

Synthesis and Photoluminescence Studies on Nanocrystalline Content ZnS Film

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Abstract

Semiconductor nanoparticles with particle sizes less than few nm to a few hundred nm size exhibit size dependent energy gap between the top of occupied states and the bottom of unoccupied states. The size quantization effect is studied by the optical absorption measurements. We have studied the optical properties of ZnS nanocrystalline semiconductors prepared by a chemical route technique by mixing aqueous solutions of ZnCl₂ and Na₂S in the presence of mercaptoethanol. The photoluminescence is a process in which the material is excited by short wavelength electromagnetic wave and de-excitation causes emission of light. In many cases, photo-luminescence is obtained by band-to-band transition and photoluminescence peaks at the same photon energy as the absorption edge. In nanocrystals, as the size of the crystal is reduced, photoluminescence peaks has been found to shift towards shorter wavelength. The size of nanoparticles can be estimated using theoretical models relating the increase in band gap with the radius of particle. ZnS nanoparticles of different sizes have been prepared and their size has been estimated by shift in photoluminescence peak using effective mass approximation model and hyper-bolic band model.

The XRD studies indicate that the nanocrystalline powder and film specimens of ZnS are cubic in nature having zinc-blende structure. The sizes have been obtained in the range of 2 to 10 nm. Absorption spectra of powder and film specimens have shown blue-shift in absorption edge as compared to their bulk counterpart indicating increased band gap energy due to quantum confinement effect.

It can be seen from the spectra that there is practically uniform absorption in the Visible range (800 nm - 390 nm). Absorption increases suddenly in the UV region. For ZnS-I, sample sudden increase in the absorption occurred at

about 260 nm similarly onset of absorption is obtained at 250 nm, 240 nm, 230 nm and 220 nm for ZnS-II, ZnS-III, ZnS-IV and ZnS-V samples, respectively. The values of E_g are obtained as 4.7 eV, 4.9eV, 5.2eV, 5.4eV & 5.6eV, respectively for the samples ZnS-I to ZnS-V corresponding to the absorption edge with increasing the capping agent concentration.

Introduction

Nanostructured materials have drawn considerable interest and are currently being investigated by the scientists in various laboratories all over the world [1-2]. Ultra fine particles, whose physical dimensions are comparable to Bohr exciton radius, show quantum size effect, which leads to discrete energy levels and widening of band gap [3]. The study of optical properties of nanocrystals has become the topic of both theoretical and experimental interest due to its wide technological importance. Among them Zinc Sulfide (ZnS) is one of the important materials.

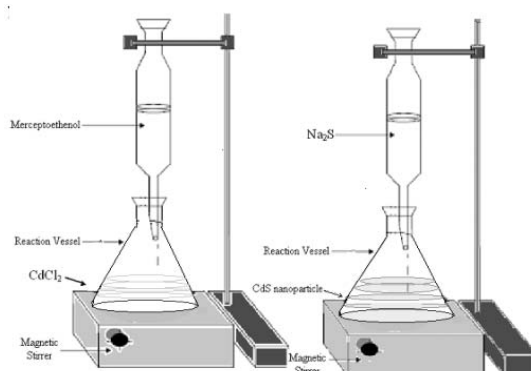
In nanocrystallites, the electron, holes and excitons have limited space to move and their motion is possible for definite values of the energy. Thus, their energy spectrum is quantized. As a result, the continuum of states in the conduction and valance band respectively are broken down into discrete states with energy spacing relative to the band edge which is approximately inversely proportional to the square of particle size and reduced mass [4]. The highest occupied valance band and the lowest unoccupied conduction band are shifted to a more negative and positive values respectively resulting in widening of the band gap. This leads to a effective band gap larger than its bulk value that can be observed through optical absorption studies. In all cases, as the crystalline size is narrowed down, there will be a blue shift in the absorption spectra along with the oscillatory structure which is a signature of the size quantization effect [5]. From the blue shift the average radius of the nanocrystallites can be estimated.

Synthesis of nanoparticles with narrow size distribution imposes a great challenge to the scientists. Various methods have been attempted such as chemical deposition, sol-gel technique, evaporation and electro-deposition etc. [6]. Presently ZnS nanocrystals have been synthesized by chemical precipitation method and their photoluminescence studies have been carried out.

Experimental Support

Nanocrystals of ZnS have been obtained by precipitation technique and deposited on glass substrate. 0.01M dilute solution of zinc chloride ($ZnCl_2$) and sodium sulfide (Na_2S) were mixed in presence of capping agent mercaptoethanol (C_2H_5OSH). The aqueous solution of mercaptoethanol was added drop wise in the solution of $ZnCl_2$ at the rate of 1ml per minute, while stirring the solution continuously with magnetic stirrer. Thereafter 0.01M solution of Na_2S was mixed drop wise into the solution. Subsequently, a milky color solution was obtained and kept for 24 hours. Precipitate was washed 2 to 3 times. In this reaction NaCl was formed which was removed by washing the solution. The unreacted mercaptoethanol and Na_2S are removed also.

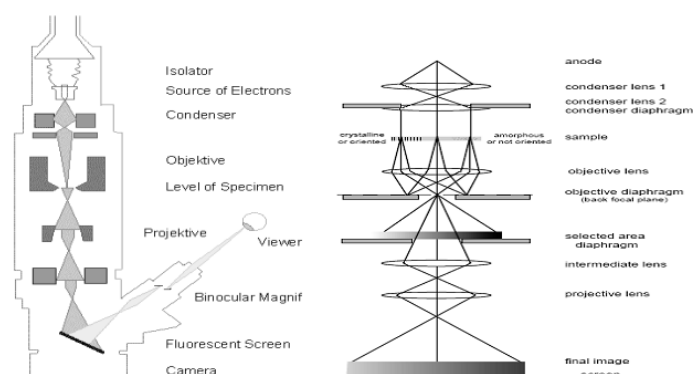
This washed solution was centrifuged for 30 minutes at 3500 rpm. Finally the precipitate was kept in a constant temperature bath at 300K, which gave different particle sizes.



In order to investigate the micrographics and crystalline size, were analyzed by transmission electron microscope (TEM). The photoluminescence of the samples was studied using monochromator and photo multiplier tube (PMT). The excitation was done with the help of mercury lamp.

Transmission Electron Microscopy

- Its principle is just like slide projector.
- Instead of light, electron beam shines on the sample. Part of it is transmitted and projected on screen.
- The lenses and apertures are electrical or magnetic.
- Sample is thin so that electrons can pass through it.
- Low wavelength gives high resolution. (~ .2 nm) & magnification 350000.
- Due to high spatial resolution it gives detailed crystallography of fine grains.

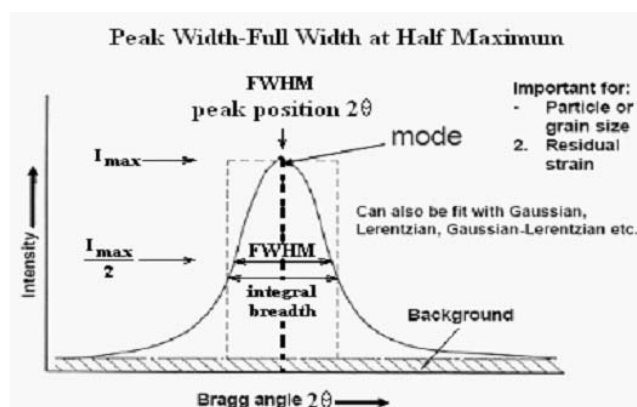


X-Ray Diffraction (XRD)

X-ray diffraction is a most powerful tool for crystal analysis. X-ray diffraction by crystals gives sharp intense lines because of regular arrangement of atoms. For small

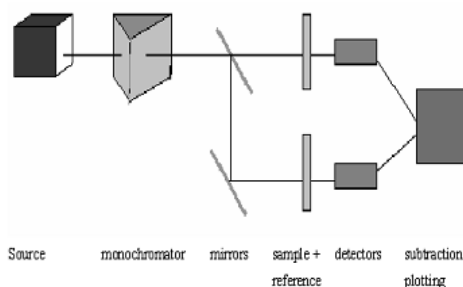
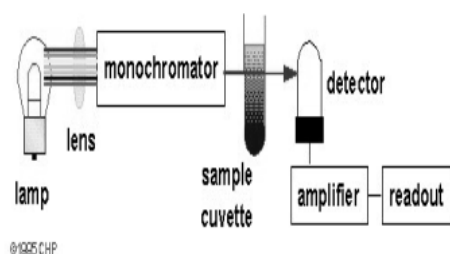
crystal sizes, x-ray beam is diffused. This decreases the peak intensity and increases the width of the line. From XRD of nanocrystals one can determine-

- Crystal structure
- Crystallite size and
- Lattice parameter



Optical Absorption

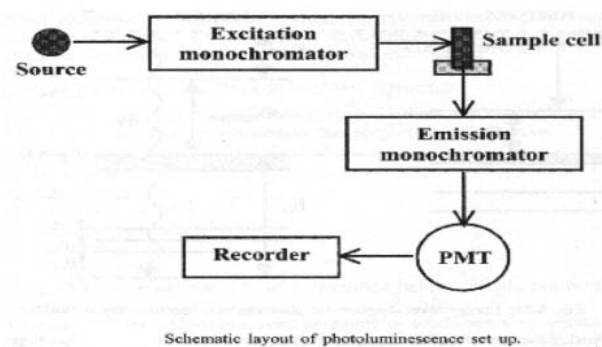
Photons of energy($h\nu$) less than the forbidden energy gap (E_g)of the crystal are not absorbed. Absorption starts at $h\nu=E_g$ and then increases rapidly. It is known that reduction in size of crystals to nanometer range causes increase in effective forbidden gap of crystals due quantum confinement effect. In case of nanocrystals absorption starts at higher energy. In small monodispersed nanocrystals stepwise absorption or absorption peaks are obtained. Absorption spectra of powder and film specimens have shown blue-shift in absorption edge as compared to their bulk counterpart indicating increased band gap energy due to quantum confinement effect. Figure shows the UV/VIS optical absorption spectra for ZnS-I, ZnS-II, ZnS-III, ZnS-IV and ZnS-V samples prepared with capping agent concentration of 0M, 0.005M, 0.01M, 0.015M and 0.02M respectively.



Photoluminescence

When excitation is done by photons, it is called photoluminescence (PL). Optical absorption and PL spectra are commonly used in characterization of size of

semiconductor nanocrystals. In case of band edge luminescence, it is seen that absorption edge and luminescence peak are at the same energy. Both shift towards higher energy as particle size of nanocrystals is reduced.



Results and Discussion

TEM image of ZnS Nanocrystals

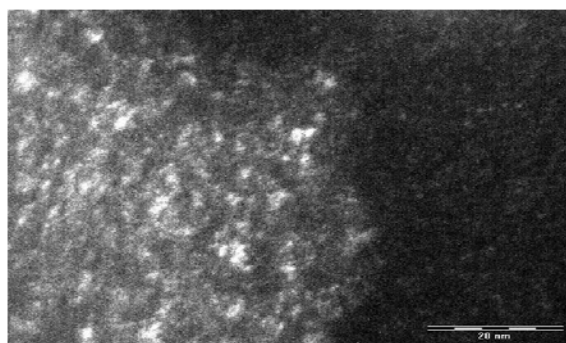


Figure 1: Particle size 2-3 nm.

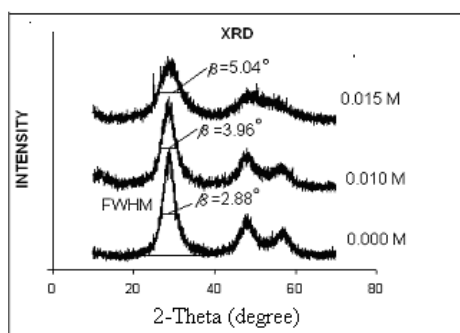


Figure 2: XRD of ZnS nanoparticles.

Figure-1 shows a typical TEM micrograph of ZnS nanocrystals. The particle size obtained by transmission electron microscope. Figure-2 shows the X-ray diffraction

of ZnS nanoparticles prepared by chemical precipitation method with different capping agent concentrations. From this, it is clear that the nanocrystalline powder and film specimens of ZnS are cubic in nature having zinc-blende structure. The broadening of peaks is indicative of small particle size. The sizes have been computed by using Scherrer formula $D = k\lambda/\beta \cos \theta$. The sizes have been obtained in the range of 2 to 10 nm. Figure-3 shows the optical absorption spectra for different concentration of ZnS.

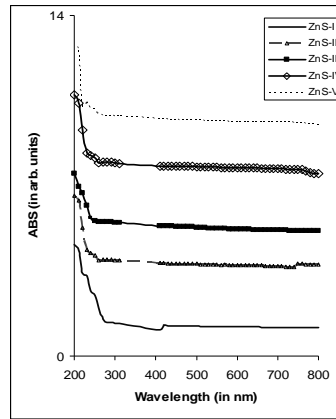


Figure 3: Optical absorption spectra For different concentration of ZnS.

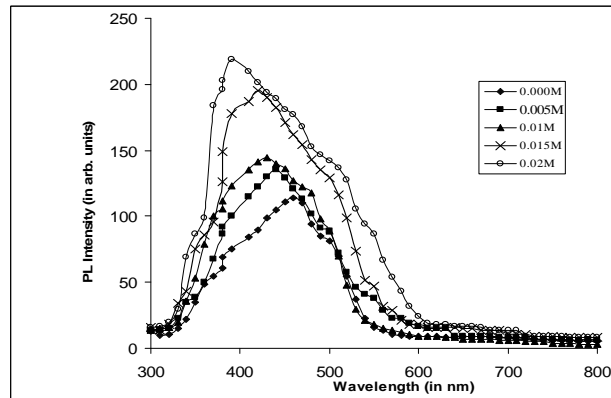


Figure 4: PL spectra for ZnS nanoparticles at various concentration of capping agent.

It can be seen from the absorption spectra that there is practically uniform absorption in the visible range (800 nm - 390 nm). Absorption increases suddenly in the UV region. For ZnS-I, sample sudden increase in the absorption occurred at about 260 nm similarly onset of absorption is obtained at 250 nm, 240 nm, 230 nm and 220 nm for ZnS-II, ZnS-III, ZnS-IV and ZnS-V samples, respectively. The values of E_g are obtained as 4.7 eV, 4.9 eV, 5.2 eV, 5.4 eV & 5.6 eV, respectively for the samples ZnS-I to ZnS-V corresponding to the absorption edge with increasing the capping agent concentration.

Table: Absorption Results for ZnS nanocrystals for various Concentration of capping agent.

Sample	Capping Agent Concentration	Absorption Wavelength	Band Gap
ZnS- I	0.000M	260 nm	4.76 eV
ZnS- II	0.005M	250 nm	4.96 eV
ZnS- III	0.01M	240 nm	5.16 eV
ZnS- IV	0.015M	230 nm	5.39 eV
ZnS- V	0.02M	220 nm	5.63 eV

Table: PL emission peak for ZnS nanoparticles at various concentration of capping agent.

Samples	Concentration	Wavelength	Energy	Relative Intensity
ZnS- I	0.000M	460 nm	2.69 eV	119
ZnS- II	0.005M	440 nm	2.82 eV	135
ZnS- III	0.01M	430 nm	2.88 eV	144
ZnS- IV	0.015M	420 nm	2.95 eV	195
ZnS- V	0.02M	390 nm	3.35 eV	219

The photoluminescence studies of ZnS nanocrystals shown in figure-4. The intensity corresponding to different wavelength given in table below. The intensity is high as the energy is high that is at lower energy low intensity was obtained. The maximum PL peak is obtained at maximum. There have been a number of reports on the photoluminescence spectra of bulk ZnS, but relatively less effort has been expended on PL studies ZnS nanoparticles. Kanemoto have studied the photophysical and photocatalic properties of ZnS nanoparticles. Their work has indicated that the defect levels play a crucial role in determining the luminescence characteristics of quantum particles. Recently, Chen has investigated the nature and properties of surface states of ZnS nanoparticles using optical techniques [6]. Yanagida have reported synthesis and spectroscopic studies of cubic and hexagonal ZnS nanoparticles. High emission quantum efficiency and very short luminescence decay times have been observed in doped ZnS nanoclusters.

References

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