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Characteristics of CdSe Nanocrystalline Thin Films at Two Immiscible Liquids

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Abstract

In this paper, we report a simple method for the assembly of CdSe nanocrystals into thin films at water-hexane interface. The size and morphology of the CdSe nanocrystals were found to be dependent the reaction temperatures. The decrease in band gap and the increase in particles size with rising reaction temperatures are found to be gradual. The growth of CdSe thin films were characterized with scanning electron microscopy, transmission electron microscopy as well as UV-vis spectroscopy.

Key words: Nanocrystals; Cadmium selenide; Thin film; Two immiscible liquids.

1. Introduction

Inorganic nanocrystals have attracted a great deal of research interest because of their use in technological applications in field effect [1-8] solar cells, optoelectronic devices, high efficiency thin film transistors [9-14]. A various of methods of it's preparation have been grown. They include chemical vapour deposition, spray pyrolysis, and chemical bath deposition [15-19]. The interface of two immiscible liquids has not investigated sufficiently, and lately, there has been a lot of effort to understand the structure and properties of the liquid-liquid interface. This possesses properties different from the bulk phases due to Surface tension, density, and viscosity effects as well as interfacial emulsification [20].The potential use of the organic –aqueous interface to assemble nanocrystals has been studied [20]. Because of the quality of the medium, assembly by the use of two immiscible liquids is less prone to defects than assembly utilizing other techniques.

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Cadmium selenide (CdSe) is a semiconductor material important for the advancement of a number of modern technologies. Recently, much effort has been devoted to the electrical and optical properties of CdSe thin film in order to improve device's performance such as solar cells and related optoelectronic devices, high efficiency thin film transistors [21-26].

Another area of interest is CdSe nanoparticles. Researchers are concentrating on improving controlled synthesis of CdSe nanoparticles. Polycrystaline thin films of CdSe have been created at the liquid/liquid interface via reacting cadmium cupferronate in organic phase with dimethyl selenourea in the aqueous phase [27]. Bawendi and co-workers [28] have synthesised CdSe nanocrystals via reacting of dimethyl cadmium and trioctyl phosphine selenide.

Here, we have successfully formed CdSe nanocrystals thin film at the interface of two immiscible liquids and describe how various reaction temperatures affect the films formed.

A metal precursor dissolved in a solvent such as hexane is held in contact with sodium seleno sulfate. The reaction yields at the interface of liquids and results in deposits suspended in the interface region.

2. Experimental section

2.1 Synthesis of sodium selenosulfate

Sodium selenosulfate was prepared utilizing method reported previously [29]. A 50 ml aqueous dispersion containing 1 g Se powder and 10 g sodium sulphite was heated under reflux in round bottomed flask at 70°C for 24 h to obtain a nearly clear reddish solution. The solution was cooled to room temperature and a small quantity of insoluble particles filtered to obtain a solution of sodium selenosulphate as shown in the following equation

$$Na_2SO_3\,(aq) + Se\,(s) \rightarrow Na_2SeSO_3\,(aq). \qquad (1)$$

2.2 Synthesis and assembly of CdSe thin films

Thin film of CdSe nanocrystal was prepared by layering 30 ml of hexane containing 0.05 g of cadmiumdiethyl dithiocarbamate over 30 ml of freshly prepared solution of Na_2SeSO_3 whose pH was adjusted to less than 10 using aqueous KOH. The beaker containing the liquids was moved into an oven held at 50°C and left undisturbed for 10 h. At the end of this time, a brown film was found adhered to the interface of the two liquids as shown in figure 1. Before the transfer, the organic layer at the top was decanted. The reactions happened are:

$$Na_2SeSO_3\,(aq) + 2OH^-\,(aq) \rightarrow Se^{2-}\,(aq) + Na_2SO_4\,(aq) + H_2O \qquad (2)$$

$$Cd(S_2CNEt_2)_2\,(if) + Se^{2-}\,(if) \rightarrow CdSe\,(if) + (S_2CNEt_2)_2^{2-}\,(ol) \qquad (3)$$

It is possible to influence the structural and optical properties of films by changing the reaction temperatures. The effects deposition temperature on the properties of CdSe deposits were studied.

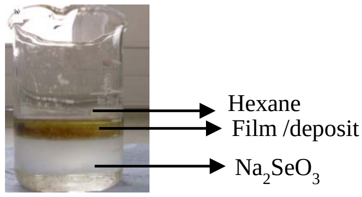

Figure 1: Nanocrystalline films of CdSe formed at the water –hexane interface.

3. Characterization of CdSe

CdSe films at the water-hexane interface were transferred to glass substrates and Transmission electron microscopy (TEM) grids. TEM was carried out with a Philips CM200 electron microscope operating at 200 keV. Samples for TEM were prepared by drop casting dispersions of the film in ethanol on holey carbon coated copper grids. Scanning electron microscopy (SEM) was performed using Philips Excel SEM equipped with a 30 kV field emission gun. Extinction spectra were recorded using Cary 5000 UV-vis-NIR spectrophotometer.

4. Results and discussion

Figure 2 SEM images of the synthesized CdSe thin films formed at the interface, it displays the morphology of CdSe films. It clearly shows the changing morphology of the thin films as the temperature varies from 40ºC to 60°C. At 40ºC consists of spherical grains were adorned with smaller, granules with critical size ranging from several nanometers to a micrometer. While films obtained at 60°C were composed globular clusters with microscopic dimensions

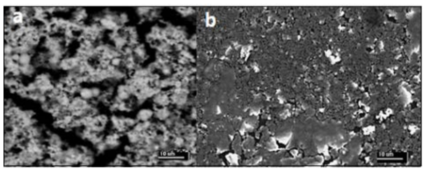

Figure 2: SEM images of CdSe thin films deposited at the water – hexane (a) at 40°C and (b) at 60°C

TEM images of CdSe, synthesised at two different temperatures are shown in figure 3. The dimension of these grains is controlled by the temperature, with the rise of reaction temperatures from 40ºC to 60ºC diameter of CdSe appears to nanocrystals increases from 10 nm to 18.74 nm.

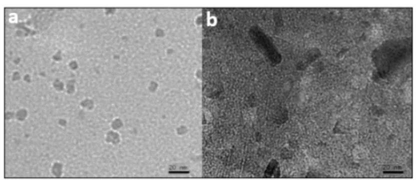

Figure 3: TEM images of CdSe thin films nanocrystals formed at interface (a) at 40°C and (b) at 60ºC

Previous reports have been successful in depositing cubic CdSe films of CdSe nanocrystals with diameters ringing from 8-20 nm [30] .

The absorption spectra exhibited by rising reaction temperatures from 40°C to 60°C the band edge blue shifts from 1.80 eV to 1.71 eV. The adsorption edge was calculated using the Tauc relation [31].

$$(\alpha h\nu) = \text{constant}\ (h\nu - E_g)^{n}$$

Here, Eg is the band gap, n is a constant equal to 0.5 for direct band gap semiconductors. Employing this relation, a graph is plotted between the $(\alpha h\nu)^2$ against hν to obtain a straight line figure 4. The extrapolation of straight line to square of (αhν) =zero axis gives the value of the absorption edge. The edge blue shifted from 1.80 eV at 40°C to 1.71 eV at 60°C According to Sarma and Sapra [32-34] method, the change in band edge corresponds to an increase in diameter from 14 to 19 nm. This is higher than estimates from TEM images, possibly because the nanocrystals for small conglomerates.

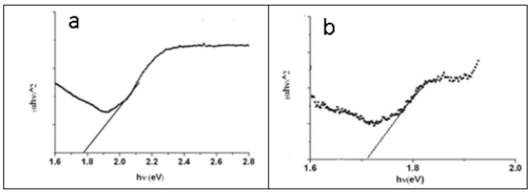

Figure **4:** Absorption spectra of CdSe thin film formed at water-hexane interface ,the plots used to determine the optical band gaps of CdSe thin film obtained (a) at 40°C and (b) at 60°C.

5. Conclusion

CdSe thin films have been formed at the interface of water and hexane, utilizing cadmium diethyldithiocarbamate as metal source and Na_2SeSO_3 as selenium source.The reaction occurs at the interface of two immiscible liquids is sensitive to reaction temperatures, increasing the temperature from 40°C to 60°C almost doubles the nanocrystal diameter from 10 nm to 18.74 nm. SEM images showed sub-microscopic features in deposits at the interface while rising temperatures plays an important role in changing the surface morphology from globular to thinner deposits of similar morphology. From UV-visible spectroscopy is found that the band gap decreases while the wavelength of absorbance shifts to longer wavelengths. The deposits grown at the interface of two immiscible liquids is a facile method to create nanocrystalline thin films of CdSe.

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References

[1] Y. A. Akimov, W. S. Koh, S. Y. Sian, S. Ren, Appl. Phys. Lett. 96 ,2010, 073111

[2] Yu A Akimov , W. S. Koh, Nanotechnology. 21 (2008) 235201.

[3] Han L, Qin D, Jiang X, Liu Y, Wang L, Chen J, Cao Y. Nanotechnology. 2006;**17**:4736–4742

[4] Bailey R E, Smith A M, Nie S. Physica E. 2004;**25**:1–12

[5] Niitsoo O, Sarkar S K, Pejoux C, Ruhle S, Cahen D, Hodes G. J Photochem Photobiol, A: Chem. 2006;**181**:306–313

[6] Nozik A. Physica E. 2002;**14**:115–120

[7] Robel I, Subramanian V, Kuno M, Kamat P V. J Am Chem Soc. 2006;**128**:2385–2393

[8] Chu K C, Su W S, Chen Y F. J Appl Phys. 2006;**100**:024516

[9] Al-Ani S K J, Mohammed H H, Al-Fwade E M N. Renewable Energy. 2002;**25**:585–590

[10] Qiu J, Cheng H, DePuydt J M, Haase M A. J Cryst Growth. 1993;**127**:279–286.

[11] Oduor, A.O. and R.D. Gould, "A comparison of the DC conduction properties in evaporated cadmium selenide thin films using gold and aluminum electrodes". Thin Solid Films, 1998. **317**(1,2): p. 409-412.

[12] Mohanchandra, K.P. and J. Uchil, ”Thermoelectric power of CdS and CdSe films deposited on vibrating substrates". Thin Solid Films, 1997. **305**(1,2): p. 124-129

[13] Lee, M.J. and S.-C. Lee, "Extraction of the trap density and mobility in poly-CdSe thin films. Solid-State Electronics", 1999. **43**(4): p. 833-838.

[14] Samanta, D., et al., "Electrical characterization of stable air-oxidized CdSe films prepared by thermal evaporation". Semicond. Sci. Technol., 1996. **11**(4): p. 548-53.

[15] P.O’Brien, chemistry,1991.**5**.61.

[16] C.M.Rouleau,D.H.Lowndes,Appl.Surf.Sci.127-129 1998.**418**.

[17] K.Subbaramaiah and V.S.Raja,Sol.Energy Mater.Sol.Cells,1994,**32,**1.

[18] P.O’Brien and T.Saeed,J.Cryst.Growth,1996.**158**,497

[19]Y.J.Change,C.H.Munse,G.S.Herman,J.F.Wager,P.Mugdur,D.H.Leeand C.H.Change,Surf.Interface Anal,2005,**37**,398

[20] O'Brien, P. and R. Nomura, "Single-molecule precursor chemistry for the deposition of chalcogenide(S or Se)-containing compound semiconductors by MOCVD and related methods". J. Mater. Chem., 1995. **5**(11): p. 1761-73.

[21] Oduor, A.O. and R.D. Gould, "A comparison of the DC conduction properties in evaporated cadmium selenide thin films using gold and aluminum electrodes". Thin Solid Films, 1998. **317**(1,2): p. 409-412.

[22] Mohanchandra, K.P. and J. Uchil, "Thermoelectric power of CdS and CdSe films deposited on vibrating substrates". Thin Solid Films, 1997. **305**(1,2): p. 124-129.

[23] Lee, M.J. and S.-C. Lee, "Extraction of the trap density and mobility in poly-CdSe thin films". Solid-State Electronics, 1999. **43**(4): p. 833-838.

[24] Samanta, D., et al., "Electrical characterization of stable air-oxidized CdSe films prepared by thermal evaporation". Semicond. Sci. Technol., 1996. **11**(4): p. 548-53.

[25] Dolocan, V., "Electrical, photoelectrical and optical properties of cadmium selenide thin films". Rev. Roum. Phys., 1983. **28**(7): p. 647-54.

[26] Pal, U., et al., "Optical constants of vacuum-evaporated polycrystalline cadmium selenide thin films". J. Appl. Phys., 1993. **74**(10): p. 6368-74.

[27] Kalyanikutty, K.P., U.K. Gautam, and C.N.R. Rao, "Ultra-Thin Crystalline Films of CdSe and CuSe Formed at the Organic-Aqueous Interface". Journal of Nanoscience and Nanotechnology, 2007. **7**(6): p. 1916-1922.

[28] Murray, C.B., D.J. Norris, and M.G. Bawendi, Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. J. Am. Chem. Soc., 1993. 115(19): p. 8706-15.

[29] Lifshitz, E., et al., "Optical properties of CdSe nanoparticle films prepared by chemical deposition and sol–gel methods". Chem. Phys. Lett., 1998. **288**(2-4): p. 188-196.

[30] Agrawal Ved, V., G.U. Kulkarni, and C.N.R.Rao, "Nature and properties of ultrathin nanocrystalline gold films formed at the organic-aqueous interface". J Phys Chem B, 2005. 109(15): p. 7300-5.

[31] Tauc, J. and Editor, "Amorphous and Liquid Semiconductors". 1974. 441 pp.

[32] Sapra, S. and D.D. Sarma, "Evolution of the electronic structure with size in II-VI semiconductor nanocrystals". Physical Review B, 2004. **69**(12): p. 125304.

[33] Viswanatha, R., et al., "Electronic structure of and quantum size effect in III-V and II-VI semiconducting nanocrystals using a realistic tight binding approach." Physical Review B, 2005. **72**(4): p. 045333

[34] Sapra, S., N. Shanthi, and D.D. Sarma, "Realistic tight-binding model for the electronic structure of II-VI semiconductors". Physical Review B, 2002. **66**(20): p. 205202.