Synthesis of Nano-Structures by Hydrothermal Method

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Abstract: Solid substances can exist in different forms such as: single crystalline materials, polycrystalline powders, nanocrystalline materials, nanostructure materials, thin films and amorphous systems. Materials with dimensions in the nanometre relm generate immense interest due to their novel physical and chemical properties as well as potential applications based on their shape and size. Hence, synthesis and fabrication of nanomaterials form an integral part of nanotechnology. Synthesis of nanoparticles with specific properties has attracted a great deal of attention from material scientists. The properties of nanoparticles depend largely on the synthesis procedure and physical conditions involved during synthesis. Nanoparticle growth mechanism is enough complex and depend on many parameters (temperature, viscosity, concentration of medium, etc.) Materials scientists have made significant contribution in the development of methods of synthesis of nanoparticles. In this review different method of synthesis of nanomaterials discussed. Polycrystalline materials are synthesized through solid-state reaction route and Sol-Gel technique. Nanomaterials can be prepared using top-down and bottom-up approaches. Top-down approach includes sculpting from bulk by mechanical attrition or lithography. Bottom-up technique usually deal with the self-assembly of atoms.

IndexTerms— NanoMaterials, Sol_Gel, Hydrothermal method, lithography *(Keywords)*

I. Introduction

Materials having dimensions in the nanometer realm are very important due to their physical properties as well as potential applications based on their shape and size. The optical, electrical and chemical properties of nano-materials can be modulated by changing the particle size. Zinc Oxide (ZnO) is a II-VI semiconductor with a wide and direct bang gap of 3.37 eV and large excitation binding energy of 60 meV. It has been widely used in near U-V emission, gas sensors and piezoelectric applications. Conventional high temperature solid state methods for preparation of ZnO nano particles are expensive and particle size cannot be controlled by those methods. ZnO nanoparticles can be prepared by simple solution based methods, such as chemical precipitation, sol-gel method and hydrothermal methods. The study of correlation of nano architecture morphology with deposition parameter and physical properties is a challenging task.

The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. Suspensions of nanoparticles are possible because the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in liquid. Nanoparticles often have unexpected visible properties because they are small enough to scatter visible light rather than absorb it. Nanoparticles have a very high surface area to volume ratio. This provides a tremendous driving force for diffusion, especially at elevated temperatures. Annealing can take place at lower temperatures over shorter time scales than for larger particles. Noticeable change in band gap energy of semiconductors occurs as the dimension of material is varied. For silicon nanowires, the band gap energy increases from 1.1 eV for 7 nm to 3.5 eV for 1.3 nm. Materials having larger band gap, higher electron mobility, large exciting binding energy and gas sensing properties are very important for applications in optoelectronics, photovoltaic and biological sensing. Metal oxide nanostructures offer those potential properties. So on making investigation about such a material the name of compound come out is Zinc Oxide (ZnO). Zinc Oxide (ZnO) is a unique material with a direct band gap (3.37 eV) and a large exciton binding energy of 60 meV. It has been widely used in near-UV emission, gas sensors and optoelectronic applications. ZnO crystallizes in three different forms: (i) Wurtzite (hexagonal), (ii) Zincblende, and (iii) Rock salt (NaCl) structures. Under normal pressure and temperature Wurtzite structure is thermodynamically the most stable structure. The ZnO Wurtzite structure consists of two interpenetrating hcp sublattices of cation (Zn) and anion (O). The important physical properties of ZnO are given in Table: 1

Physical property	Value
Structure	Wurtzite
a (nm)	0.32495
c (nm)	0.52069
c/a	1.602
Melting point	1975^0 C
Thermal Conductivity	1-1.2
Refractive index	2.008
Dielectric constant	8.656
Carrier concentration (Intrinsic)/cm^3	10^6
Bandgap (ev)	3.4
Binding energy (meV)	60

Table 1: Physical properties of ZnO

Most of the ZnO crystals have been synthesized by traditional high temperature solid state method which is energy consuming and difficult to control particle properties. ZnO nanoparticles can be prepared on a large scale at low cost by simple solution based methods, such as chemical precipitation [1, 2], sol-gel synthesis and solvothermal/hydrothermal reactions [3-10]. In the last decade hydrothermal processing technique has become one of the most powerful tools for synthesizing many organic materials. It has several advantages over other methods which are listed below.

- Powders are directly formed from solutions
- It is possible to control particle size by the hydrothermal temperature
- It is possible to control particle shape by the starting materials
- It is possible to control its chemical composition by reaction time, reaction temperature etc.

II. Synthesis of metal-oxide nanostructures (ZnO) by Hydrothermal Method

Hydrothermal synthesis is a process that utilizes single or heterogeneous phase reactions in aqueous media at temperature of the order of 60-100^{0}C and pressures (P>100 kPa) to crystallize materials directly from solution. Hydrothermal synthesis of nanomaterials can be realized by the following five sequential steps: Selection of materials, Optimization of molarity of reactants, pH of reactants, temperature of reaction, Synthesis of materials in auto clave, Centrifuging the sample and drying the sample. In this study the materials used are Znic Nitrate Hexahydrate [$Zn(NO_3)_2$, $6H_2O$], Ammonium Hydroxide (NH_4OH) for pH adjustment, deionised water as reaction medium.

Hydrothermal synthesis of ZnO was carried out using aqueous solution of $Zn(NO_3)_2$, $6H_2O$ and NH_4OH as a hydrolytic catalyst. The concentration of the solution was kept in the range 0.5M-0.05M. The amount of Zn $(NO_3)_2$.6$H_2$0 needed for various concentrations in the range 0.5M-0.05M was calculated in grams and then completely dissolved in 20 ml of distilled water. The pH of the solution was adjusted by the amount of NH_4OH. The resulting colloidal mixture is put into a teflon-lined stainless steel autoclave at room temperature. The autoclave used in these experiments is shown in Figure 2. The autoclave with the solution is then placed in a conventional oven and heated for 2 to 6 hours at temperatures 100^{0}C or 140^{0}C for different samples.

III. Collection of samples by centrifugation and drying of samples

The solution was transferred to a test tube and placed in a carousel for centrifuging. The centrifuge was carried for 45-55 minutes and the supernatant solution was discarded. The centrifuge (REMI- 8C) is shown in figure 4. Due care was taken to load the samples in the centrifuge. The centrifugation process was carried out for 50 minutes. The supernatant solution is discarded. The sample is thoroughly cleaned from the test tubes with DI water. Approximately 25 ml of powder sample suspended in DI water is obtained. The samples collected after centrifuging and washing with distilled water was transferred to a ceramic crucible and was heated for 2-3 hours at around 130-140^{0}C until it is dried. The sample was then ready for characterization. The samples were annealed at higher temperature of the order of 1000-1400^{0}C.

IV. CONCLUSIONS

This method revealed reproducible materials for the same experimental conditions. There is enough scope for study of effect of variation of experimental conditions on the properties of nanomaterials. The XRD pattern of prepared samples confirmed the formation of ZnO nanoparticles. Materials are also can be characterized by SEM, TEM.

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