

Effects of solution concentration and pH value on the density of flower shaped nanoparticles of In_2O_3

Rajendra Kumar Sharma¹, Moti Ram^{2*}, Vaibhav Jain³

^{1,2}Department of Physics, Shri Venkateshwara University, Gajraula, U. P., India.

³Department of Physics, DAV (PG) College, Bulandshahr, U. P., India.

*Corresponding author, E-mail address: motiram05@yahoo.co.in

Abstract: Indium oxide nanoparticles were prepared by solution process method. It was observed that for fix formation temperature and constant value of pH, density of nanoparticles increases with concentration of solution. The variation of pH value at constant value of temperature and solution concentration indicates that the pH value of the solution strongly affects the obtained surface. For low pH values, spherical assemblies were not observed, but nano films were obtained on the sample. With increasing pH value, setups formed by self-assembly of In_2O_3 platelets are more frequently found. Finally, surface of the obtained nanoparticles was influenced by the solution concentration and pH value.

Keywords: Indium oxide, Solution process method, pH value.

1. Introduction

Indium oxide is an amphoteric oxide of indium. Indium oxide nanoparticles are graded as an irritant and could possibly causes skin and eye irritation, and allergy or asthma symptoms or breathing difficulties if inhaled [1]. Indium oxide (In_2O_3) is an n-type transparent semiconductor with a wide band gap (~3.0 eV). In_2O_3 exhibits a number of interesting attributes and has been studied extensively. In_2O_3 films are also used as heat mirrors for solar energy applications [2]. The crystalline form exist in two phases, the cubic (bixbyite type) and rhombohedral (corundum type) [3]. These interesting attributes make In_2O_3 an important material for a different of practical functions, such as substitute for mercury as a battery inhibitor, hot mirrors, optical coatings, and some antistatic coatings. A different of In_2O_3 nanoparticles have been reported, such as nanowires, nanobelts, nanosheets, nanocrystals etc [4]. Shape-controlled growth of Indium oxide nanostructures can be achieved by one step electrodeposition process [5].

A layer of indium oxide on a silicon substrate can be deposited from an indium trichloride solution, a method useful for manufacture of solar cells [6]. A number of different fabrication techniques have also been reported, such as thermal oxidation [7], fusion by laser beam [8], electrochemical deposition method [9] etc. Bulk samples of Indium Oxide nanoparticles can be prepared by heating indium (III) hydroxide or the nitrate, carbonate or

sulfate [10]. Among many fabrication techniques, crystallizing substance from liquid solutions are of interest because they are safe and atmospherically friendly, and may be performed at relatively low temperatures (< 250 °C) [11].

The structure and properties of amorphous indium oxide was studied by D. Bruce Buchholz, and others [12]. Fundamental understanding of the chemical and structural origins of transparent conducting oxides (TCOs) has allowed TCOs to evolve into important materials for photovoltaic devices and optoelectronic applications [13-16].

Also, there are still some issues on In_2O_3 nanoparticles which are not understood completely. So lots of effort needs to be done in order to understand its fundamental attributes and enhance its performance in functions. In this introduction, some basic attributes of In_2O_3 will be introduced. Then a different of reported In_2O_3 nanoparticles will be described in detail.

Amorphous indium oxide is insoluble in water but soluble in acids, whereas crystalline indium oxide is insoluble in both water and acids. In_2O_3 is a basic oxide, so it mixes in mineral acids such as sulfuric acid or hydrochloric acid to give the corresponding Indium (III) salts. It may also be reduced to Indium metal using hydrogen or carbon monoxide.

Thin polycrystalline films of indium oxide doped with Zn are highly conductive (conductivity $\sim 10^5$ S/m) and even superconductive at helium temperatures. The

superconducting transition temperature T_c depends on the doping and film structure, which is below 3.3 K. These studies motivated us to prepare the Indium oxide nanoparticles using solution process method and its study as effect of solution concentration and pH value on the density of flower shaped nanoparticles.

2. Experimental procedures

In this work, In_2O_3 nanoparticles were fabricated by solution processed method. The chemicals used in this operate include Indium (III) nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.999 % purity) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, 99 % purity) obtained from Aldrich, and In_2O_3 nanoparticles (size in the range of 50-60 nm) used for making In_2O_3 seed layers obtained from nano and amorphous materials. Equimolar solution of Indium (III) nitrate hydrate and hexamethylenetetramine with known concentration were prepared. The prepared solutions were transferred into a vial and samples (Si or ITO/glass) were placed at the bottom of the vial. The vial was then heated at 120°C for 3 h. After the reaction, the samples were dried in an oven at 100°C . However, the obtained products from a dilute solution did not adhere well to the sample. Also, the presence of the sample did not seem to affect the surface of obtained In_2O_3 nanoparticles, as very similar surfaces were observed by examining the leftover solution. While the measurement of the products grown on the sample could be performed, the grown In_2O_3 could be partly washed away by rinsing the sample with deionized water, which would not be ideal for practical functions. Before fabrication, the sample was seeded with In_2O_3 nanoparticles. The seeding was performed by dispersing the nanoparticles in deionized water in ultrasonic bath for 1-2 h, putting a decrease of the dispersion on the sample and drying the sample in an oven at 150°C for 2 h. Then, the sample was sonicated for several seconds to remove the excess nanoparticles on the surface, and finally dried at 100°C . After uniformly coating the sample with In_2O_3 nanoparticles, fabrication of In_2O_3 nano-particles was carried out. The surface of indium oxide nanoparticles by solution-phase growth strongly depends on the pH value of the solution. So the influence of pH value on the surface of In_2O_3 nanoparticles has also been investigated. The pH value of the solution may be changed by the addition of hydrochloric acid (HCl) or Potassium hydroxide (KOH).

3. Results and discussion

The influence of solution concentration on the surface of obtained In_2O_3 nanoparticles was investigated in detail. The

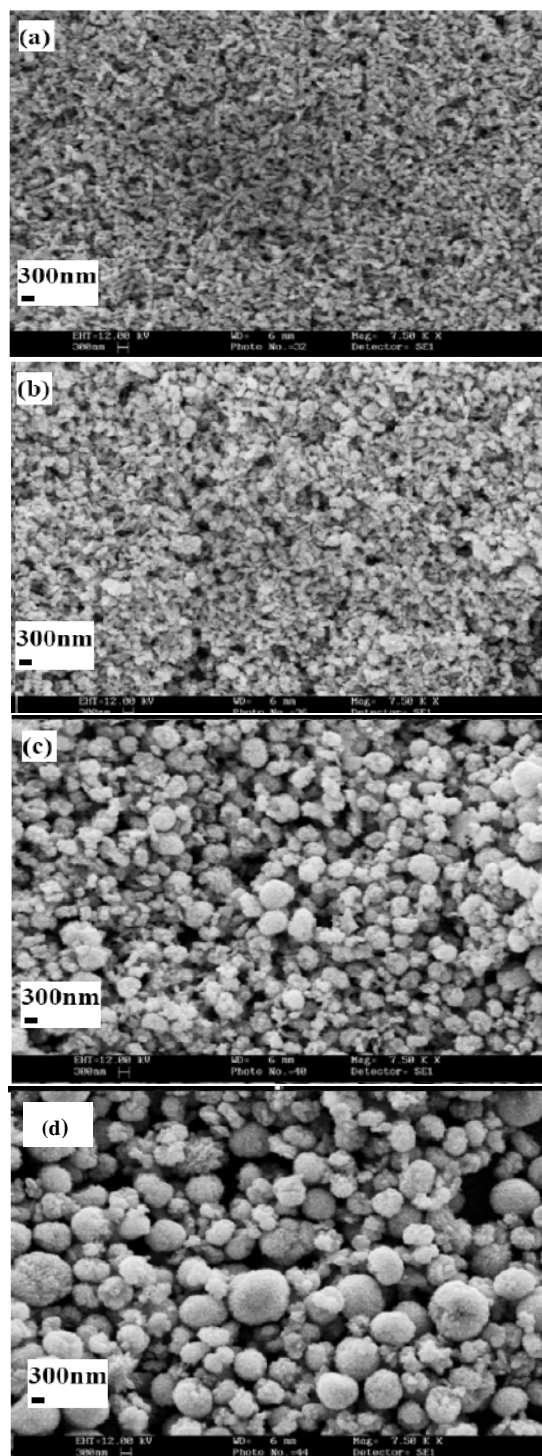


Figure 1: SEM images of In_2O_3 nanoparticles obtained at 120°C and $\text{pH} = 6$ from solution concentrations 1 mM (a), 2 mM (b), 3 mM (c) and 5 mM (d).

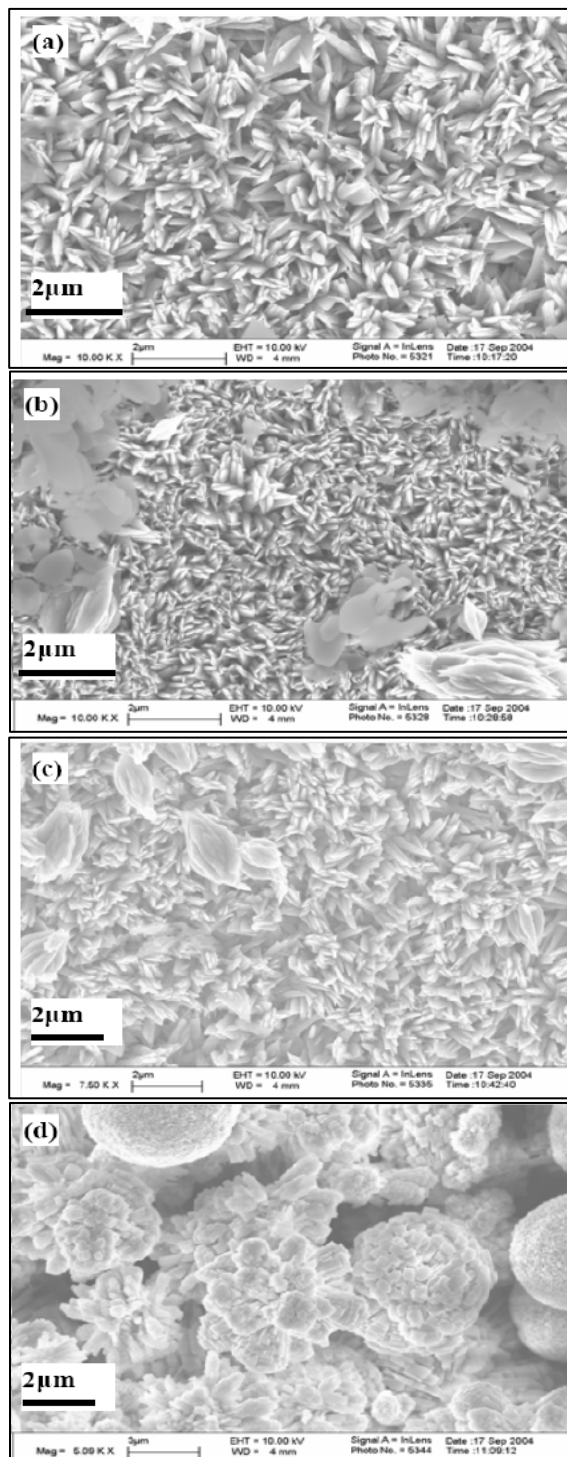


Figure 2: SEM images of In_2O_3 nanoparticles obtained from solution concentration 25 mM at 90 °C with pH = 3 (a), pH = 4 (b), pH = 5 (c) and pH = 6 (d).

solution concentration has significant impact on the obtained surface. For fabrication temperature 120 °C and pH = 6, different In_2O_3 nanoparticles were fabricated from solutions with different concentrations varying from 1 mM to 5 mM. Figure 1(a) to 1(d) show the representative SEM images of In_2O_3 nanoparticles obtained from different solution concentrations.

It may be observed that solution concentrations 1 mM and 2 mM do not result in formation of spherical ensembles. The obtained setups are irregular and very small (the largest dimension < 300 nm). For 3 mM concentration, some spherical setups may be observed, but the individuals appear to be more closely packed for concentration near 4 mM. This density is further increased for 5 mM concentration. Similarly properties of Indium Tin Oxide (ITO) nanoparticles affected by growth conditions [17].

For fabrication concentration 25 mM and temperature 90 °C, different In_2O_3 nanoparticles were fabricated from solutions with different pH values varying from 3 to 6. Figure 2(a) to 2(d) show the representative SEM images of In_2O_3 nanoparticles obtained from different pH values on a silicon sample with In_2O_3 seed layer. It may be observed that the pH value of the solution strongly affects the obtained surface. For low pH values, spherical assemblies were not observed, but nano films were obtained on the sample. With increasing pH value, setups formed by self-assembly of In_2O_3 platelets are more frequently found.

Finally, for pH value of 6, some spherical assemblies may be found. From the incomplete assemblies, it may be seen that there is no common core. However, the distance between the ends of In_2O_3 platelets is smaller. Also, for pH = 6, thicker platelets with a rectangular cross-section may be observed in the spherical assemblies, which is different from previously reported rhombic crystal strips. We see that the surface of obtained nanoparticles is influenced by the solution concentration and pH value has been investigated intensively. It was proposed that the growth of the nanoparticles is determined by the chemical potential of hydroxyl ions (OH^-). The chemical potential is determined by the pH value and monomer concentrations. Thus, it is expected that both pH value and solution concentration will affect the obtained surfaces. Also, the surface electrification of an oxide depends on the solution pH value: decreasing the pH value will steer to adsorption of protons, while increasing the pH value will steer to the absorption of hydroxyl ions (OH^-). The presence of surface charges will affect the aggregation and ripening of the nanoparticles. The aggregation of the nanoparticles is dependent on the

presence or absence of electrostatic repulsion, while the negative surface charge may hinder Oswald ripening way.

4. Conclusions

Solution process method was used to prepare Indium oxide nanoparticles. SEM micrographs of prepared sample show that density of nanoparticles increases with concentration of solution at constant formation temperature and constant value of pH. SEM micrographs of the sample, which was prepared with different pH value at constant value of temperature and constant solution concentration show that the pH value of the solution strongly affects the obtained surface. Therefore, surface of the obtained nanoparticles was influenced by the solution concentration and pH value.

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