

ROLE OF TEMPERATURE IN THE FORMATION OF ZnSe NANOMATERIALS BY CHEMICAL REDUCTION METHOD

SATYAJIT SAHA, TAPAN KUMA DAS & RAHUL BHATTACHARYA

Department Of Physics And Technophysics, Vidyasagar University, Midnapore, West Bengal, India.

ABSTRACT

ZnSe nanorods are grown by varying temperature and keeping ratio of reagent constant. The samples are characterized using electron diffraction techniques. Simultaneously optical absorption, photoluminescence and longtime photorelaxation of these samples are studied at room temperature. An increase in band gap is observed in each case as compared to bulk ZnSe. Also the formation of nanorods is found to be favourable at particular temperature. An attempt is made to explain the growth & correlate the structural, optical & electrical properties

KEYWORDS: Synthesis of nanomaterials, Structural properties, Optical properties.

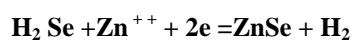
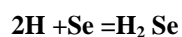
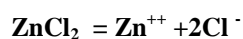
INTRODUCTION

The semiconductor nanomaterials exhibit structural, optical, luminescence and photo conducting properties that are very different from their bulk properties. 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 [1-7]. A_2B_6 semiconductor nanorods play an important role having application in nano devices [8, 9]. ZnSe (bulk band gap 2.6 eV at 300K) 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 nanorods [10-19]. 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 reduction method is followed at room temperature. Sodium borohydride is used to initiate the reaction between $ZnCl_2$ and selenium at room temperature. The grown samples are dispersed in ethanol to characterize it structurally & optically. Nanofilm is also grown from the dispersed medium on glass substrate & is used for photorelaxation study. An attempt is made to explain the formation of nanorods at certain ratio of reducing agent.

EXPERIMENTAL SECTION

Anhydrous $ZnCl_2$ (360mg), Selenium powder (208 mg) and stoichiometric amount of sodium borohydride (150mg, 300mg, 450mg, 600mg, 750mg) were taken to prepare different samples. To prepare different samples the temperature of the medium of reaction are kept as $30^{\circ}C$, $45^{\circ}C$, $60^{\circ}C$ and $70^{\circ}C$ respectively. Ethylene-di-amine used as capping agent. Sodium borohydride were taken to initiate

the reaction at room temperature.. The stirring was continued for three hours at a particular speed. The reaction are as follows.



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 nanosamples was acquired using JEOL-JEM-200 operating at 200kV. The SAD pattern and EDX analysis of the said nanosamples 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 in ethanol. The photoluminescence spectrum of the as prepared samples was obtained by using Hitachi-F7000-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 ohmic contact. I-V characteristics are found to be linear. The photoelectrical characteristics have been studied using Keithly 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 25 lux.

RESULTS AND DISCUSSIONS

The structural morphology of as prepared samples were obtained from SAED and TEM pattern. The TEM and SAED images are shown in figure 1. The images clearly show that there is formation of nanoparticles for the reaction temperature 60°C and 70°C respectively. Mainly randomly oriented nanorods of different diameter and length were obtained for reaction temperature 30°C and 45°C. EDX pattern shows that nanorods are formed when the weight ratio of Zn and Se is approximately 1:1.

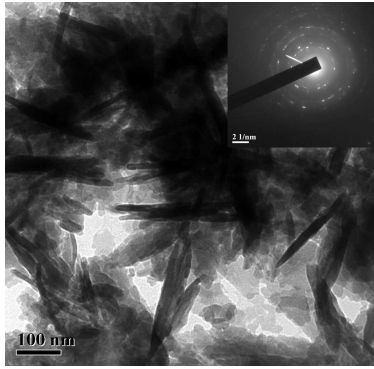


Figure 1(a)

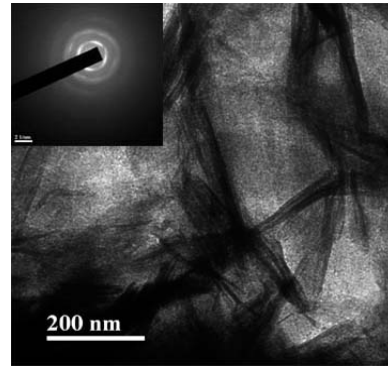


Figure 1(b)

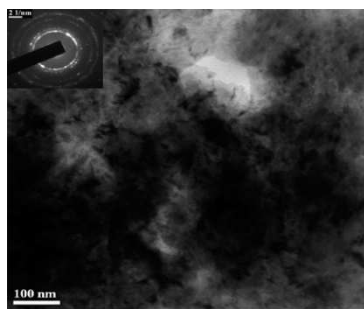


Figure 1(c)

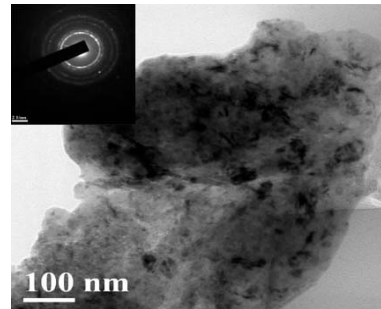


Figure 1(d)

Figure 1(a) (b) (c) (d) The TEM and SAD pattern of as synthesized ZnSe samples having reagent temperature 30°C (room temperature), 45°C, 60°C and 70°C respectively

The diffraction peaks of the XRD pattern of the as prepared sample is shown in figure 2. The XRD pattern of the as synthesized samples show a mixture of hexagonal phase and cubic phase at different condition.

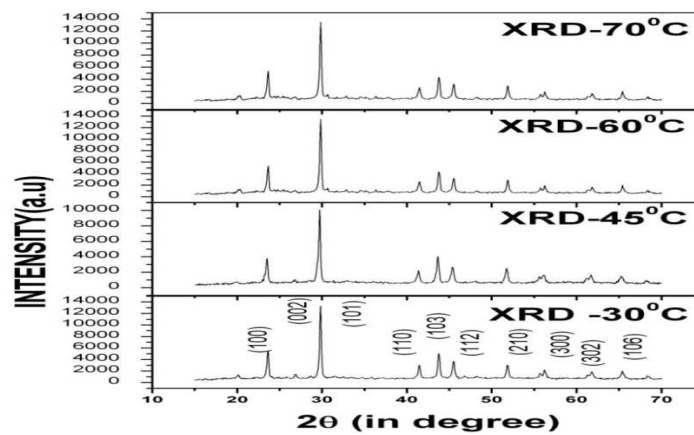


Figure 2 The XRD pattern of the sample ZnSe- nanomaterials

Figure 3 displays the variation of optical absorbance with wavelength of nanomaterials. Optical absorption coefficient has been calculated in the wavelength region 350-700nm.

The band gap of the as-prepared nanorods is determined from the relation

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

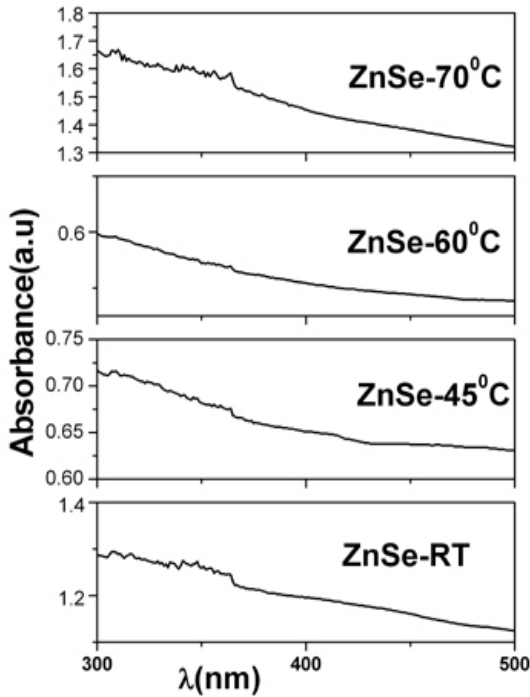


Figure 3 Optical absorption spectra of for different samples

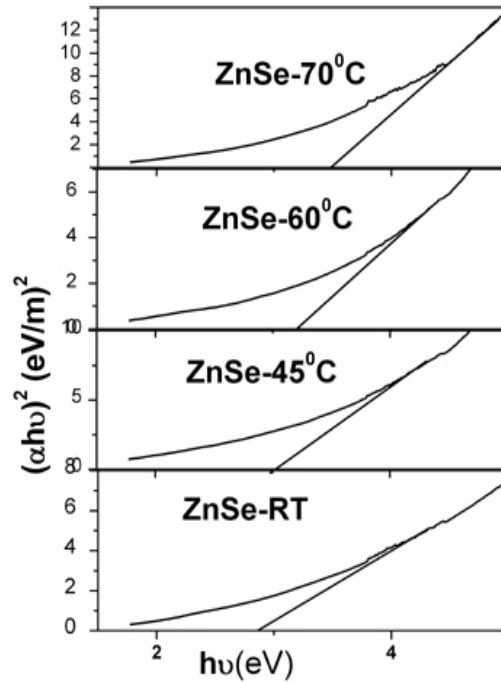


Figure 4 The band gap determination curve different samples

where C is a constant. E_g is the band gap of the material and α is the absorption coefficient. A plot of $(ah\nu)^2$ vs. energy ($h\nu$) is shown in figure 4 and is used to determine band gap. The band gap is found to be $E_g = 2.92\text{eV}$, 3.00 eV , 3.2eV and 3.5eV for the temperature 30°C , 45°C , 60°C , and 70°C respectively

Hence band gap is found to be maximum at grown temperature 70°C . This is due to the more quantum confinement at that particular reaction temperature. The photoluminescence spectra of ZnSe sample are displayed in the figure 5.

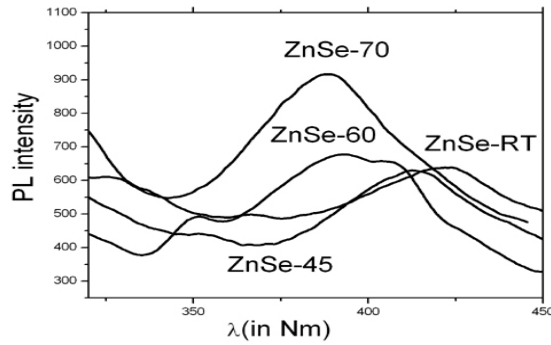


Figure 5 The photoluminescence spectra of as synthesized samples

The photoluminescence spectra show the shift of peak towards lower wavelength as the temperature is increased This is in agreement with the optical absorption data. These peaks are due to surface states appearing in the range 380-430 nm. The growth of photocurrent is shown in figure 6. After the steady current is reached the light is off. Relaxation times are measured from long time photodecay graph.. Relaxation time is measured using the relation

$$\Delta n = \Delta n_s \exp (-t / \tau) \dots\dots\dots(2)$$

This relation can be correlated to experimentally measurable parameter by

$$\frac{\Delta n_s}{\Delta n} = \frac{\Delta I_{ph(s)}}{\Delta I_{ph(t)}} = \exp (t / \tau) \dots\dots\dots(3)$$

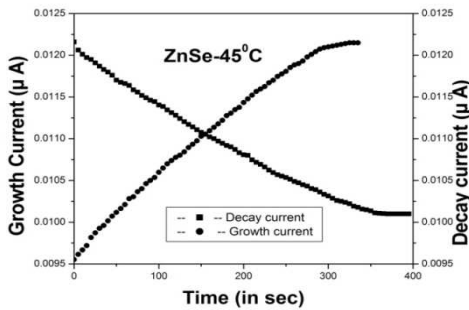


Figure 6(a)

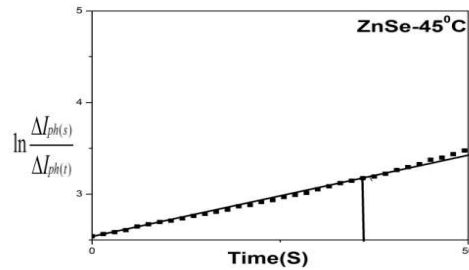


Figure 6(b)

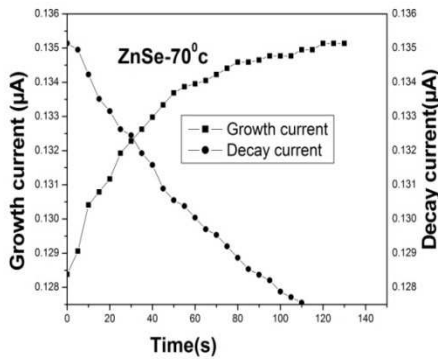


Figure 6(c)

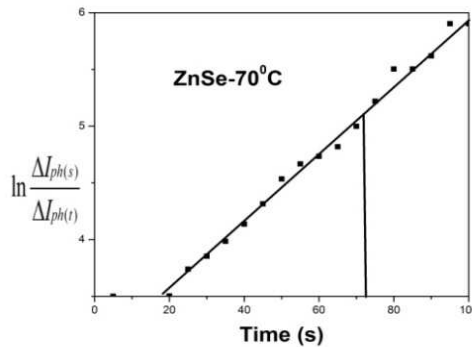


Figure 6(d)

Figure 6 (a) (b) (c) (d) The photoconductive growth, decay current and determination of relaxation time graph for two typical samples.

$\Delta I_{ph(s)}$ 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.

The plot of $\ln \frac{\Delta I_{ph(s)}}{\Delta I_{ph(t)}}$ vs. t gives the straight line. Two typical plot are displayed in figure 6(a) (b)

The long time relaxation is estimated from the slope of the respective curve.

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.

CONCLUSIONS

The ZnSe nanoparticles and nanorods are synthesized by chemical method at different temperature. The XRD pattern shows mixture of hexagonal & cubic phase for all cases. The TEM images shows that nanorods are formed when growth temperature are at room temperature & at 45⁰C. With increasing growth temperature the probability of formation of nanorods are reduced & formation of particles are increased. It is observed that smaller particles are formed at higher growth temperature. The tendency of formation of nanoparticles at higher temperature is probably due to the decrease of free energy. Band gap energy of that sample becomes maximum at higher reaction temperature. Also the peak of the PL spectra is shifted towards higher energy for greater reaction temperature & long time relaxation shifts towards lowest value. All these effects clearly show more and more quantum confinement at the greater growth temperature.

ACKNOWLEDGEMENTS

Authors are acknowledging Department of Physics of Vidyasagar University for XRD measurement. Authors are thankful to IIT Kharagpur for graciously allow the use of TEM measurement.

Table 1. Summarisation Table

Name of the samples	Temperature	Size of the nanoparticles/nanorods (nm)	Relaxation time in (sec)	Band gap (eV)
	(in ⁰ C)			
ZnSe-1	30	Rods length 229.74-267.01 diameter 11.44-16.24	77	2.92
ZnSe-2	45	Rods length 100-215, diameter 7-14	54	3
ZnSe-3	60	Diameter 19.73-38.04	45	3.2
ZnSe-4	70	diameter 8.58-26.26	38	3.5

REFERENCES

- [1] Lv. R, Cao .C, Zhai. H, Wang. D, Liu. S, Zhu .H, (2004), Solid state Commn,130, 241
- [2] Orr. G.W, Larbaur.J. B, Atwood. J.L, (1999),Science 285, 1049
- [3] Goldberger. J, Zhang. R. He ,Y, (2003),Nature, 422, 599
- [4] Wang .Z.L, Gao. R. P , Gole .J. L, (2000),Adv. Mater, 12 ,1938
- [5] Rao .C.N.R, Gobindaraj. A, Deepak. F.L, (2001), Appl.Phys.Lett, 78 ,1853
- [6] Xiong .Y, Xie. Y, Yang. J, (2002), J.Mater.Chem, 12 ,3712
- [7] Dloczik .L, Engelhardt. R, Ernst. K, (2001) ,Appl.Phys.Lett, 78 ,3687
- [8] Collins. P.G, Zettl .A , Bando. H, (1997),Science, 278, 100
- [9] Wong. E.W, Sheehan .P.E , Lieber .C M, (1997),Science ,277 ,1971
- [10] Chen. T .Y, Ding .J.B , Guo. Y, (2002),Chem.Phys Mater, 77 ,734
- [11] Xu.D, Xu .Y, Chen. D, (2000),Adv.Mater, 12, 520
- [12] Yang .J , Zeng. J.H, Yu. S.H, (2000),Chem. Mater, 12 ,3259
- [13] Li.Y.D, Liao .H.W, Ding Y, (1998),Chem .Mater, 10, 2301
- [14] Liao. X.H, Wang. H, Zhu. J, (2001), Mater. Res.Bull, 36, 2339
- [15] Chopra N.G, Luyken. R.J, Cherry K, (1995),Science, 269, 966
- [16] Korgel. B.A, Fitzmaurice. D, (1998),Adv. Matter, 10, 661
- [17] Ray. O, Sirenko .A.A, Berry. J.J, (2000),Appl. Phys.Lett ,76 ,1167
- [18] Wagner .H.P, Tranitz. H.P, Schuster .R, (2001),Phys. Rev. B ,63, 155311
- [19] Wallace. C.H.C, Sha. X., Yuxiu .S, (2009),J.Phys.D: Appl.Phy, 42,125410