, gelation, ripening, drying, densification⁸.

Sol-gel process is a wet chemical technique (chemical solution deposition) for the manufacture of a material (especially metal oxide) starting from a chemical solution that is part of the sol, or colloidal particles (sol to nano-sized particles) to the creation of a piece of gel. Precursor or starting material in the manufacture of metal are metal alkoxides and metal chlorides, which then undergoes hydrolysis reaction and poly condensation reactions to form a colloid, which is a system that consists of solid particles (particle size between 1 nm to 1 μ m) dispersed in a solvent.

The starting material or precursor can also be stored on a substrate to form the film (such as through the dip-coating or spin-coating), which is then inserted into a suitable container with the desired shape for example to produce a monolithic ceramics, glass, fiber or fibers, membrane, air gel, or also for both granular powder synthesis micro and nano³.

Of the several stages of the sol-gel process, there are two general stages in the manufacture of metal oxide via sol-gel process, the hydrolysis and poly condensation. At this stage an attack hydrolysis of water molecules (nucleophilic attack), the oxygen atoms in the water, on the atom at the center of positive charge, which is generally in the form of metal⁵.

The sol-gel reaction mechanism can be seen in Figure 1 with an acid catalyst and Figure 2 with the base catalyst. The hydrolysis process can be catalyzed by an acid or base in order reaction rate becomes faster. Part sol or colloidal particles are formed subsequent to the hydrolysis reaction. Part of this sol is a colloidal substance in the solid phase dispersed in the water phase. Hydroxy groups will be formed in the precursors that undergo hydrolysis, both the catalyst and the acid-base catalyst. As an example of precursors used are silicone compounds.

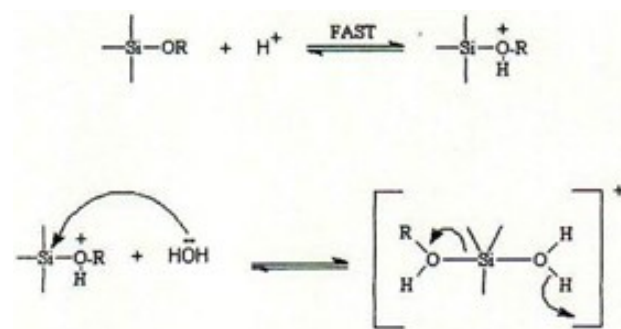


Figure 1: Mechanism of sol-gel reaction with acid catalysts

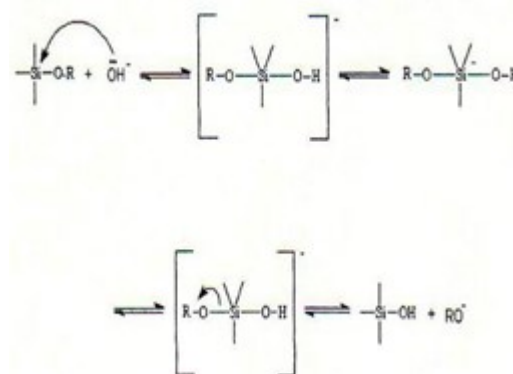


Figure 2: Mechanism of sol-gel reaction with base catalyst

Hydroxy group formed to carry out attacks on other precursors or reactants are known as a condensation reaction (Figure 3).

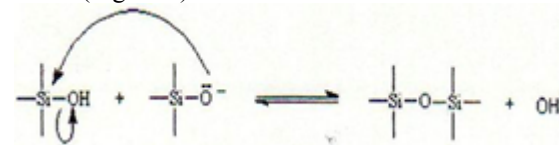


Figure 3: Mechanism of condensation reactions in the sol-gel

Increasing the viscosity of the solution indicates that the process of polymerization or condensation has occurred. By changing the charge on the surface of the particles (zeta potential) or an increase in the concentration of particles which are then followed by the agglomeration process, the gel will form part [8].

The sol-gel process is very lucrative and attractive for low cost and uses a low temperature so it is quite safe in the process, and can be easier to control in the determination of the chemical composition of the desired product.

4. Experimental Procedure

The tools used in the experiments are the means glasses, crucibles, electric heating (hot plate), oven and furnace. While the characteristics of the test equipment crystals or powder is scanning electron microscope (SEM) and X-ray Diffractometer (XRD).

The materials used consisted of Indium Acetate (Aldrich 99.99%), Diethylene Glycol (DEG), Nitric Acid (HNO_3), and demineralized water (de-ionized H_2O). The process of making Indium Oxide (In_2O_3) can be seen in Figure 4 (experimental flowchart). At first by weighing as much as 0.6695 grams Indium Acetate / In (CH_3COO)₃ dissolved in diethylene glycol (DEG). Then the mixture is heated at a temperature of 130°C to obtain a homogeneous solution. After it was added 2 ml of 3N Nitric Acid (HNO_3) into the solution and stirred rapidly. Results of stirring and then heated at 180°C during 5 hours. Fine grains Indium Oxide (In_2O_3) yellow obtained after drying at a temperature of 400°C for 2 hours and calcined at 500°C for 1 hour.

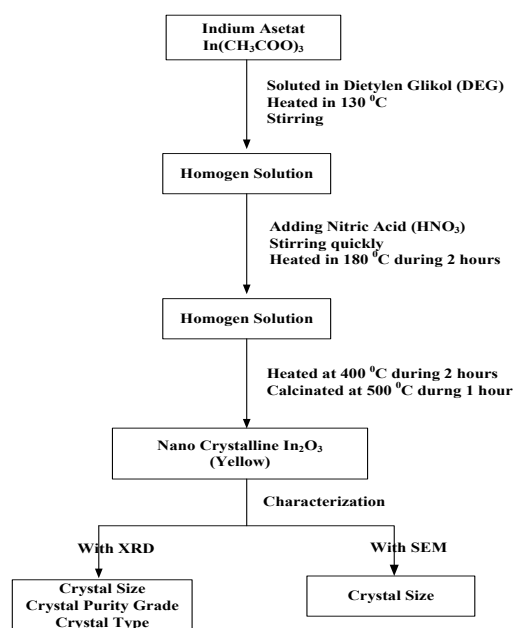


Figure 4: Flowchart of the experimental manufacture of In_2O_3

Material synthesis results in the form of powder or crystal form crystal structure characteristics tested, the degree of purity of crystal and crystal types have been characterized using X-ray diffraction (XRD), while the size of the crystal is characterized by using a scanning electron microscope (SEM).

5. Results and Discussion

5.1. Synthesis of Indium Oxide (In_2O_3)

Sol-gel process is one method that had been developed in the field to produce a nanometer-sized metal oxides with high purity level. The sol-gel process is often used to produce nanometer-sized metal oxides, coupled with sol-gel processing is fairly simple, fast, and does not require an expensive cost.

Nanometer-sized In_2O_3 powders were synthesized by using a sol-gel process, as a precursor in the synthesis of In_2O_3 powder used Indium Acetate / In (CH_3COO)₃, and Diethylene Glycol (DEG) as solvent. These two ingredients are then mixed and the result thereof is heated at 130°C . During heating, stirring until dissolved acetate obtained indium perfect. It aims to increase the solubility of indium acetate Diethylene Glycol in the solvent because the solubility of indium acetate Diethylene Glycol in the small, so that the necessary heating and stirring to increase its solubility. After that, add Nitric Acid (HNO_3) 3N, into the resulting mixture and heated at a temperature of 180°C and then stirred rapidly for 5 hours. This stage is the beginning of hydrolysis and polymerization with nitric acid and the acid acts as a catalyst to produce a colloidal system called Sol.

After heating and stirring for 5 hours, the results obtained colloid dried using an oven at 400°C for 2 hours. This stage is the stage of drying to remove most of the solvent and the acid catalyst and polymerization process occurs simultaneously advanced from Colloidal Sol system and then generating system called Xerogel Colloidal Gels. After drying for 2 hours, then made the final stage, the stage calcination at 500°C for 1 hour. Phase Calcination is a thermal treatment process using. In the calcination process occurs several reactions, namely the Thermal Decomposition of the resulting compound In_2O_3 , the phase transition from a liquid to a solid and removal of volatile fractions or remaining solvent and other compounds produced by side reactions, such as gas Carbon Dioxide and Acetic Acid, CH_3COOH .

During the synthesis of In_2O_3 , the results obtained mixture changes color from white to light brown result of hydrolysis and polymerization, and subsequent color changes to yellow from the calcination process and the yield of crystalline In_2O_3 obtained as 0.5145 g with a yield of 76.8 %.

To characterize the resulting powder In_2O_3 , used X-ray diffractometer tool (XRD) to determine the crystal structure, crystal purity levels and types of crystals are generated and then compared against the standard. In addition to using XRD, also the tool used electron microscopy (SEM) to determine the crystal morphology of the particles, such as crystal size and uniformity of the crystal In_2O_3 .

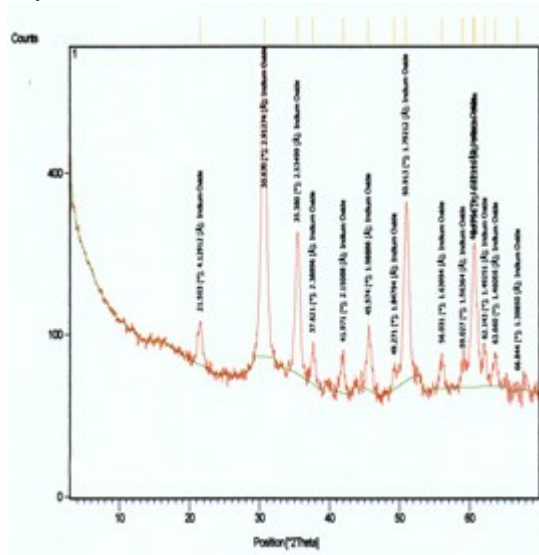


Figure 5: Results of powder XRD In_2O_3

Figure 5 shows the results of XRD characterization of In_2O_3 powder. Through comparison of the pattern of In_2O_3 peak synthesis results with standard peak pattern that indicates a considerable similarity, as shown in Figure 6, it can be believed that the resulting powder is powder In_2O_3 which have a cubic crystal structure with a peak value of 2 θ similarity of 71.

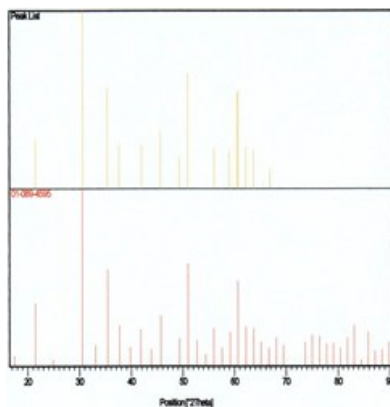


Figure 6: Plot comparison between standard In_2O_3 (above) with the synthesis of In_2O_3 (below)

Value peak from the XRD patterns for powder Indium Oxide synthesis results can be seen in Table-1 below.

Table-1: The peak value of the results of the XRD patterns for the synthesis of In_2O_3 powder

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	Value-d [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
21,5033	49,69	0,4896	4,12912	7,63	0,5875	01-089-4595
30,6696	651,33	0,6528	2,91274	100,00	0,7834	01-089-4595
35,3800	208,27	0,2448	2,53499	31,98	0,2938	01-089-4595
37,6213	40,46	0,3264	2,38896	6,21	0,3917	01-089-4595
41,9711	39,19	0,6528	2,15088	6,02	0,7834	01-089-4595
45,5741	67,52	0,3264	1,98886	10,37	0,3917	01-089-4595
49,2708	20,30	0,4896	1,84794	3,12	0,5875	01-089-4595
50,9129	270,35	0,5304	1,79212	41,51	0,6365	01-089-4595
56,0311	33,54	0,6528	1,63994	5,15	0,7834	01-089-4595
59,0274	27,26	0,6528	1,56364	4,19	0,7834	01-089-4595
60,4962	186,05	0,2448	1,52914	28,56	0,2938	01-089-4595
60,7576	194,73	0,2448	1,52319	29,90	0,2938	01-089-4595
62,1431	35,87	0,4896	1,49251	5,51	0,5875	01-089-4595
63,6597	30,37	0,4080	1,46056	4,66	0,4896	01-089-4595
66,8443	7,60	0,2448	1,39850	1,17	0,2938	01-089-4595

5.2. Characterization using SEM

Figure 7 is the result characterization using SEM showing the morphology of the structure of In_2O_3 powder. The results of SEM mapping, with 20.000x magnification, indicating that the In_2O_3 powder obtained has a particle size reaches the nanometer scale, which is about 100 nm, and are homogeneous or uniform.

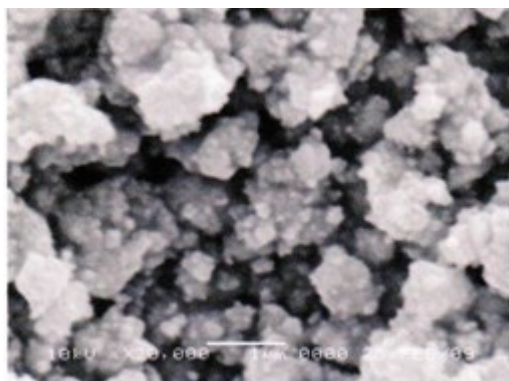


Figure 7: SEM Results for In₂O₃ powder with magnification (b) 20.000x.

6. Conclusions

Powder Indium Oxide (In₂O₃) can be synthesized by Sol-Gel process using Indium Acetate materials / In (CH₃COO)₃, Diethylene Glycol (DEG) and Nitric Acid (HNO₃) and de-ionized water. Indium oxide powder obtained by Sol-Gel has reached the scale of size approaching 100 nanometers with peak 2θ similarity value of 71. Results of the synthesis of indium oxide powder is ready for use as an ingredient / active layers of gas sensors. With the results of the nano scale grains become larger surface area that would be more sensitive gas sensors.

7. References

1. B.M.C. Carotta, S. Galliera, A. Giberti, C. Malagu, *Sensors and Actuators*, B 100, pp. (2004) 277-282..
2. S.D. Han, S.Y. Huang, M.C.R. Shastry, Portier, *Active and Passive Elec. Comp.*, 1 (1995), 39-51.
3. L.L. Hench, and J.K. West, *The Sol-Gel Process Chem.*, 90 (1990), pp. 33-72.
4. J. Hildenbrand, *Simulation and Characterisation of a Micromachined Gas Sensor and Preparation for Model Order Reduction*, Diploma Thesis, Albert Ludwig University Freiburg Germany, 2003.
5. R.K. Iler, *The Chemistry of Silica*, John Wiley & Sons Inc., New York, (1979).
6. Jones, J. Alan, *Sensor Technology, Part One-Materials and Devices*, Departement of Industry, Technology and Commerce, Australia (1990).
7. J. Koplin Tobias, Maik Siemons, Cesar Ocen Valentine, *Sensors*, 6, (2006) 298-307.
8. M. Mulder, *Basic Principles of Membrane Technology*, Springer, New York (1996).
9. S. Widodo, "Studi Sintesis Timah Oksida (SnO₂) Nano Partikel Dengan Metode Sol Gel Sebagai Bahan Aktif Pada Sensor Gas", Prosiding Seminar Nasional Tjipto Utomo, ITENAS Bandung, (2012).
10. Kil Dong Lee, *Journal of the Korean Physical Society*, 38, (2001), 33-37.
11. S. Shishiyana, L. Chowb, O. Lupana, and T. Shishiyana, *ECS Transactions*, 9 (2006), 65-71.
12. Sung – Jei Hong and Jeong-In Han, *Journal of the Korean Physical Society*, 45, (2004), 634-637.
13. J.F.Q. Rey, T.S. Plivelic, R.A. Rocha, S.K. Tadokoro, I. Torriani and E.N.S. Muccillo, *Journal of Nanoparticle Research* 7 (2005) 203–208.
14. S. F. Hasany, I. Ahmed, J. Rajan, Rehman, *Nanoscience and Nanotechnology* 6 (2012), 148-158
15. Mahtab Gholami et al., *Chem. Phys. Letter* 48 (2012) 9626-9628.