Development of ZnS Nanostructure Based Luminescent Devices

Upamnayu Das
Department of Physics, Rajiv Gandhi University, Doimukh, Arunachal Pradesh, INDIA

Abstract: The fabrication of ZnS nanocrystalline dots (NCD) doped with Transition metals (Cu, Mn, Cr, Fe, Co etc.) by simple chemical method is reported. These ZnS nanocrystallines dots encapsulated in the polymer matrix show better stability. The X-ray diffraction and AFM signified the formation of ZnS nanostructures. Transmission electron microscopy confirms the formation of nanostructures of average size 10 nm. Enhancement and up-conversion of luminescence due to doping is observed from Photoluminescence spectra. A schematic diagram of a luminescent device using these nanostructures is reported.

1. Introduction

Semiconductor nanostructure, which uses the principle of three dimensional carrier confinement, have emerged as important technological assets for their dimensional dependent opto-electronic properties. The nanoscaled systems exhibit properties e.g. quantum size effect or three dimensional carrier confinement, quantization of the bulk electronic states. In addition, energy gap enhancement occurs with decreasing crystallite size. In recent years, size dependent electronic and optical properties of nanostructures [1-4] have been studied by different workers. In fact that the band gap of these materials varies with crystallite size makes them and interesting category of materials for potential optoelectronics and photonics application. Among binary semiconducting systems, ZnS are the most widely investigated system having a direct band gap of 3.7 eV at 3000K.

Again, doped nanomaterials provide improved functionality for prospective applications in nanotechnology [5-9]. The properties of intrinsic nanomaterials or host nanomaterials can be tuned by doping with some impurity. It is an important phosphorescent material both in doped and undoped form. It has been established that when doped with some magnetic impurities, the nanostructures develop a unique class of material called diluted magnetic semiconductors (DMS) which are promising candidates for magnetic memories, sensors and other spin-based devices [10, 11]. Such semi-magnetic and semiconducting structure, where carrier and spin confinement is possible provides a matchless system for spin manipulation and spin transportation [12]. Fabrication of doped a nanostructures is difficult. Here we have used solution growth technique because they provide a homogeneous distribution of impurity atoms in the host nanoparticle, easy to control the size and shapes, higher production yields and low costs.

2. Experimental

First, 5 % (w/v) transparent polyvinyl alcohol (PVOH) matrix was prepared under moderate stirring (~200 rpm) and heating (65 0C) for 3 hours. Next, 0.15 M ZnCl$_2$ was added to the PVOH matrix under stirring environment. The solution was immediately brought back to ice cold temperature and left undisturbed overnight. H$_2$S gas was allowed to diffuse through the solution for maximum absorption. The solution is than kept in cool and dark environment for 24 hours to form stable ZnS nanostructures. To synthesis TM (Mn, Co, Cu, Fe, Ni) doped nanostructures same method is slightly modified. For this purpose instead of only ZnCl$_2$ a mixture of ZnCl$_2$ and chloride or oxide of the transition metal is added to the PVOH matrix etc. For proper doping it is necessary to maintain suitable environmental condition.

Figure 1: XRD diffraction pattern of (a) Bulk ZnS (b) PVOH film (d) PVOH embedded ZnS nanostructure
The phase of the as-grown samples and their crystallographic orientation was identified by X-ray diffraction (XRD) analysis as shown in Fig. 1(c) which suggests formation of a cubic structure. The XRD also gives an idea of rough estimation of average particle size ~10 nm, obtained by measuring full-width-at half maxima (FWHM) and Scherrer formula $d = 0.9\lambda /w\cos\theta$. The 2D-topological view of nano-ZnS, taken by atomic force microscopy (AFM) and shown in Fig. 2 agree well with it.

Figure 2: AFM image showing 2D-topological view of nano-ZnS in Atomic force microscopy (AFM)

More clear evidence on the formation of ZnS nanostructures is being depicted in Transmission electron micrograph in figure 3.

Figure 3: TEM image ZnS nanostructure

A Photoluminescence spectrum is used to study the optical properties of doped and undoped ZnS nanostructures on Perkin Elmer LS 55 operating at 325 nm Xeon light as excitation source. Normally, the photoluminescence study provides information relating to different energy states available between valence band and conduction band responsible for radiative recombination. It is well known that when emission peak energies are less than the band gap energy of the material, these bands ascribe to transition involving donors, acceptors, free electrons and holes. The appearance of the PL peaks at energies substantially lower than the band gap suggests band edge emission. The photoluminescence spectra of ZnS nanostructure in figure 4 show instance luminescence around 430 nm which is due to surface states in the nanoparticles. This peak is show instance that is quenched out the band-edge emission peak which is responsible of phosphorescence bulk ZnS. The spectra of doped ZnS nanostructures are shown the figure 5,6,7,8,9 and 10 at different doping level.

In doped ZnS nanoparticle any impurity can lead to impurity levels in the band gap and which leads to modification of luminescence. The luminescence property of the materials enhanced/ suppressed depending upon the position of the defect states in ZnS nanostructures after doping.

Figure 4: Photoluminescence spectra of ZnS nanostructures

Table 1: PL results doped & undoped ZnS

Figure 5: Photoluminescence spectra of ZnS:Mn nanostructures

Figure 5(a) : PL of ZnS:Mn nanostructure

Figure 5(c) : PL of ZnS:Cu nanostructure

Figure 6: Photoluminescence spectra of ZnS:Co nanostructures
Among the transition metals Mn\textsuperscript{++}, Cu\textsuperscript{++}, & Co\textsuperscript{++} doping show enhancement in luminescence in the visible range while Fe\textsuperscript{++} & Ni\textsuperscript{++} show suppression of luminescence. From application point of view ZnS:Mn, ZnS:Co, and ZnS:Cu in nano form are promising candidate for luminescent devices.

One most promising application of these materials are as phosphors in Light Emitting Diode (LED) and other display devices. By using a blue/uv emitting diode the nanoparticle phosphor embedded in polymer excites/stimulate to illuminate particular color of light depending upon the kind of the nanoparticles. Again, there is also possibility to produce different color using these by mixing these nano phosphors at different ratios.

3. Conclusion

In conclusion, I have produced doped/undoped ZnS nanostructures by simple and inexpensive chemical route. Photoluminescence shows a new emission peak due to doping and enhancement in luminescence. Again, after doping with TM impurity, I found some multifunctional material which is semi conducting & semi magnetic.

4. Acknowledgements

The author thank SAIF, NEHU, Shilong and IUAC, New Delhi for TEM and AFM images respectively.

5. References


