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Preparation and characterisation of nanocrystalline CdSe

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Abstract : Nanostructured CdSe crystals have been prepared by wet chemical method in alkaline medium at 65 - 70°C using cadmium acetate and freshly prepared sodium selenosulphite as Cd and Se ion sources. XRD pattern of the prepared sample shows cubic zinc blende structure with average particle size of 3 4 nm. EDX measurement determines nearly equal atomic concentrations of Cd and Se. The powdered sample of CdSe is characterised using SEM and AFM. Optical absorbance study of thin film of CdSe deposited on glass substrate using chemical bath deposition method shows the blue shift of the band gap of energy of 0 12 eV from the bulk value of 1 7 eV due to quantum confinement effect. The average crystallite size is estimated using effective mass approximation (EMA) as 3 8 nm which agrees well with that obtained using the XRD pattern.

Keywords : Nanoparticles, optical absorbance, semiconductors

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1. Introduction

Nanocrystalline semiconductor materials have attracted many researches for their intriguing physical properties which arise due to the spatial confinement of carriers and increase in the number of surface atoms. Among them group II-VI binary semiconductors in nanocrystalline form occupy a prominent place in the semiconductor physics as they show wide range of applications in optoelectronic devices, solar energy conversions etc. Cadmium Selenide nanocrystal among II-VI semiconductors is of great interest for its potential applications owing to its excellent optical conductivity, such as non linear optical properties, luminescent properties and quantum size effect [1, 2]. In thin film form they

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are used as thin film transistors, gas sensors [3], gamma ray detectors and large screen liquid crystal display [4]. Further, deliberate doping of impurity influences their optical, electronic, structural and other characteristic properties [5-8]. Cadmium Selenide quantum dots have also shown the sensitive dependence of their optical and electrical properties on size, shape, size distribution and morphologies. Such properties attract research workers [9, 10] for fundamental and technological interest.

Among a number of methods for the preparation of the CdSe, wet chemical method offers an inexpensive and simple means to synthesize such particles with good control over size and size distribution by optimising various parameters. Many workers [1, 3, 7, 8] use ammonia for its dual role of forming complex metal ion and varying the pH of the reaction bath and thereby slowing down the reaction rate.

Preparations of CdSe in various shapes, namely, nanorods, nanocables, nanoballs, hollow nanospheres have been investigated by a number of workers [9-12]. R Maity and K K Chattopadhyay reported the preparation of nanocrystalline ZnS and ZnS:Mn by chemical synthesis process without using any capping agent [13]. Ghosh *et al* [14] have also reported the chemical bath deposition of transparent polycrystalline ZnS nonobelts within the pores of polyvinyl alcohol on glass and Si substrates. In this paper we report the synthesis and characterisation of nanostructured CdSe crystals and thin films using wet chemical method without using capping agent. Cadmium Acetate and freshly prepared sodium selenosulphite are used as cadmium and selenium ion sources and liquor ammonia (25%) solution is used as a complexing agent as well as to make the bath alkaline. XRD, SEM and AFM are used to characterize the air-dried powder sample. Thin film of CdSe has been deposited onto the glass substrate using chemical bath deposition method for study of optical absorbance properties. The band gap of CdSe calculated using the absorbance is found to be 1.82 eV. The size of the nanograins of CdSe has been determined using both XRD pattern and effective mass approximation (EMA) using the increase in the value of bandgap from the value of bulk CdSe (1.7 eV). The values are found to agree well.

2. Experimental details

2.1 Sample preparation :

All reagents used are of analytical grade. Cadmium Acetate $Cd(CH_3COO)_2$ and freshly prepared sodium selenosulphite Na_2SeSO_3 are used as the sources of Cd and Se ions respectively. To prepare fresh Na_2SeSO_3 solution 3 gm of Na_2SO_3 is dissolved in 250 ml of distilled water. 0.5 gm of Se metal powder is added to this solution and heated at 90^0C under constant stirring for 8 hours and cooled to room temperature to obtain fresh Na_2SeSO_3 solution. To 250 ml of 0.005M $Cd(CH_3COO)_2$ is added 0.05M NH_4COOCH_3 buffer solution in which 25% liquor ammonia is then added to this until the pH of the bath becomes 9.6. Glass substrates are cleaned following the steps reported by Oladeji and Chow [15]. The cleaned glass substrates are held vertically in the solution with the help of teflon holders and tapes. The solution is now heated upto 65^0C and 30 ml of the

freshly prepared Na_2SeSO_3 is then added slowly at the rate of 1 ml per minute. The reaction continues for 4 hours while red CdSe thin film gets deposited on the glass substrate. The glass substrate with the thin film of CdSe is taken out of the bath, cleaned with distilled water in an ultrasonic bath and air dried at room temperature for its optical absorbance measurement. The temperature of the bath is now increased to 70^0C for the homogeneous reaction to start and precipitation of CdSe starts taking place in the solution. The CdSe colloids in the bath is centrifuged and extracted with methanol. The CdSe precipitate is washed with several times with distilled water and air dried at room temperature and kept in desiccators for its characterisation.

2.2 Reaction mechanism

The reaction mechanism involved in the formation of CdSe [16, 17] is as follows :

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \quad (1)$$

$$Cd^2 + 4NH_3 \leftrightarrow Cd(NH_3)_4^{2+} \quad (2)$$

In an alkaline solution, the inorganic sodium selenosulphite hydrolyses to give Se^{2-} ions and reacts with Cd^{2+} to form the CdSe.

$$Na_2SeSO_3 + 2OH^- \leftrightarrow Na_2SO_4 + H_2O + Se^{2-} \quad (3)$$

and $$Cd^2 + Se^{2-} \leftrightarrow CdSe \quad (4)$$

If the ionic product $[Cd^{2+}][Se^{2-}]$ exceeds the solubility product, K_{sp}, of CdSe (4.0×10^{-35}), then CdSe will form as solid phase [4,16].

2.3 Characterisation :

The particle size and crystal structure of the samples are determined from XRD data using a Rigaku 18 kW Rotating X-ray generator equipped with Rigaku D-Max-300 $\theta - 2\theta$ Goniometer with CuK_α X-radiation. The ionic composition is determined using energy dispersive X-rays (EDX) data. The micrographs of the sample dispersed on the glass substrate are recorded using SEM (JSM-5600) and a Digital Instruments Nanoscope AFM (E Verson-245). The optical absorbance of CdSe deposited on glass substrates is recorded using UV-Visible Spectrophotometer (Systronics-2202).

3. Results and discussions

Figure 1 shows the XRD pattern of the nanostructured CdSe crystals. The diffraction peaks are observed at the 2θ values of 25.665^0, 42.650^0, 49.650^0, 67.709^0 and 78.021^0 corresponding to the crystal planes of (111), (220), (311), (331) and (422) respectively, showing the cubic zinc blende structure of CdSe [18]. CdSe has been reported to exist both in cubic phase [1,3,6,10] and in hexagonal phase [19]. Different workers have revealed the co-existence of hexagonal and cubic CdSe crystallites with preferential orientation

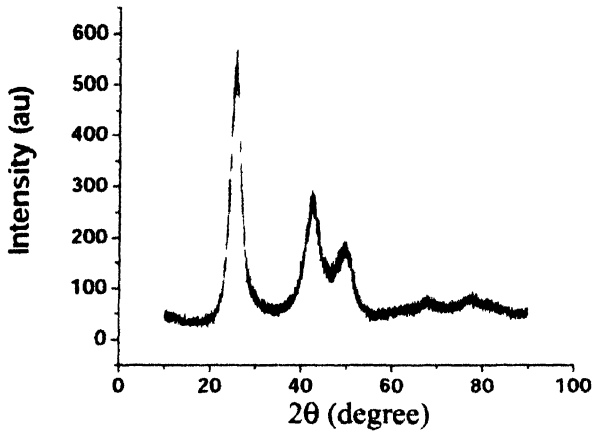

Figure 1. XRD pattern of nanostructured CdSe crystals

along *c*-axis and (111) direction respectively [4,20]. In this work, CdSe nanocrystals are found to exist only in cubic phase. The prominent peaks have been utilised to estimate the grain size of the samples with the help of Scherrer formula [21], $D = K\lambda/\beta\cos\theta$, where D is the average crystallite size, K is a constant (~1), β is the full width at half maximum and θ is the Bragg's angle. The grain size estimated using the (111) peak is found to be 3.4 nm The ionic concentrations of cadmium and selenium of the prepared CdSe sample are determined using EDX. Cadmium ion concentration exceeds slightly that of the selenium ion by about 9% with a small trace of sulphur ion of about 6%. Figure 2 shows the SEM picture of the powdered sample of CdSe. The picture shows that the 3 4 nm nanograins have agglomerated to form a bigger particle of nearly 1 micron size with sharp boundaries. The SEM picture shows that bigger agglomerated particles are homogeneous in size.

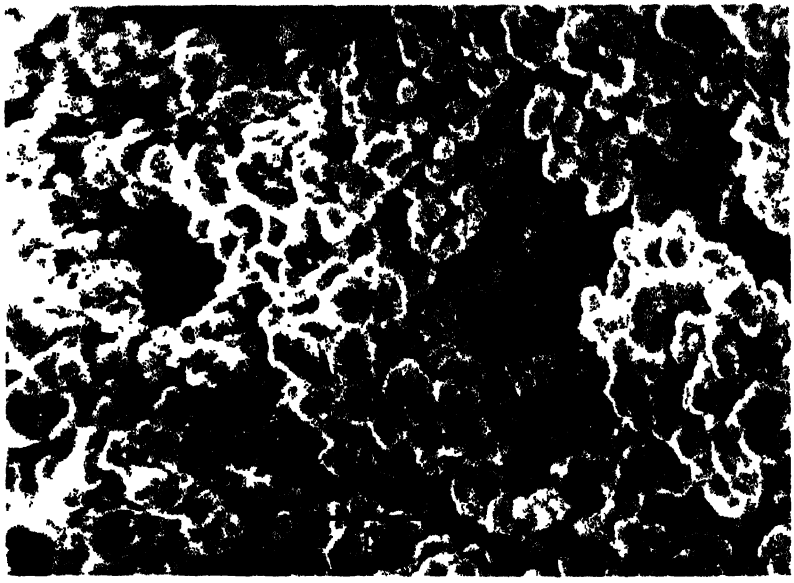

Figure 2. SEM picture of CdSe powder.

Figures 3(a) and 3(b) shows two dimensional (2D) and three dimensional (3D) AFM images of CdSe powder samples dispersed in acetone over a glass substrate. The particles are found to form small spherical islands of an average diameter of 150 nm. However, section analysis of two spherical islands shows that the islands have vertical distances of

5.991 nm and 11.701 nm. This shows that although a single particle could not be selected for the AFM observation the particles lie in the range of 6-12 nm. Kale *et al* [22] attributed the formation of small islands of ZnSe to the indication of three dimensional growth of the film of ZnSe deposited using modified chemical bath deposition method.

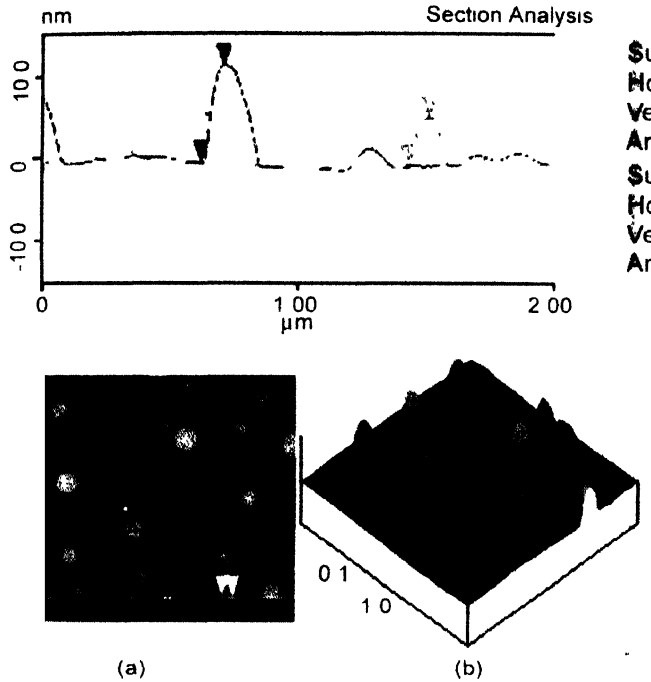

Figure 3. Two dimensional (2D) and three dimensional (3D) AFM images of CdSe powder

The absorbance of the CdSe thin film deposited on the glass substrate is shown in figure 4. The band gap of the sample is calculated from the absorption spectra shown in figure 4 using the relation [23] $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$ where α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant and E_g is the band gap of the material. The value of n in the exponent is 1/2 for direct, allowed transitions.

Figure 5 shows the plots of $(\alpha h\nu)^2$ *versus* $h\nu$. The linear portion of the plot of $(\alpha h\nu)^2$ *versus*

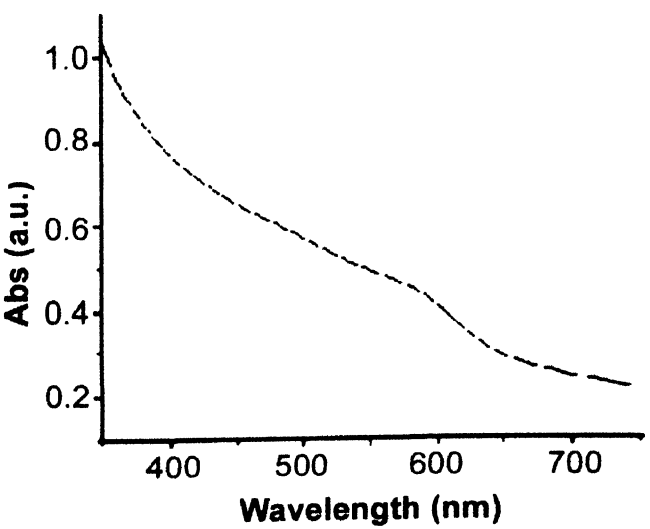

Figure 4. Absorbance spectra of thin film of CdSe deposited on a glass substrate.

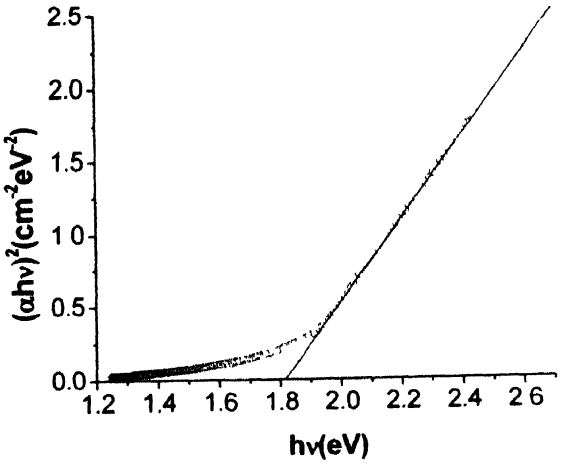

Figure 5. Curve showing $(\alpha h\nu)^2$ *versus* $h\nu$ (open circles) of CdSe thin film. The solid line shows the extrapolation of the linear portion of the strong absorption region.

$h\nu$ in the region of strong absorption has been extrapolated to obtain the intercept on the $h\nu$ axis. The intercept gives the value of the band gap E_g. The value of E_g is found to be 1.82 eV, which exceeds the band gap 1.70 eV of bulk CdSe. This is attributed to the quantum confinement effect as the particle size becomes smaller [24]. The grain size of 3.4 nm obtained from the XRD data shows that it is appreciably smaller than the Bohr exciton radius 5.6 nm of CdSe. The exciton energy E_s obtained using effective mass approximation (EMA) for strong confinement is given by [23, 25] $E_s = E_g + \hbar^2\pi^2/2\mu R^2 - 1.786e^2/4\pi\varepsilon_0\varepsilon R - 0.248E^*_{Ry}$, where μ is the reduced effective mass, ε is the dielectric constant of CdSe and ε_0 is the permittivity in vacuum, E^*_{Ry} is the effective Rydberg energy. Using this relation the grain size of the prepared CdSe is found to be 3.8 nm, which is quite near to the size 3.4 nm obtained from XRD data.

4. Conclusion

Nanostructured CdSe both in powder form and thin film has been prepared using chemical method. The grain sizes obtained using XRD (3.4 nm) and EMA (3.8 nm) are found to agree well. The particles are found to be in cubic phase. SEM pictures shows the grown samples are homogeneous in size. AFM picture of the sample shows spherical islands having heights of 6-12 nm. The band gap calculated using the absorbance spectra of the deposited CdSe film gives a value of 1.82 eV.

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