Australian Journal of Basic and Applied Sciences, 7(4): 31-34, 2013
ISSN 1991-8178

Liquid Phase Synthesis of indium tin oxide (ITO) nanoparticles using In(III) and Sn(IV) salts

Majid Farahmandjou

Department of physics, Varamin Pishva Branch, Islamic Azad University, Varamin, Iran

Abstract: Indium tin oxide (ITO) nanoparticles are prepared by two hydrothermal and liquid-phase co-precipitation methods under given conditions with solution of indium chloride (InCl3·4H2O), tin chloride (SnCl4·5H2O) in ethylenedyamine solution. The samples were characterized by XRD and SEM analysis after heat treatments. The SEM results showed that, the size of ITO particles prepared by ethylendiamide co-precipitation are increased from 35 nm to 120 nm. The XRD results revealed that the size and crystallity of the ITO particles is increased by hydrothermal method. The XRD results indicated that the intensity ratio of I_{400}/I_{222} has a decrease of 21.67% by hydrothermal method.

Key words: ITO nanoparticles, Liquid phase, Crystallity, Hydrothermal method PACS: 73.63.Bd, 78.67.Bf, 78.67.Sc

INTRODUCTION

Indium oxide is a wide band gap material (3.3 eV), which can have a high optical transparency in the visible wavelength range and a high conductivity due to the oxygen vacancies, acting as donor states (Babu, P.M., *et al*, 2004). To increase the conductivity up to the metallic conductivity (10^3-10^4 $\Omega^{-1}cm^{-1}$), a solid solution of indium-thin oxide (ITO) with a few percent of tin is used. Indium tin oxide, a kind of n-type semiconductor material, has a wide forbidden band. ITO thin films have high transparency in the visible light region and lower electric resistivity (Cheng, G., *et al*., 2006; Adurodija, F.O., *et al*., 2006). It has been used as electrodes in manufacturing of solar cells, flat panel displays, and gas sensors. The tradition deposition techniques of ITO film are DC sputtering, RF sputtering, or electron beam evaporation. It is the first step to fabricate indium and tin alloy target or ITO ceramic target. Afterwards the target is sputtered to glass substrate by the controlled electron beam. These techniques need costly equipments, and the utilization rate of the target materials is low (Wang, S.L. and D.L. Xia, 2006). Because indium is a rare metal, it is necessary to explore a new route to deposit ITO thin film with high-Indium utilization rate. The synthesis nanoparticles of metal oxide from aqueous solutions and deposition thin films at low temperatures are an important way for preparation of transparent conductive film (Niesen, T.P. and M.R. De Guire, 2001). Dip-coating or spray deposition of light transparent, good conductive and low-membrane resistant ITO film has been studied by the researchers (Betz, U., *et al*., 2006; Ogi, T., *et al*., 2006; Chang, W., *et al*., 2008). The fabrication of ITO nanoparticle is important in emulsion preparation for spray deposition or dip-coating ITO film. The ITO thin film's quality is related to the size and morphology of the nanoparticles.

With the development of nanometer material research, several kinds of preparation methods for nanosized ITO emerged. The current methods for nanometer indium tin oxide preparation mainly include solid-phase method, liquid-phase method, and gas-phase method (Zhang, Y., *et al*., 2004; Soulantica, K., *et al*., 2003; Kim, H.S., *et al*., 2008). The liquid-phase method, with the advantages of simple operation and controllable granularity, can realize the atomic scale level of mixing. The doping of components achieves easily, and the nanoscale powder material has high-surface activity. The liquid-phase methods include liquid phase precipitation, hydrothermal (high temperature hydrolysis), Sol-gel (colloidal chemistry), radiation chemical synthesis (Arfsten, N.J., 1984; Xu, J.J., 1988; Yamamoto, O., *et al*., 1992; Bisht, H., *et al*., 1999; Toki, M. and M. Aizawa, 1997).

In this paper, the ITO nanoparticles are first fabricated by two hydrothermal and liquid-phase co-precipitation methods with composition solution of $InCl_3{\cdot}4H_2O$ and $SnCl_4{\cdot}5H_2O$ and ammonia precipitant. Then, the structural characterization of ITO nanoparticles is studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD). The effect of ethylenediamine and ammonia precipitant on the size of ITO nanoparticles is studied. Finally, the penetration of Sn atoms into the indium oxide by both liquid-phase co-precipitation and hydrothermal methods has been investigated.

Experiment Method:

The synthesis of ITO nanoparticles was carried out by two methods: liquid phase co-precipitation and hydrothermal. In liquid phase co-precipitation a certain quality of indium chloride ($InCl_3{\cdot}4H_2O$ 99%, Aldrich) and tin chloride ($SnCl_4{\cdot}5H_2O$ 99%, Aldrich) was dissolved in pure de-ionized water or ethanol, keeping the ratio

Corresponding Author: Majid Farahmandjou, Department of physics, Varamin Pishva Branch, Islamic Azad University, Varamin, Iran
E-mail: farahmandjou@iauvaramin.ac.ir

of In_2O_3: SnO_2 = 9: 1. Certain concentrations (5.00%) of ammonia solutions were made by mixing certain amount of ammonia ($NH_3 \cdot H_2O$, 25%) with pure water. The prepared $InCl_3$ solution (0.3mol/L) was transferred into fixed three-neck flask, keeping in 40°C to 50°C temperatures under electromagnetic agitation. The ammonia solution was added to the flask, controlling the stirring speed and testing the pH value till the required pH value was added as dispersant. The precipitate precursor of ITO was aged a certain time and washed with de-ionized water and absolute alcohol for three times, respectively. After washing, the precipitates were dried at 120°C for 1 hour. The dried samples were calcinated at 600°C for 1 hour to get the indium tin oxide nanopowder. In this approach, tin hydroxide was first precipitated at PH=1.5 and then indium hydroxide formed at PH=3.5.

ITO nanoparticles were also synthesized by hydrothermal method as follows. In this method, the acidity of indium ($InCl_3 \cdot 4H_2O$) and tin chloride ($SnCl_4 \cdot 5H_2O$) were first controlled by ammonia and then hexamethylenetetramine was added to the solution as precipitant agent. The reaction was transferred into fixed three-neck flask, keeping in 110°C temperatures under electromagnetic agitation for 6 hours and then the solution was filtered and calcinated. The product was finally annealed at 500°C for 2 hours to achieve the indium tin oxide nanoparticles.

The morphology and structure of the prepared nanoparticles were characterized by means of a SEM and XRD. The microstructure of the ITO samples was analyzed by a KYKY-Ammray 2800 type SEM with 200 kV acceleration voltages. To determine the nanoparticles' structure, the XRD measurement of nanopowder were performed using a Seifert with Cu-Kα radiation (wavelength = 1.54 A°).

RESULTS AND DISCUSSION

Figures 1 show the SEM images of the ITO nanoparticles prepared by two co-precipitation and hydrothermal methods. Figure 1(*a)* indicates the ITO naoparticles prepared by co-precipitation method with ethylendyamide solution. Figure 1(*b)* show the ITO naoparticles prepared by hydrothermal method. As you can see, the size of ITO prepared by co-precipitation method is about 35-120 nm whereas; the size of ITO nanocrystals prepared by hydrothermal method is more than 100 nm. In fact, high temperature and pressure lead to increase the size and quality of the crystalline ITO nanoparticles in hydrothermal method. Also, ITO particles are rapidly precipitated by increasing reaction temperature and the size and uniformity of the crystals are increased in hydrothermal method as you can see in figure 1(b).

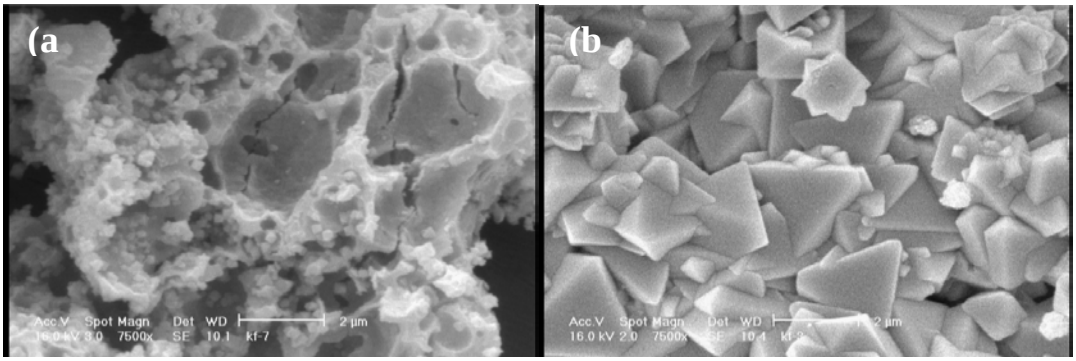

Fig. 1: SEM images of ITO prepared by (a) co-precipitation and (b) hydrothermal method.

In Table 1, the lattice parameters according to XRD patterns are listed, including the size of nanocrystals, D(nm), atomic planar distance d_{222} (Å), the intensity of diffraction peak, I_{222}, and the intensity ratio I_{400}/I_{222}. In 1998, Quaas and co-workers reported that if tin oxide penetrates into the indium oxide by 5%, the atomic planar distance will decrease, and for penetration more than 5%, the atomic planar distance will increase (Quaas, M., *et al*., 1998) Compared to the atomic planar distance for the In_2O_3 sample d_{222} = 2.92 (Å), it is realized that the penetration of Sn atoms into indium oxide is more than 5% for ITO prepared by both co-precipitation with ethylenediamine and hydrothermal methods with atomic planar distance d_{222} = 2.917 (Å) and d_{222} = 2.923 (Å), respectively. Also in comparison of the I_{400}/I_{222}, it is found that the ratio I_{400}/I_{222} for ITO particles prepared by coprecipitation and hydrothermal methods is less than 29.3%. The results show that the crystallite ITO particles have more growth in ⟨400⟩ preferential orientation. In fact, the ITO crystal growth is increased at the preferential orientation with more atoms at higher temperatures. Therefore, the penetration of Sn atoms into the indium oxide prepared by h approach is more than the ITO prepared by the co-precipitation method.

Table 1: The data of lattice parameters for In_2O_3 and ITO nanoparticles

sample name*	Preparation Method	D(nm)	d_{222}(Å)	I_{222}	I_{400}/I_{222}
In_2O_3	Actual value	---	2.921	----	29.3
ITO	Hydrothermal	>100	2.923	8653.51	21.67
ITO	Etylendyamide	46.5	2.917	8747.53	29.07

* D=crystallite size, d222 =atomic planar distance of 222

Figures 2 shows the XRD pattern of SnO_2 and ITO nanoparticles are calcinated for 1 hour at 600 ^oC. The large wide of the picks for SnO_2 pattern indicate that these particles have the amorphous structure (Fig. 2*a*), while the ITO prepared by hydrothermal method (Fig. 2*b*) and ITO prepared by co-precipitate method (Fig. 2*c*) are crystalized after the annealing process. The sharp picks indicate the body centered cubic structure after heat treatment. The XRD results also indicate that the intensity of I_{400}/I_{222} is increased to 29.07 percent by the co-precipitation method with ethylendyamine.

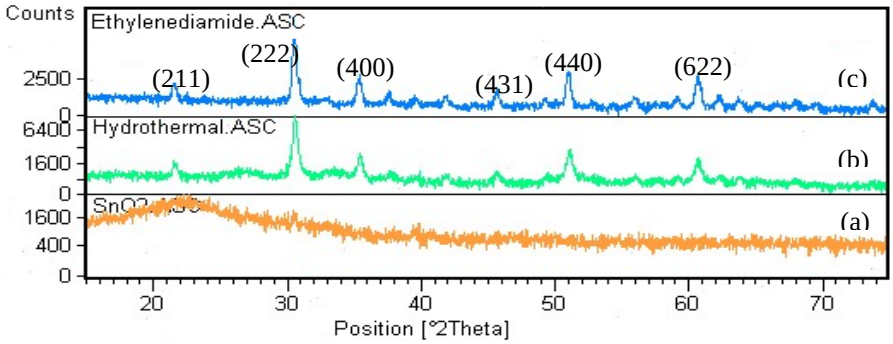

Fig. 2: X-ray diffraction pattern of (a) SnO_2 (b) ITO prepared by hydrothermal and (c) ITO prepared by co-precipitation method with ethylendyamide precipitant.

Conclusion:

In conclusion, indium tin oxide (ITO) nanoparticles have been successfully synthesized by liquid phase co-precipitation and hydrothermal method under given conditions with reactants of indium chloride, tin chloride in the presence of ethylenediamine precipitant. The results indicate that the size of ITO prepared by co-precipitation method is about 46.5 nm in the presence of ethylenediamine precipitant while the size of ITO nanocrystals prepared by hydrothermal method is more than 100 nm, because of increased reaction temperature. The XRD results indicated that the ITO particles are finely crystallized body centered cubic structure. The penetration of Sn atoms into indium oxide is more than 5% for the ITO prepared by both co-precipitation and hydrothermal method. The atomic planar distance is d_{222}=2.923 (Å) for hydrothermal and 2.917 (Å) for co-precipitation synthesis. Finally, the preferential growth and orientation of the ITO prepared by the hydrothermal method is the <400> orientation.

ACKNOWLEDGMENTS

The author acknowledges the financial support of Karaj for material and the energy research center for analysis and the discussions on the results.

REFERENCES

Babu, P.M., B. Radhakhrishna, G. Venkata, P.S. Reddy and S. Uthanna, 2004. Bias voltage dependence properties of dc reactive magnetron sputtered indium oxide films. Journal of Optoelectronic and Advanced Material, 6(1): 205-210

Cheng, G., E. Stern, S. Guthrie, M.A., R. Klie, Y. Hao, G. Meng and L Zhang, 2006. Indium Oxide Nanostructures. Appllied Physics A, 85(3): 233-240.

Adurodija, F.O., L. Semple and R. Br¨uning, 2006. Crystallization process and electro-optical properties of In_2O_3 and ITO thin films. Journal of Material Science, 41(2): 7096-7102.

Wang, S.L. and D.L. Xia, 2006. Fabrication techniques and development of ITO film. GLASS & ENAMEL. 32(5): 51-54.

Niesen, T.P. and M.R. De Guire, 2001. Review: deposition of ceramic thin films at low temperatures from aqueous solution. Journal of Electroceramics, 6(3): 169-207.

Betz, U., M. Kharrazi Olsson, J. Marthy, M. F. Escol´a, and F. Atamny, 2006. Thin films engineering of indium tin oxide: large area flat panel displays application. Surface and Coatings Technology, 200(20-21): 5751-5759.

Ogi, T., F. Iskandar, Y. Itoh, and K. Okuyama, 2006. Characterization of dip-coated ITO films derived from nanoparticles synthesized by low-pressure spray pyrolysis. Journal of Nanoparticle Research, 8(3): 343-350.

Chang, W., S. Lee, C. Yang, and T. Lin, 2008. Opto-electronic properties of chromium doped indium-tin-oxide films deposited at room temperature. Materials Science and Engineering B, 153(1–3): 57-61.

Zhang, Y., H. Ago, J. Liu, M. Yumura, K. Uchida S. Ohshima and S. Iijima, 2004. The synthesis of In, In2O3 nanowires and In2O3 nanoparticles with shape-controlled. Journal of Crystal Growth, 264(1-3): 363-368.

Soulantica, K., L. Erades, M. Sauvan, F. Senocq, A. Maisonnat, and B. Chaudret, 2003. Synthesis of indium and indium oxide nanoparticles from indium cyclopentadienyl precursor and their application for gas sensing. *Advanced Functional Materials*. 13(7): 553-557.

Kim, H.S., P. D. Byrne, A. Facchetti, and T. J. Marks, 2008. High performance solution-processed indium oxide thinfilm transistors. *Journal of the American Chemical Society*, 130(38): 12580-12581.

Arfsten, N.J., 1984. *Sol*-gel derived transparent IR-reflecting ITO semiconductor coatings and future applications. Journal of Non-Crystalline Solids., 63: 243-249.

Xu, J.J., A.S. Shaikh and R.W. Vest, 1988. Indium tin oxide films from metallo-organic precursors. Thin Solid Films., 161: 273-280.

Yamamoto, O., T. Sasamoto and M. Inagaki, 1992. Indium tin oxide thin films prepared by thermal decomposition of ethylene glycol solution. Journal of Material Science, 7(9): 2488-2491.

Bisht, H., H. Eun., A. Mehrtens and M.A. Aegerter, 1999. Comparison of spray pyrolyzed FTO, ATO and ITO coatings for flat and bent glass substrates. Thin Sold Films, 351(1-2): 109-114.

Toki, M. and M. Aizawa, 1997. *Sol-gel* formation of ITO thin Film from a Sol Including ITO Powder. Journal of *Sol-Gel Science* and *Technology*, 8: 717-720.

Quaas, M., C. Eggs and H. Wulff, 1998. Structural studies of ITO thin films with the Rietveld method. Thin Solid Films, 332(1-2): 277-281.