

Growth time dependence of size of nanoparticles of ZnS

Satyajit Saha, Kamal Bera, Paresh Chandra Jana

Abstract—Growth time is an important factor in the growth of nanoparticles of a semiconducting material. With this view ZnS is synthesized at different duration of times by chemical method. Nanocrystalline ZnS is synthesized at room temperature by a cost effective chemical reduction method. The dispersed as grown samples in ethanol are characterized using electron diffraction techniques. Simultaneously optical absorption, photoluminescence of these samples is studied at room temperature. The increase of particle sizes and decrease of band gap of the as prepared ZnS nanoparticles are observed with increase in growth time. The size of the nanoparticles depends on growth time. An increase in band gap is observed in each case as compared to bulk ZnS. An attempt is made to correlate the structural, optical properties.

Index Terms— ZnS nanoparticles, Microstructural properties, Optical properties, Photoluminescence

I. INTRODUCTION

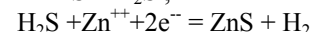
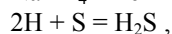
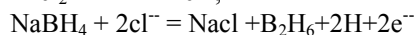
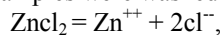
Nanocrystalline semiconductor particles have attracted considerable interest in recent years, because of their novel properties, such as large surface-to-volume ratio and the three dimensional confinement of the electrons^[1-7]. The degree of confinement of the electrons are changed due to the change of the size of the particles and hence affects the electronic structure of the solid especially the band gap edges. Among the family of II–VI semiconductors, ZnS are the foremost candidates because of their favorable electronic and optical properties for optoelectronic applications. Among those ZnS is a commercially important II–VI semiconductor having a wide optical band gap, rendering it a very attractive material for optical application especially in nanocrystalline form. ZnS can have two different crystal structures (zinc blende and wurtzite); both have the same band gap energy (3.68 eV) and the direct band structure. ZnS has been extensively used for the cathode ray tube, field emission display, and scintillators as one of the most frequently used phosphors^[8-10], thin-film electroluminescent devices^[11], infrared windows, flat panel displays^[12], sensors, and lasers^[13] etc.

Nanocrystalline ZnS can be prepared by various methods like sputtering^[14], coevaporation^[15], wet chemical^[16-18], sol-gel^[19, 20] solid state^[21], micro-wave irradiation^[22,23], ultrasonic irradiation^[24] or synthesis under high-gravity environment.^[25]

In this work, nano crystalline ZnS structures are formed via a chemical reduction route^[26] in room temperature. In the present method sodium borohydride is used as reducing agent to initiate the reaction between zinc chloride and sulphur at room temperature. Duration of growth time are varied to study the effect of growth time. The used method is cost effective and free from experimental hazards. The structural optical and photoluminescence properties of as grown samples are characterized by XRD, TEM, SAD, EDX, optical absorption and photoluminescence techniques.

II. EXPERIMENTAL

Anhydrous ZnCl₂ (99.999%) (817.68 mg), sulphur powder (99.999%) (196.36 mg) and stoichiometric amount of sodium borohydride (99%) were taken to grow ZnS. Tetrahydrofuran was used as solvent. The reaction was carried out at 30 °C. ZnCl₂ and sulphur powder were added in tetrahydrofuran and the solution was magnetically stirred for different duration of time 3 hours, 6 hours, 9 hours and 12 hours. The stirring speed was same for all samples. The grown samples were washed and dried.



For microstructural study, as prepared ZnS nanoparticles were dispersed in ethanol by ultrasonification. A small drop of this dispersed samples were placed on a thin carbon film supported on the carbon grid and kept for some time for drying. The transmission electron micrograph (TEM) of the prepared nanoparticles was acquired using JEOL-JEM-200 operating at 200 kV. The SAD pattern and EDX analysis of the said nanoparticles were also carried out. The XRD patterns of the said samples were obtained by using Rigaku MiniFlex-II X-ray diffractometer.

The optical absorption spectrum of the samples was taken by using Shimadzu-Pharmaspec-1700 UV-VIS after ultrasonification in ethanol. The photoluminescence spectrum of the as prepared samples was obtained by using Perkin Elmer LS 55 Fluorescence spectrophotometer.

III. RESULTS AND DISCUSSION

The morphology of as prepared samples was obtained from SAED and TEM pattern. The TEM and SAED images are shown in Figure 1.

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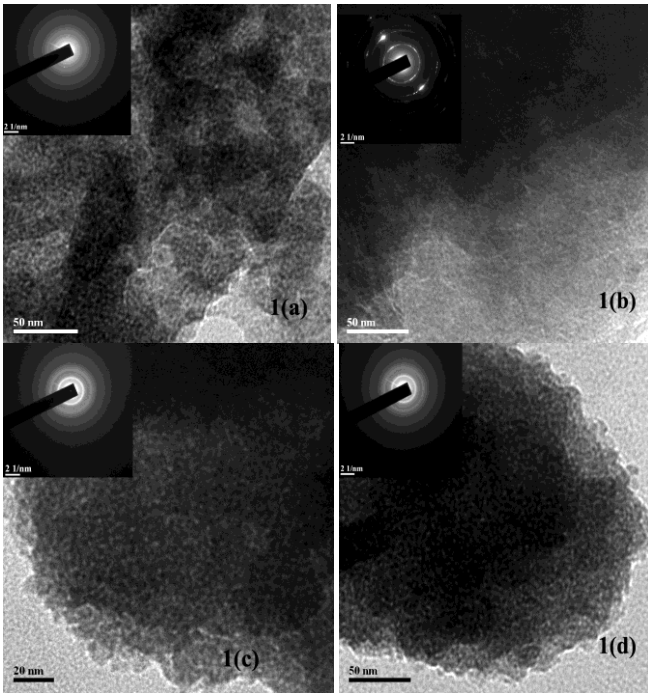


Fig.1 (a) (b) (c) (d) The TEM and SAD pattern of as synthesized ZnS nanoparticles grown at 3 hour, 6 hour, 9 hour and 12 hour time duration respectively.

The images clearly show that the particle size depends on the growth time. The particle sizes of the as prepared samples increase as increase in growth time shown in table 1. The smallest particle size has observed 4 nm in case of three hours. EDX analysis show that the ZnS ratio increases as increase of growth time.

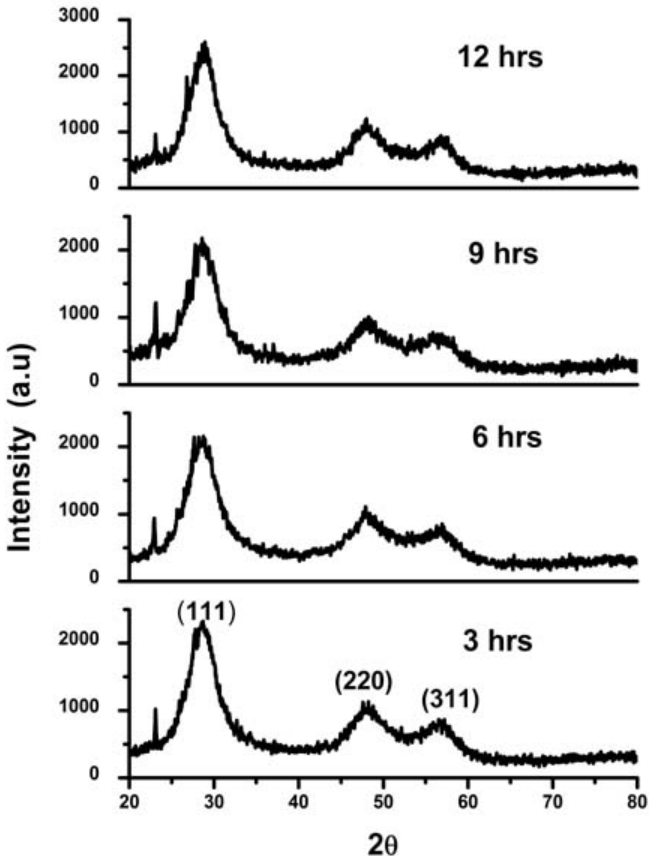


Fig. 2 The XRD pattern of the samples grown at different duration of time.

The diffraction peaks of the XRD pattern of as prepared the samples are shown in Figure 2. The XRD pattern of as prepared nanoparticles exhibit the peaks at scattering angle (2θ) 28.56°, 48.14°, 56.56° corresponds to (111), (220), (311) planes respectively. Diffraction peaks of the XRD pattern of the as synthesized samples show cubic phase. The lattice constant $a=5.4039\text{\AA}$ calculated from the XRD pattern of as synthesized ZnS nanoparticles are in good agreement with the reported value of bulk ZnS with cubuic structure $a=5.345\text{\AA}$.

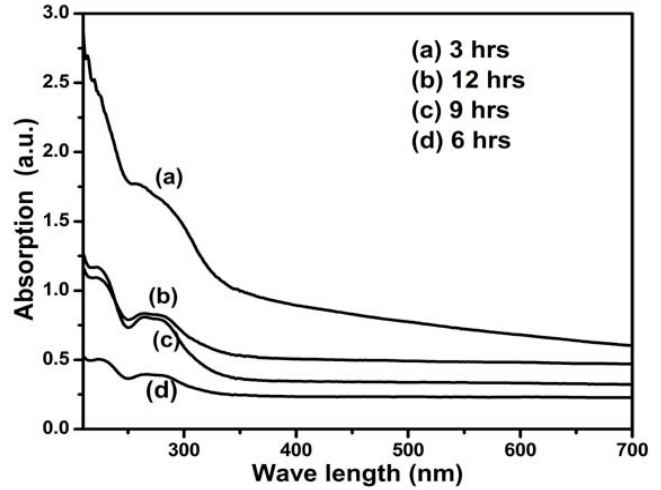


Fig.3 Optical absorption spectra of as prepared samples.

Figure 3 shows the variation of optical absorbance with wavelength of the as prepared nanoparticles. Optical absorption coefficient has been calculated in the wavelength region 200–700 nm. Optical absorption coefficient (α) is calculated at each wave length.

The band gaps of the as-prepared nanoparticles are determined from the relation^[27]

$$(\alpha h\nu)^2 = C(h\nu - E_g) \dots \dots \dots (1)$$

where C is a constant. E_g is the band gap of the material and α is the absorption coefficient.

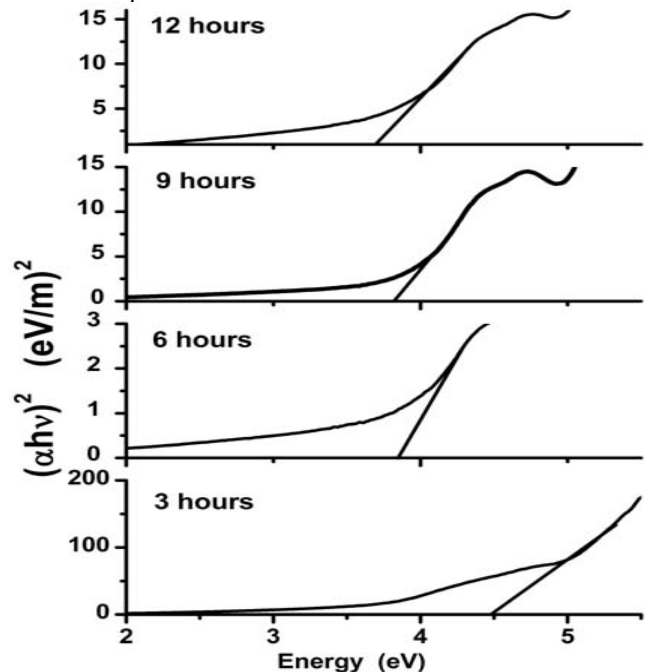


Fig.4 Band gap determination of as prepared samples.

Fig. 4 shows the plot of $(ahv)^2$ vs. energy ($h\nu$) and it is used to determine band gap in each case. The band gap of as prepared samples decreases as growth time increases.

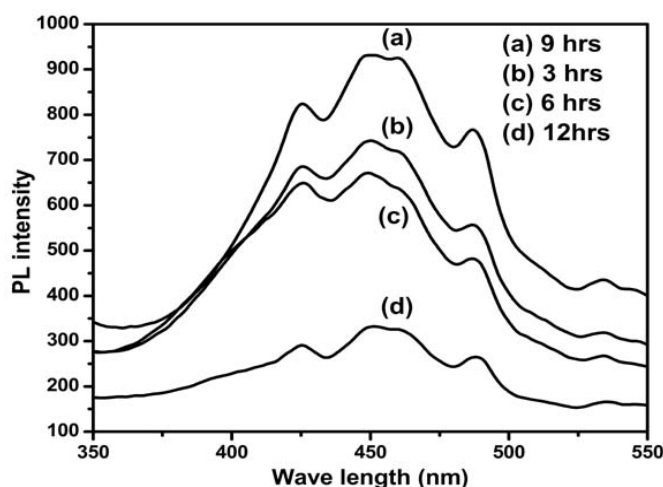


Fig.5 Photoluminescence spectra of as prepared samples.

Fig .5 shows the PL spectra of the samples dispersed in ethanol. The excitation wave length is 266 nm in each case. PL peaks are found to be broad around 450 nm. PL study indicates that observed broad peaks centred on 450 nm are commonly attributed to the recombination of charge carriers within surface states. Appearance of a broad peaks centered at 450 nm is attributed to the presence of sulphur vacancies in the lattice . This emission results from the recombination of photo generated charge carriers in shallow traps .Table 1 summarizes the observed results.

Table 1 Summarisation Table

Name of samples	Growth time (hours)	Weight % EDX analysis	Size (nm)	Band gap (eV)
ZnS-1	3	Zn-51.56 S-48.44	4	4.48
ZnS-2	6	Zn-56.06 S-43.94	7	3.86
ZnS-3	9	Zn-61.76 S-38.24	9	3.81
ZnS-4	12	Zn-63.16 S-36.84	13	3.68

IV. CONCLUSIONS

The ZnS nanoparticles are prepared by chemical reduction method at room temperature. The XRD patterns show cubic phase for all cases. The TEM images show that size of the nanoparticles depend on growth time. Experimental results shows that lower dimension of nanoparticles with higher band gap energy are obtained in case of shorter growth time. Also the peaks of the PL spectra are shifted towards lower energy for longer growth time. The structural, optical properties indicate that there is formation of more and more nanoparticles with more quantum confinement in the case of shorter growth time.

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