Comparative study on synthesis of Indium Tin Oxide nanoparticles

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Abstract- In recent years indium tin oxide (ITO) coating has been widely used in touch screens, LCD and plasma display, etc. ITO thin films are main precursors over suitable substrates for making such devices. ITO is n-type semi conducting material which is transparent in visible light. Various preparation methods of ITO are compared on the basis of size of nanoparticles obtained and the cost effectiveness. The conductive properties of ITO depend on its preparation method. Generally, ITO can be prepared by solid phase method, liquid phase method and gas phase method. The solid-phase and three liquid phase methods using different reactants and techniques for preparation of ITO have been reviewed. It is observed that liquid phase method is simple in preparation and give particle of better conductivity and good crystalline structure that would be required for thin film fabrication.

Keywords: Indium Tin Oxide, nanopaticles, liquid phase method, solid phase method

I. INTRODUCTION

ITO is a n-type transparent conducting oxide (TCO) which is widely used in the manufacture of transparent electrode, photo electronic devices, photo sensors, LCD display, solar cells, etc. It has a wide band gap of 3.3eV - 4.3eV [1]. ITO has many applications in optical and electronic devices owing to its high conductivity and high optical transparency in visible region. It also reflects infrared radiation and therefore sometimes it is used as heat mirrors to reduce energy consumption. Most of the times ITO is used as thin films and various techniques of thin film formation are used according to the required application [2-4]. Sometimes it is also used as particles added in small amount in polymer to increase its electrical conductivity.ITO nanoparticles influence the formation of thin films, thus it is very important to study the characteristics of ITO particle as their size and shape vary with its technique of synthesis. In recent years, ITO nanoparticles synthesized are of controlled size and shape so that these can be used in various devices. Most of the times particle are bixbyite structure of cubic unit cell and sometimes corundum structure of rhombohedral or hexagonal unit cell. Normally ITO nanoparticles are made in ratio of 9:1 for tin to indium metal oxides. This is done because increase in the doping ratio increases the band gap thus decreasing the resistivity [5].

In this paper , various methods of preparation of ITO have been reviewed viz. solid phase method with microwave heating and conventional heating, liquid phase co-precipitation method, liquid precipitation method without chlorine contamination, hydrothermal method, urea based hydrothermal method and sol gel method.

Description

ITO nanoparticles are generally prepared by three methods namely solid phase, liquid phase and gas phase methods.

1. Solid phase method

In solid phase method [6-7], the effect of temperature and mode of heating on conductivity have been discussed . In this method, indium oxide and tin oxide powder are used to synthesize ITO , using microwave heating and conventional heating. High purity indium oxide and tin oxide with mass median diameter of 9.0 µm and 0.12 µm were used as precursors in ratio of 10:1. A mixture of In_2O_3 and SnO_2 was mixed in a pot rotator and then set into a glass tube to remove intercellular space as the packing fraction influences the conductivity of ITO nanopowder. Then it was heated in a microwave heating equipment**.** Microwave at 2.45 GHz was generated at 750 watts through magnetron, to irradiate and heat the cylindrical powder layer in silica glass plate. A thermocouple was used to measure the temperature at the centre of the powder which was considered as reaction temperature and was maintained by controller. The electrical conductivity of ITO was measured to evaluate the reaction progress. The electrical conductivity was measured from electrical resistance. The reaction time for microwave heating was about 20 min. Same Packing fraction was used in heating with electrical furnace. The reaction time required by conventional heating was about 15 hours. ITO was prepared at 800℃ and 1200℃ through microwave and conventional heating respectively and the conductivity was compared.

It was observed that at higher temperature, the conductivity obtained was higher than at lower

temperature. The packing fraction also contributed to the conductivity. As the packing fraction increases the electrical conductivity reduces.

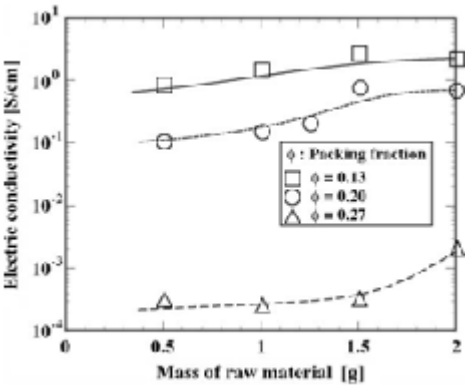

Fig.1 Electric conductivity of the product powder layer obtained by using the microwave heating as a function of the mass of raw material for various packing fractions [5]

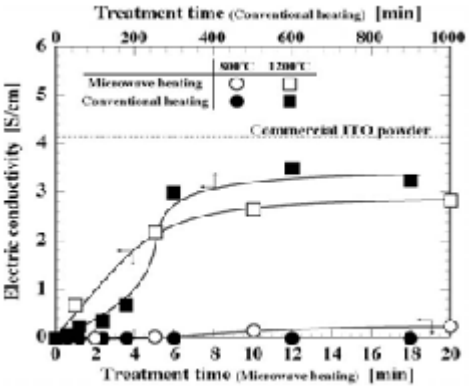

Fig.2 Change in electric conductivity of the product powder layer with treatment time for microwave and the conventional heating methods [5]

The comparison of conductivity is depicted in plots given above. The amount of ITO produced was less in microwave heating than in conventional heating.

This method is not so efficient because it gives large size nanoparticles which do not give a homogeneous film, also it requires large reaction time and temperature which eventually increase the heating cost of the nanopowder.

2. Liquid Phase method: In liquid phase method we have reviewed liquid co-precipitation method, hydrothermal method and sol-gel hybrid method.

2.1 Liquid co-precipitation method [8-10]

In this method indium chloride and tin chloride are used as precursor for synthesis of ITO. This method is simple in operation and the granules obtained are of good quality. $InCl_3 .4H_2O$ and $SnCl_4.5H_2O$ are dissolved in ethanol or deionised water in the ratio of 9:1. This solution is transferred into a three-neck flask, maintained at 40℃-50℃ under electromagnetic agitation. 5% ammonia solution was prepared and added to this mixture with continuous and controlled stirring as dispersant. The pH was checked in between to control acidity. Ethylene diamine solution was added as precipitant. The precipitate obtained was aged for a certain time, and then it was washed with deionised water and absolute alcohol three times. After washing, the precipitate was dried at 120℃ for 1 hour. Then it was calcinated at 600℃ for 1 hour to get ITO nanopowder. The sample obtained was characterized by XRD and SEM [7-9]. The nanoparticles obtained were in the range of 35nm-120nm.

In this method, it was found that the crystal size was about 46.6 nm in the presence of ethylene diamine precipitant. Sharp peaks observed in XRD shows the body centred crystal structure. This method is simple in operation but it requires calcinations which lead to agglomeration of particles thus the homogeneity is difficult to control.

II METHODS

2.2 Hydrothermal method [8-10]

In this method, $InCl_3.4H_2O$ and $SnCl_4.5H_2O$ are dissolved in ethanol or deionised water in ratio of 9:1. This solution is transferred into a three-neck flask, maintained at 110℃ under electromagnetic agitation for 6 hours. 5% ammonia solution was prepared and added to this mixture with continuous and controlled stirring as dispersant. The pH was checked in between to control acidity by adding ammonia. Hexamethylenetetramine was used as precipitating agent. The precipitate was filtered and calcined, then the product was annealed at 500℃ for 2 hours. Crystal size obtained was more than 100 nm. SEM and XRD analyses were done to characterize the product.

High temperature and pressure increase the size and quality of crystals. The particles obtained were uniform in size.

2.2.1 Hydrothermal method without chlorine contamination [11]

ITO nanoparticles were synthesised by novel hydrothermal method from stable indium tin acetyl acetone complex. Metal indium(5N purity) was dissolved in Con. HNO_3 and metal tin was dissolved in 8mol/lit HNO_3 in ice water bath. Then these solutions were mixed and a calculated amount of acetyl acetone (acac) was added such that molar ratio was (acac):[In +Sn] =2:1. Then, 25% ammonia was added drop wise to maintain pH ~7. The solution was transferred to a teflon coated stainless steel furnace where it was kept at 200℃ for 10 hours. The black particles obtained were washed with distilled water and absolute alcohol three times. Then, a yellow coloured ITO was obtained after heat treatment at 600℃ for 3 hours in muffle furnace. This method provided the product of homogeneous nucleation. The calcination step was eliminated which decreases the degree of aggregation. While in conventional hydrothermal methods, where chlorides

were used give impure ITO nanoparticles. As chloride ion in oxides forms high agglomerates and are difficult to remove from colloids even after 10 times washing. It was observed that with the increase in atomic % of tin, the size of ITO nanoparticles decrease. In this method, the size of ITO nanoparticles obtained was about 15 nm. This method has avoided chlorine contamination which gives various advantages like improved product quality, decrease the particle agglomeration and increase the particle sinterability with reduced washing time.

2.2.2 Urea based hydrothermal synthesis of ITO [12]

Two methods are designed for synthesis of ITO nanopowder by using urea as mineraliser. In the first method, precipitates of Indium and tin hydroxide (Sn:In=8:92) were obtained from aqueous solution of indium and tin salts where ammonia is added gradually to maintain the pH value~9. This solution is then washed with distilled water to remove anionic species and chlorine. The precipitates are then mixed with distilled water along with 10 wt% urea. This mixture was then stirred for 2 hours at room temperature and the solution is shifted in Teflon lined vessel. This suspension is then hydrothermally treated at 250℃ for 48 hours; product powder obtained is centrifuged, washed and then calcined at 600℃ for 1 hour which resulted in fine ITO nanopowder. Second method of urea based hydrothermal directly uses metal salt solution with urea in which the pH was maintained at 1.5 by adding ammonia. This was then hydrothermally treated at 240℃ for 48 hours. Then the solution was centrifuged, washed and calcined at 600℃ for 1 hour. A mixture of rhombohedral and cubic forms of ITO was obtained. This study revealed that the presence of urea suppressed the conversion of rhombohedral to cubic ITO. Spherical particles with size ranging 30-60 nm are obtained from first method and these are weakly aggregated. From second method rod like structures are obtained. These methods have revealed the results that urea can be used to control the morphology as well as crystal form of ITO powders.

2.3 Sol-gel combustion hybrid method [13-14]:

In sol gel method, aqueous solutions of indium nitrate and tin chloride were dissolved in deionised water. The quantity of metal ions was adjusted in such a ratio to get a final oxide composition of In_2O_3/SnO_2 = 9:1(by weight). Acetylene black was added to indium tin solution with drop by drop addition of ammonia solution under constant stirring at ambient condition. The bath temperature was maintained at 30℃; the sol obtained was then heated to 120℃ for 120 min to get dried sol. The dried sol was transformed into gel and then was ignited at 650℃ in air. An auto combustion process took place and the burnt product obtained was calcined at 750℃ for 30 min to get ITO nano powder.[13]

The size of the nanoparticle obtained was 16nm-33nm. The method involved low temperature self propagating ignition process which is safe, simple and rapid. The product formed by this method is fine and homogeneous.

2.3.1 Preparation of Highly Crystalline Sol-Gel Derived Nano-Sized ITO Powders by Supercritical Carbon Dioxide Drying [14]

Supercritical carbon dioxide drying replaced the conventional heat treatment in sol-gel process to produce xerogel precursors. By this method, highly crystalline sol-gel nano-sized powder of indium tin oxide was directly produced by supercritical carbon dioxide drying without calcination. Gas anti-solvent process (GAS) was used for preparing ultrafine ITO nanopowder by supercritical drying.

In this method, Indium nitrate tri-hydrate ($In(NO_3).3H_2O$, purity, 99.99%) and anhydrous tin chloride ($SnCl_4$ purity, 99.99%) were dissolved in methanol and clear solution was made by continuous mixing at 0℃. The solubility of solvent in supercritical carbon dioxide was increased by using ethanol instead of methanol; this also increased the drying efficiency through solvent exchange by reduced pressure distillation. This method provided with ITO precursor solution. Carbon dioxide (CO_2) was used as the anti-solvent for removal of solvent from the sol-gel derived precursors. The ITO precursor solution was kept in the drying chamber in a glass container. The chamber was then tightly sealed, when supercritical condition was achieved i.e. temperature & pressure of CO_2 exceeds its critical point 31 &1070.4 psi) CO_2 was supplied through gas chamber to remove the solvents from it. Finally after proper heat treatment, product was characterized by XRD and TEM.

III CONCLUSION

From all the above methods, it was found that the solid phase method was quite simple but had a very large reaction time, very high temperature and gave product of large size which is not suitable for producing thin films. The liquid co-precipitation method was simple in operation and gave granules of good quality but homogeneity was difficult to control. Hydrothermal method also gave good crystal quality but size of particles is large. Hydrothermal method without chlorine contamination gave homogeneous nucleation. The calcinations step which decrease the degree of aggregation was eliminated . The urea based hydrothermal method gave a mixture of rhombohedral and cubic forms of ITO. This study revealed that the the presence of urea suppressed the conversion of rhombohedral to cubic form of ITO. This gives an idea that urea can be used to control the morphology as well as crystal form of ITO powders. In hybrid sol-gel method the size of nanoparticle obtained was very small. The method involved low temperature self propagating ignition process which is safe simple and rapid. The product formed by this method is fine and homogeneous. In CO_2 drying sol-gel method, the supercritical CO_2 drying not only can be incorporated into the sol-gel process to replace conventional drying heat treatment but also has the potential to produce

highly-crystalline and conductive ITO powders by completely avoiding both conventional drying and calcination heat treatments. The mechanism and the precise conditions for the formation of these black conductive well-crystallines ITO powders are currently being investigated. But this involves large production cost.

Mainly liquid co-precipitation method is used for producing ITO widely because of simple operation as well as cost effectiveness.

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