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SYNTHESIS OF ZnO:Mn NANOPARTICLES, NANOBELTS AND NANORODS

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Doping is a widely used method to improve the electrical and optical properties of semiconductors. However synthesis route is also very important to get different type of nanostructures with different properties. Different types of ZnO nanostructures doped with Mn having variable doping concentrations by weight percentage have been synthesized in the laboratory using wet chemical synthesis technique. Scanning Electron Microscope(SEM) image shows the nanobelt around one millimeter and Transmission Electron Microscope(TEM) studies shows that the average diameter of the particles is 25-100 nm and the diameter of the rod is 66nm.

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1. Introduction

Earlier people synthesized different type of ZnO nanostructures using sol-gel synthesis template synthesis, hydrothermal technique, pulsed laser ablation etc. However wet chemical synthesis technique offers many advantages in comparison to other techniques such as easy to synthesize, lower temperature required for reaction to be carried out, higher yields and well defined nanostructures. Doping of Mn in to the ZnO offers an interesting way to alter various properties [1,2] for example the band gap of host material can be tuned from 3.37eV to 3.70eV. Additionally it also alter the emission properties by providing an efficient channel for the recombination of electron and hole via the dopant Mn d levels. The optical and electronic properties of semiconductors can further be tuned by varying the size of the particles in the range below 10nm. It is found that Mn doped ZnO thin films exhibit ferromagnetism at room temperature [3]. Studies on various Mn –doped semiconductor nanocrystals[4] have revealed that the properties of these samples, like the band gap, are influenced by the quantum confinement of electronic states [5]. These interesting changes in confined dilute magnetic semiconductors(DMSs) have enlarged the scope of research activity in this field, prompting us to study the confinement effects in Mn-doped ZnO nanostructures with different shapes.

Also, one dimensional nanostructures like nanobelts, nanowires nanosprings, nanotubes etc. have stimulated interest for scientific research due to their importance in mesoscopic physics and their potential application in nanotechnology. The development of nanodevices might be benefited from the distinct morphology, and high aspect ratio of nanotubes and nanowires in particular nanotubes possess several different areas of contact (borders, inner and outer surfaces and structured tube walls) which can be functionalized in several ways such as, incorporation of nanorods in the nanotubes and more generally used as nanoscale host materials. Therefore the explorations of new fabrication methods have become an active subject. Up to now many kinds of

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nanobelts such as sulfides nitrides and oxides have been reported[6,7,8]. Spanhel and Anderson have explained the synthesis of nanocrystals of ZnO using distillation set up starting with products of Zinc acetate and ethanol[7] using this technique. They have obtained highly concentrated colloidal nanocrystals of ZnO of size varying from 3.5nm-5.5nm. with ageing and shown that these crystals remain in a dispersed state for weeks. Hossain et.al [10-11] have further modified this technique successfully to obtain nanobelts of ZnO of length 700 micrometer using refluxing technique. However our group produced a nanobelts up to 2 mm with increasing reaction time using the refluxing technique starting with Zinc acetate and absolute ethanol. Several workers have used capping agents such as poly (N-vinyl-2pyrroledone)(PVP), polyethylene glycol (PEG) to stop particles agglomeration to obtain nanoparticles of size less than 20 nm [11-12]. Sol-gel and thin film deposition are other best alternates to obtain particle size less than 5nm. In this paper using wet chemical synthesizing techniques we obtained different type of ZnO nanostructures. Fig. 1 represents the overview of various synthesis routes for preparing nanostructures of ZnO using wet chemical synthesis technique.

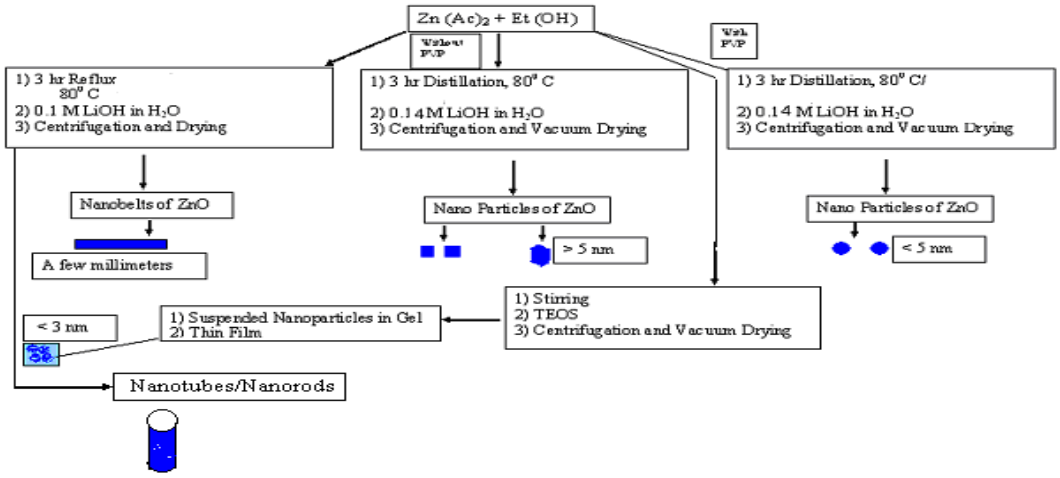

Fig. 1. Various synthesis routes for ZnO nanostructures.

2. Experimental

Synthesis of ZnO nanoparticles

Colloidal solution was prepared from Zinc acetate and absolute ethanol. 0.1M Zn^{2+}, prepared from Zinc acetate in absolute ethanol; was refluxed under distillation and stirred for 3hours at 80^{o}C. This is initially based on the method given by Spanhel et al.[7]. Desired proportion of manganese impurity obtained from 0.1M Mn^{2+}, prepared from Mn acetate, in 100 ml of ethanol, 0.1gm of poly (N-vinyl-2pyrroledone)(PVP) were also added in the reaction during the synthesis process. The concentration of PVP, the capping agent was kept at 0.1gm per 10 ml of ethanol. The remaining hygroscopic product was mixed with 0.1M LiOH prepared in 100 ml deionized water in which precipitates started forming then precipitates were separated out using centrifugal machine at 5000 rpm and then sample were dried in vacuum oven at 80^{0}C.

Synthesis of ZnO nanobelts

The precursor was prepared from Zinc acetates and absolute ethanol was refluxed at 80 ^{0}C for 3hours . The remaining hygroscopic product is mixed with Mn impurity obtained from 0.1M Mn^{2+} were separated out and mixed with 0.14M LiOH prepared in 100ml deionized water. The precipitates were separated out using centrifugal machine at 3500rpm. Samples were then dried in

the oven at 80^{o}C for 4 hours. We increase the concentration of LiOH from 0.1 M to 0.14 M by doping so that the near neutral clusters are formed and pH values comes out to be 8. This will helps to form long length nanobelts.

Synthesis of ZnO rods

The precursor prepared from Zinc acetates and absolute ethanol was refluxed at 80^{o}C for 1hour under oxygen atmosphere. The remaining hygroscopic product is mixed with Mn impurity obtained from 0.1M Mn^{2+} was separated out and mixed with 0.14 M LiOH prepared in 100 ml deionized water. The precipitates were separated out using centrifugal machine at 4500rpm. Samples were then dried in the oven at 80^{o}C for 4 hours.

Structural characterization

Nanostructures of manganese doped ZnO have been studied by scanning electron microscopy(SEM) and transmission electron microscopy(TEM). Scanning electron microscope(SEM) images of the samples were obtained from JSM-6100 type microscope. Transmission electron microscope(TEM) images of the samples were obtained using JEOL JEM 2000Ex type microscope.

3. Results and discussion

Mn doped ZnO nanocrystals were synthesized using wet chemical synthesis technique. ZnO nanophosphor doped with variable concentration of Mn have been synthesized in the lab and characterized using TEM and SEM. Figs-(2-4) shows the fabricated ZnO nanostructures. Scanning Electron Microscope(SEM) image shows the nanobelt which have a size around one millimeter. Transmission Electron Microscope(TEM) studies shows that the average diameter of the particles is in between 25-100 nm and the diameter of the rod is around 66 nm. It is clear from the results that ZnS:Mn nanostructures are very sensitive to the preparation conditions and we can fabricate any desired nanostructure.

Fig. 2 TEM of ZnO:Mn nanoparticles

Fig. 3 SEM of ZnO:Mn nanobelt

Fig. 4 TEM of ZnO:Mn nanorod.

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