ABSTRACT

Globally there is a lot of interest in the nanostructured crystalline zinc oxide for its multiple properties, wide range of applications and possibilities in tuning their properties suitable to the application. A variety of physical and chemical methods are adopted for the preparation of nanocrystalline ZnO with various shapes. Among them Bottom-up and Top-down approaches are two basic larger classifications of the synthesis or growth methods. Each and every method has its own advantage and disadvantages. In the Bottom-up approach most of the methods which are having a lot of scope for research in synthesis of nanomaterials. The common methods available for the preparation of nanostructures by bottom up approach are

♦ Hydrothermal method

♦ Laser ablation method

♦ Electron beam evaporation method

♦ Thermal evaporation method.

Among these methods, hydrothermal method has a cost-effective advantage than the rest of the methods. In addition they can provide platforms for various possible morphologies of nanostructures which can be influenced by chemical and physical experimental conditions. Hence there is a lot of scope for tuning the growth parameters for a specific morphology. Therefore the hydrothermal method was chosen for the synthesis of zinc oxide nanostructure. In this dissertation studies on the effect of various physico-chemical conditions on the growth kinetics of the nanocrystals were the major objective. Diverse physical and chemical experimental conditions were chosen to obtain a range of dissimilar shapes of nanocrystals.
Eventually the difference in the applied experimental conditions took effect to modify the growth parameters. These tainted growth phenomena subsequently has lead to the modifications in the structure, shape and size, size distribution of the prepared ZnO nanocrystals.

On the way to chose a number of miscellaneous experimental conditions, the following alterations were chosen. Temperature and time duration of the hydrothermal experiments are the very basic parameters. When temperature is reduced the formation of the intermediate growth complexes takes time. Similarly when sufficient time is not given for the experiment, the growth of nanostructures will be in the midway. Therefore the speed of growth can be retarded to get smaller and thinner particles. These can even have influence at the lattice level. For the formation of complexes, the ionic strength of solution used is of having a major contribution. So, when this is allowed to vary it can play major alterations in the formation of growth complexes again. The differences of population of the complexes, the nucleation conditions are not the same. They eventually pave way to specific nanostructures with naturally modified aspect ratio and of dissimilar dimensions. An another way of modifying the growth complexes tested were to alter the zinc ion sources and the alkalis which produce the hydroxyl ions. Several combinations of these two can really produced newer engineered nanoshapes. Achieving multiple shapes and surface to volume ratio of nanostructures will be possible by these selection of experimental conditions.

Chemical additives are good candidates to tune the morphologies to the wish and will of the researchers since they actively take part in the growth activity. A surfactant, a chelating agent and a capping agent were different chemical additives chosen for the study in the hydrothermal growth of ZnO nanostructures. The action of a surfactant is to lower the surface tension of the
solution and to form micelles in the solution. The hydrophilic heads oriented at the peripheries of the micelle favours the seeding; as a result a bunch of nanorods in a shape of ‘arms of the wheel like’ structure is formed. Variation in the strength of the surfactant is tested on the resultant morphology nanocrystalline ZnO. Similarly, the addition of capping agent and chelating agents in different concentrations were considered. The addition of capping agents suppresses growth along certain faces. These were affirmatively exploited to study the effect of this on the growth of ZnO in hydrothermal method. The chelating agent actually slows down the reaction process than usual, by just capturing the Zn$^{2+}$ ions. So, a controlled supply of the nutrients is made available to the growth sites. This prevents arbitrarily shaped growth of nanostructures and hence controlled growth of ZnO can be achieved.

By the analysis it was examined and verified that there are variations in result due the difference in experimental conditions. The variation in temperature and time duration of the experiments, change in pH, effect of multiple ionic strengths, and changing the zinc sources all have shown up a considerable modification in the morphology of the zinc oxide nanostructures and also in the lattice parameters. In some cases, their optical properties were also tested, and confirmed to be comparable with the characteristic property of zinc oxide. But there are some slight variations due to the difference in the ways of preparation of nanocrystalline ZnO.

Similarly, the microwave heated hydrothermal experiments were also tried to analyse the growth kinetics of zinc oxide nanostructures. This microwave treated hydrothermal method has a great advantage of rapid synthesis of nanostructures. It has reduced the time required from 12 hour to 20 minutes. The effect of pH, the role of ionic liquid, substituting mono, di and tri ethanolamines of increasing concentration for alkali etc., were tested for the investigations on
growth kinetics of microwave treated hydrothermal synthesis (MWTHS). In that it was predicted by us that the growth complexes produced were different from each other when pH was increased. The complexes responsible for nucleation were higher in population in some cases and lower in some other cases where growth nutrients were in large number. The dissolution/recrystallisation process which is a common phenomena in growth of crystals from solutions predicted and confirmed to be correct. Occurrence of Ostwald ripening process was inferred, where in the growth of bigger crystals progress further at the cost of dissolution of smaller ones. In some other experiments, ionic liquids (IL), which posses both cationic and anionic part in it simultaneously are used for the synthesis of ZnO in MWTHS. The IL – 1-Butyl, trimethyl imidazolium hexafluoro phosphate could produce a brick-like morphology coated onto a seed layer. This was a peculiar and a never before seen structure for zinc oxide in our experiments.

In an attempt to test versatility of this hydrothermal method to prepare vertically oriented nanorods arrays of ZnO, seed layers prepared from aqueous solutions by dip coating method with two different thicknesses were immersed into solutions of different concentrations. The container was tightly closed, then hydrothermally treated in hot air oven. From SEM analysis, it was found that well-defined shapes of nanorods array like growth was observed on the seed layers. The arrays grown from various molar concentrations of solutions, and from different zinc sources were totally different. The texture co-efficient of the layers grown on different seed bed thicknesses were found to vary as inferred from XRD spectrum. The grown nanostructured arrays were analysed by X-ray photoelectron spectroscopy, Atomic Force Microscopy etc., The results confirmed the layer prepared was of pure ZnO, and the surface roughness of the layer consisting of nanostructured arrays was near about 350 nm. Further, this method was extended to
study the effect of the chemical additives, such as surfactant, chelating agent, and capping agent for the growth of layer of nanostructure arrays onto the seed layer. It could be confirmed that the additives had the same effect as they had in the preparation of crystalline ZnO nanoparticles.

To test this method for its suitability in the preparation of metal doped ZnO nanostructures, microwave assisted solvothermal method was adopted using ethanol as a solvent. Both metal doped nanoparticles and layer of nanostructure arrays were also tried. The XRD results exhibited some additional peaks in response to the presence of the added metal atoms. The colour of the prepared metal doped layers was exhibiting specific colours of the doped transition metal. Moreover, the formed morphologies were also different for different metal doped specimen. Hence it could be found that there is suitability for using this method to prepare transition metal doped ZnO nanorods etc., As a continuation of this dissertation, the analyses of the exact quantity of the metal doped into it and the change in crystallographic structure of the prepared specimen if any can be studied.

The above said details are divided into separate chapters of this thesis as shown below.

**Chapter I** gives an introduction in general to the material, preparation of nanostructures and method adopted for the preparation of these, the specific properties of ZnO etc.,

**Chapter II** contains the experimental details, results, predictions and inferences of the experiments in which the effects of experimental conditions, ionic concentration and different zinc sources on the morphology were tested.

**Chapter III** presents the details of the actions of capping agent, surfactant and chelating agent, on the morphologies of finally formed nanoshapes.
In **Chapter IV**, Microwave assisted hydrothermal method of synthesis of ZnO nanostructures is described. pH variation, addition of ionic liquid, role of different ethanolamines in the synthesis of ZnO by this method are vividly discussed.

**Chapter V** records the experiments, results and growth kinetics of layered nanorod arrays of ZnO. There the variation in source of Zn precursor, and the action of various chemical agents such as surfactants, capping agent and chelating agents which are tested for the preparation of the nanocrystalline ZnO particles are tested for the layered growth of ZnO nanorod array. Finally, the extension of this aqueous chemical method to transition metal doped ZnO nanocrystalline particles and layered array of metal doped ZnO nanorods.

The summary and conclusion of the overall work is presented in **Chapter VI**.