International Journal of Applied and Natural Sciences (IJANS);
ISSN(P): 2319-4014; ISSN(E): 2319-4022;
Vol. 5, Issue 1, Dec - Jan 2015; 39-44

International Academy of Science, Engineering and Technology
Connecting Researchers; Nurturing Innovations

GROWTH AND CHARACTERIZATION OF ZNSE NANOMATERIALS BY A COST EFFECTIVE CHEMICAL REDUCTION METHOD

SATYAJIT SAHA, TAPAN KUMAR DAS & RAHUL BHATTACHARYA

Department of Physics and Techno Physics, Vidyasagar University, Paschim Medinipur, India

ABSTRACT

A simple chemical reduction method is followed to grow ZnSe nonomaterials at room temperature with different duration of growth time. The dispersed samples are characterized using electron diffraction techniques. Simultaneously optical absorption, photoluminescence and longtime photorelaxation of these samples are studied at room temperature. Nanomaterials are obtained with different shape. An increase in band gap is observed in each case as compared to bulk ZnSe. Dimension of nanomaterials decreases with increase of growth time and hence there is increase of band gap with increase of growth duration. Simultaneously long time relaxation decreases with increase of growth time. An attempt is made to correlate the structural, optical and optoelectrical properties.

KEYWORDS: Microstucture, Nanomaterials ZnSe, Optical Properties, Optoelectrical Properties

INTRODUCTION

The semiconductor nanoparticles exhibit structural, optical, luminescence and photo conducting properties that are very different from their bulk properties [1-6]. It is very attractive because of their possible application in solar cell, photo detector, laser, LED, high density magnetic information storage and many others in semiconductor industries. A2B6 semiconductor nanomaterials play an important role having application in nano devices [7-12]. ZnSe (bulk band gap 2.7 eV at 300 K) has huge potential in this aspect. Their growth techniques are relatively cheap. Their characteristic absorption of light is in the visible range. There are various methods to prepare ZnSe nonomaterials [13-19]. Some of the above mentioned methods have some draw backs.

Used precursors are unstable causing environmental hazards and required very high temperatures. These methods are not cost effective also. In the present work a chemical method is followed at room temperature [20]. Sodium borohydride is used to initiate the reaction between $ZnCl_2$ and selenium at room temperature. The method used is simple and cost effective. Hence it is preferred compared to other costly processes.

EXPERIMENTAL

Anhydrous $ZnCl_2$(681.4 mg), Selenium powder (394.8mg) and stoichiometric amount of sodium borohydride (567.45 mg) were taken to prepare different samples. Ethylenediamine was taken as solvent for reaction medium. Sodium borohydride were taken to initiate the reaction at room temperature. Varying the growth time the different samples were prepared. The reaction was carried out at 27 °C. The stirring was continued for different duration of time such as -three hour, six hour and twelve hour at a particular speed using a magnetic stirrer.

For microstructural study, as prepared ZnSe nanomaterials 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 of the prepared nanomaterials 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 are 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 of the samples in ethanol. The photoluminescence spectrum of the as prepared samples was obtained by using Perkin Elmer LS 55 FL spectrophotometer. For photoconductive measurement, thin film of the ZnSe has been grown from the dispersed sample. The glass substrate has been dipped in the dispersed solution at least for 12hrs. Uniformly thin film of ZnSe is deposited on the glass substrate. Silver paint is used as ohomic contact. I-V characteristics are found to be linear. The photoelectrical characteristics have been studied using Kiethly electro-meter-6514.From long time photoconductive decay, relaxation time has been measured. Intensity of light falling on the sample is measured by luxmeter and found to be 30 lux.

RESULTS AND DISCUSSION

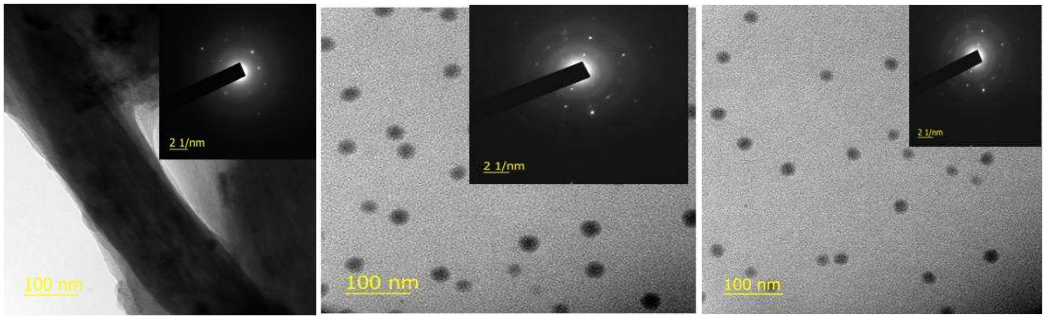
Figure 1 shows the morphology of as prepared ZnSe nano materials obtained from TEM images.

The SAD pattern shows that ZnSe samples are in hexagonal phase. The images clearly show that there is formation of nanomaterials with different shape and sizes.

Nanorods of length 650 nm and diameter of 160 nm is obtained in case sample grown at 3 hour duration.

While nanoparticles of average diameter 30 nm are obtained in case of sample grown at 6 hour duration.

Diameter of nanoparticles are reduced to 20 nm in case of sample grown at 12 hour duration.



(a) (b) (c)

Figure 1: TEM and SAD Pattern of as Synthesized ZnSe Nano Materials Grown at a) 3 h, b) 6 h c) 12 h Time Duration Respectively

Figure 2 shows the diffraction peaks of the XRD pattern of the as prepared samples with different growth time. From the XRD pattern it is clear that the as synthesized samples are in hexagonal phase.

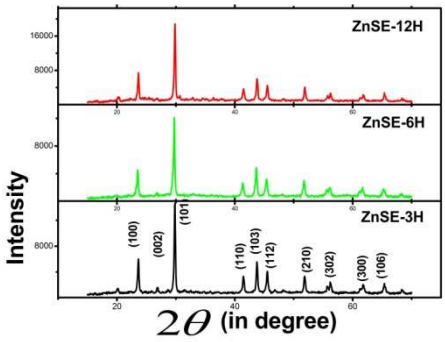


Figure 2: The XRD Pattern of the Samples Grown at Different Duration of Time for (a)3 h, (b)6 h, (c) 12h

The particles sizes are determined by measuring half width of the XRD peaks from the 2θ plot using

Scherrer's formula $D = \frac{.9\,\lambda}{\beta_{\frac{1}{2}} cos\theta}$

where D is crystal diameter, $\beta_{\frac{1}{2}}$ is half width of XRD peaks. θ is diffraction angle, λ is X-ray wavelength (1.5408 Å, Cu K_α).

Figure 3 displays the variation of optical absorbance with wavelength of the as prepared ZnSe nano materials. Optical absorption coefficient has been calculated in the wavelength region 300-750 nm. The band gaps of the as-prepared nano materials are determined from the relation $(\alpha h\nu)^2 = c(h\nu - E_g)$ where C is a constant. E_g is the band gap of the material and α is the absorption coefficient.

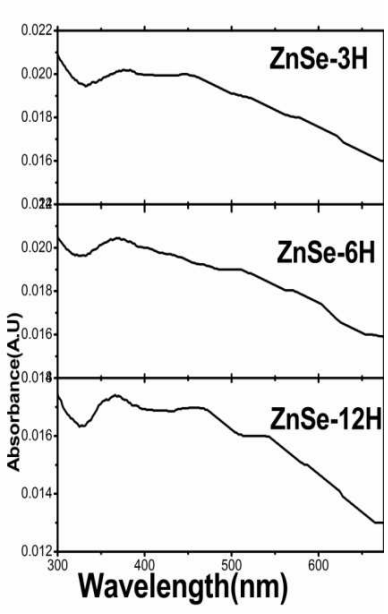


Figure 3: Optical Absorption Spectra of Different for Samples

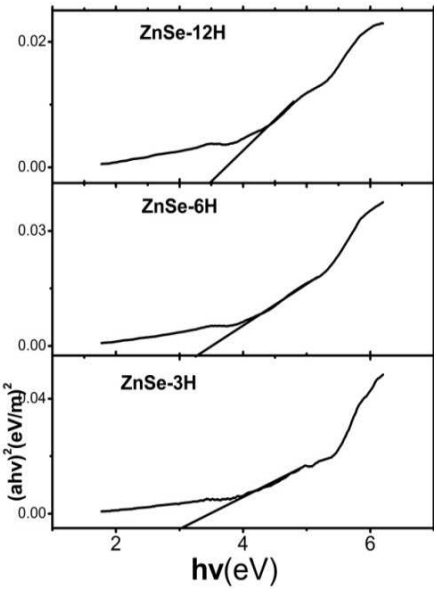


Figure 4: The Band Gap Determination of Different Samples

Figure 4 shows the plot of $(\alpha h\nu)^2$ vs. energy (hν) and it is used to determine band gap. The band gap is found to be 3.0 eV, 3.2eV and 3.5 eV for growth time 3, 6 and 12 hour respectively.

Thus with the increase of growth time the band gaps are shifted to the higher energy. Thus there is a blue shift relative to the peak absorption of bulk ZnSe indicating more and more quantum confinement with the decrease of particle size.

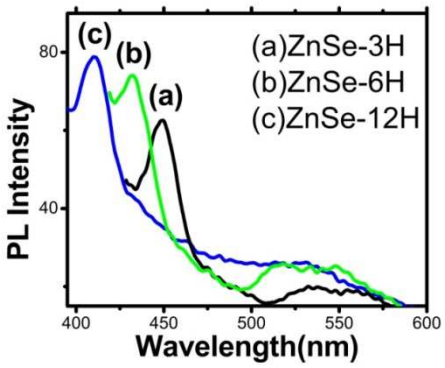
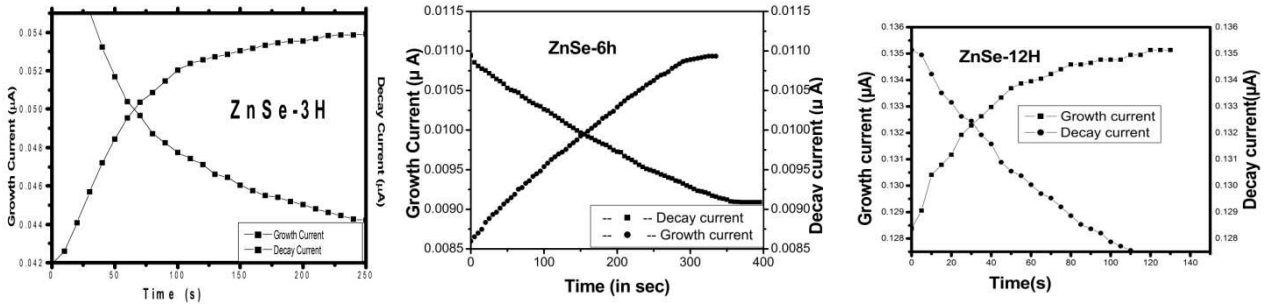


Figure 5: Photoluminescence Spectrum of As-Prepared ZnSe Samples

Figure 5 displays the photoluminescence spectrum of as-prepared ZnSe samples.

Photoluminescence spectra display peak around 430 nm due to band edge luminescence and another peak around 525 nm due to surface states. The peaks attributed to band edge luminescence are shifted towards higher energy as band gap of the nanomaterials increases with growth time.



(a) **(b)** **(c)**

Figure 6: Plot of the Photoconductive Growth and Decay of Current for the Sample Grown for 3-Hour, 6 Hour and 12 Hour Duration

Figure 6 displays the growth and decay of photocurrent. After the steady current is reached the light is off. Relaxation times are measured from long time photo decay graph.

Relaxation time is measured using the relation

$$\Delta n = \Delta n_s \exp\ (-t / \tau)$$

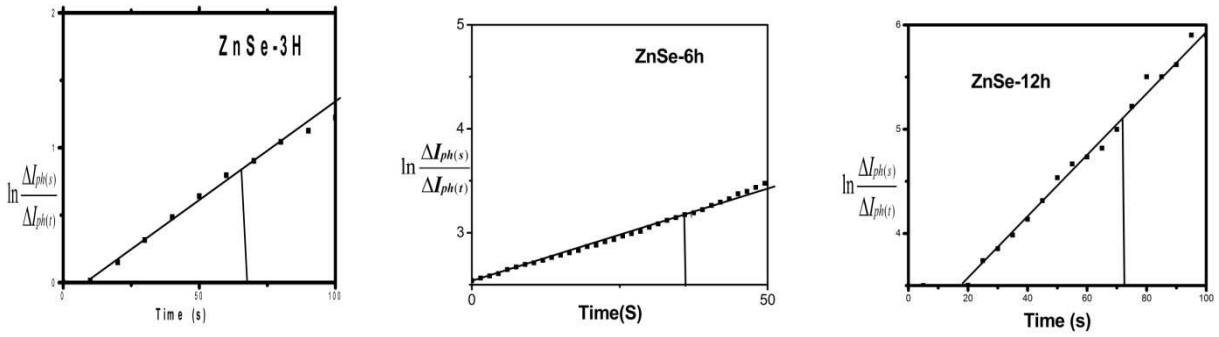
Where Δn is excess carrier concentration at any arbitrary time, Δn_s is excess carrier concentration at steady state condition and τ is relaxation time.

This relation can be correlated to experimentally measurable parameter by

$$\frac{\Delta n_s}{\Delta n} = \frac{\Delta I_{ph(s)}}{\Delta I_{ph(t)}} = \exp(t / \tau)$$

$\Delta I_{ph(s)}$ is the change in photocurrent at steady state condition with respect to dark current value.

$\Delta I_{ph(t)}$ is the change in photocurrent at an arbitrary time t with respect to the dark.



(a) **(b)** **(c)**

Figure 7: The Relaxation Time Determining Plot for the Sample Grown as 3-Hour, 6-Hour and 12-Hour Duration

Figure 7 shows the plot of $\ln \frac{\Delta I_{ph(s)}}{\Delta I_{ph(t)}}$ vs. t for sample grown for 3-hour, 6 hour and 12 hour duration. The plot leads to a straight line. From the slope, the long time relaxation is estimated and is given in the table 1.

A comparison of different characteristics of as prepared ZnSe nanomaterials with change of growth time is given in Table1

Table 1: Comparison of Different Characteristics of ZnSe Nanomaterials with Change of Growth Time

Name of the Samples	Growth Time(Hour)	Size (nm)	Relaxation Time (sec)	Band Gap (eV)
ZnSe 3H	3	Rod L=650,D=160	67	3.0
ZnSe 6H	6	Particle D=30	49	3.2
ZnSe12 H	12	Particle D=20	11	3.5

Experimental results show that the lower band gap energy sample having greater relaxation time. This is probably due to the decrease of surface states with the increase of grain size. The slow photoconductive decay is attributed here to the reconstruction of recombination recombination barrier which has spatially separated the photogenerated electron-hole pairs by trapping minority carriers. The dark conductivity is established only after equilibrium filling of the recombination barrier states, the process being self hampering because it involves the barrier being overcome by majority carriers. The exponential decay shows that recombination barrier height does not change at all under illumination & this is the case under weak illumination

CONCLUSIONS

The ZnSe nonomaterials are synthesized in chemical reduction route at room temperature. The XRD pattern shows hexagonal phase for all cases. The TEM images show that dimension of the nanomaterials decreases as the growth time of the samples are increased. The band gap energy increases with increasing duration of growth time of the samples. All these characterestics show that more and more quantum confinement with increase of growth time.

ACKNOWLEDGEMENTS

The authors are acknowledging the department of physics of Vidyasagar University for XRD measurement. Authors are thankful to IIT Kharagpur for graciously allow the use of TEM measurement.

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