OPTICAL AND STRUCTURAL PROPERTIES OF CHEMICAL BATH DEPOSITED CdSe NANOPARTICLE THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

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Room temperature chemical bath deposition of CdSe nanoparticles on glass slides has been carried out using cadmium ions (complexed with NH_3) and solution of sodium selenosulphate. Triethanolamine was employed as a pH stabilizer. The deposited nanoparticle thin films were annealed at 100°C and 150°C and then characterized using X-ray diffractometer, scanning electron microscope and spectrophotometer. Analysis of the optical characterization shows that high temperature annealing has significant influence on the absorbance, transmittance and band gap energy of the films. From the optical absorption spectra, the band gap energy for CdSe nanoparticle thin films were found to lie within 1.50eV - 1.70eV. These values are in the desired interval for the films to be used as absorber materials in solar cell architecture.

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1. Introduction

The Chemical Bath Deposition (CBD) technique has become very popular in recent decades, especially for thin film deposition, due to its low cost since no expensive and sophisticated vacuum equipments are required, ease of handling and ease of application to many compounds such as sulphides and selenides which include ZnS, CdS, PbS, CdSe, CuS_2, ZnSe, Sb_2S_3, TlS and HgS [1-9].

Presently nanocrystalline materials have opened new chapter in the field of electronic application since changing the crystallite size of film could change material properties. The technological potentialities of nanoparticles have also generated interest in CBD techniques [10].

The review of literature reveals that various research groups with a view to finding the optimum deposition condition for CdSe thin film for use in device applications have investigated a lot of parameter variation. For instance, Mahmoud and co worker [11] studied PVP-capped CdSe nanoparticles embedded in PVA matrix and found from the I-V characteristic curve that the film shows a photovoltaic cell-like behaviour. Lokhande et al [12] developed a method to synthesis CdSe from ammonia-free chemical bath and found out that the films are microcrystalline and photoactive. It has also been reported that the growth of (Cd, Hg)Se pseudobinaries depends on various preparative parameters and deposition conditions such as concentration of the starting materials, pH, temperature, time and speed of mechanical churning [12]. Other studies were focused on formation of ternary thin films based on CdSe and were tested for possible application as solar cell buffer layer [14], solar rechargeable storage cells [15] and in opto-electonic devices [16].

In this paper the influence of annealing temperature on the optical properties and band gap energy of chemical bath deposited CdSe nanoparticle thin films is presented. The films are also studied for possible application in solar cell architecture.

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2. Experimental

Glass microscope slides were cleaned by degreasing them in concentrated hydrochloric acid for 24 hours, washed in detergent solution, rinsed in distilled water and dried in oven at 50°C. The bath constituents for deposition of cadmium selenide (CdSe) nanoparticle thin films were cadmium acetate ($Cd(CH_3COO)_2$) as a source of Cd^{2+}, sodium selenosulphate (Na_2SeSO_3) as a source of (Se^{2-}) in the presence of ammonia (NH_3) as the complexing agent. Triethanolamine (TEA) was employed as a pH stabilizer.

To obtain deposition of CdSe nanoparticle thin films, the chemical bath was composed of 5ml of 1M $Cd(CH_3COO)_2$, 10ml of 7.4M TEA, 5ml of 13.4M NH_3, 4ml of 1M Na_2SeSO_3 and 40ml of H_2O put in that order into 80ml beaker. Clean microslide was then inserted vertically through synthetic foam into the mixture. The deposition was allowed to proceed at room temperature for 8hours after which the coated substrate was removed, washed well with distilled water and allowed to dry. The deposited films were annealed in air at 100°C and 150°C for one hour. The samples were then labelled as A (as-grown), B (annealed at 100°C) and C (annealed at 150°C).

The deposited films on glass substrate were characterized by using scanning electron microscope (SEM) JEOL 1600 model. The X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray diffractometer of CuKα wavelength (1.5408Å). Optical properties of chemical bath deposited CdSe nanoparticle thin films were measured at room temperature by using a double beam Perkin-Elmer UV-VIS Lambda 35 spectrometer with glass substrate as a reference in the wavelength range of 200–900 nm.

3. Results and discussion

3.1 XRD Spectra

CdSe thin films may grow with either sphalerite cubic (zinc-blende type) or the hexagonal (wurzite-type) structure [17, 18]. The hexagonal state is the stable phase while the sphalerite cubic is the metastable state. Figure 1 shows the XRD patterns of CdSe thin films deposited in this work and annealed at 100°C. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of crystalline thin films.

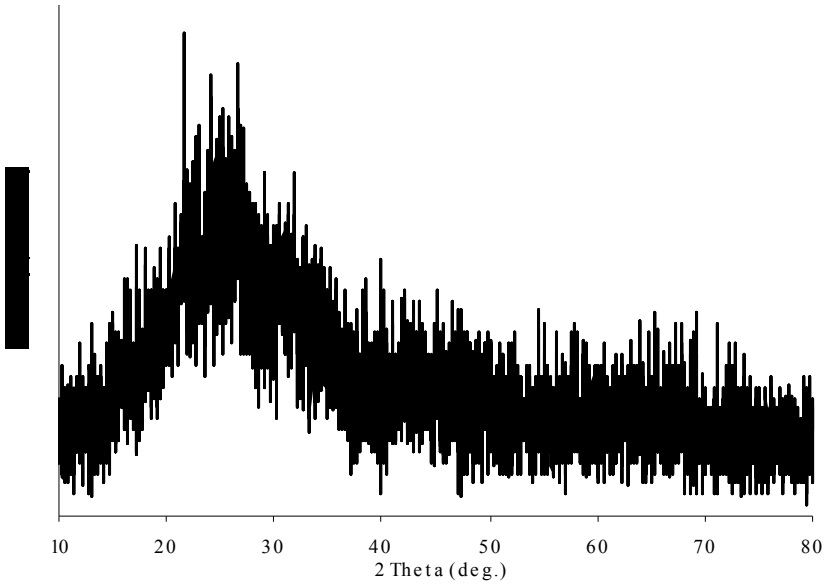

Fig. 1. XRD pattern for CdSe nanoparticle thin film annealed at 100°C

The most prominent peaks extend from 21.62°, 24.02°, 26.64°, 31.84° and 39.88° in 2θ angular units. The 21.62° peak corresponds to hexagonal (100) plane while the low intense reflection peak at 25.74° corresponds to cubic (111) plane, which agrees with the standard values [17, 18]. The low intensity peaks observed in the XRD pattern of the sample under study shows that the films are coarsely fine crystallites or nanocrystalline. The broad hump in the displayed pattern is due to the amorphous glass substrate and also possibly due to some amorphous phase present in the CdSe nanoparticle thin films.

The average crystallite size of the films was calculated from the recorded XRD patterns using Scherrer formula:

$$D = 0.89\,\lambda/\beta \cos\theta, \quad (1)$$

where D is the average crystallite size, λ is the wavelength of the incident X-ray, β is the full width at half maximum of X-ray diffraction and θ is the Bragg's angle. The average crystallite size for the thin film of CdSe was found to be 23.54nm.

3.2 SEM

Scanning electron microscopy (SEM) is a convenient method for studying the microstructure of thin films. Figure 2 show the surface morphology of CdSe nanoparticle thin films deposited at room temperature and annealed at 100°C at different magnifications. From the micrographs, it is observed that the films were formed from uniformly deposited nanoparticles and covered the substrate well. SEM image also reveals the grain boundaries around the crystallites.

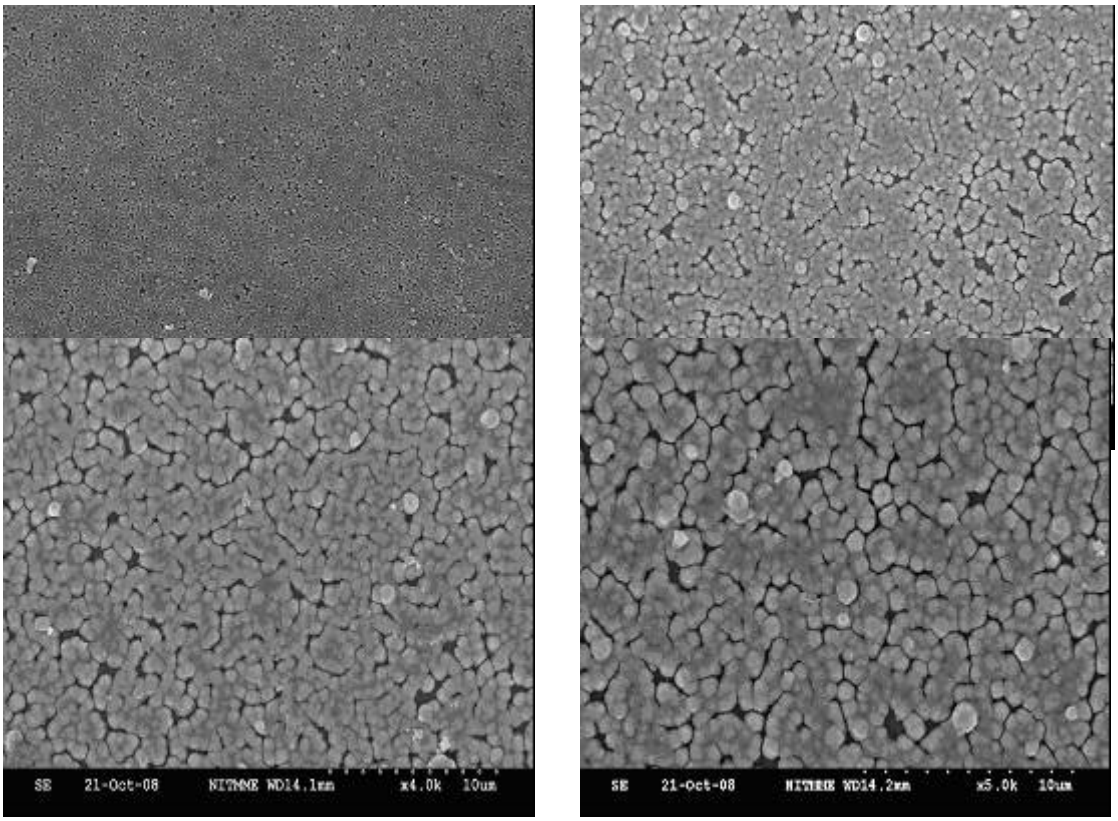

Fig. 2. SEM of CdSe nanoparticle thin film annealed at 100°C at different magnifications

3.3 Variation of the absorbance and transmittance of the films with wavelength

The optical absorption spectra of the films deposited onto glass substrate were studied in the range of wavelengths 200 – 900nm. The variation of absorbance with wavelength for the

samples annealed at different temperature and the as-grown film are shown in figure 3. The figure shows that the films have good absorption in the VIS and NIR spectrum of solar radiation. The as-grown film has the highest absorbance within the visible region of the solar spectrum. However, there is a slight lack of trend in the absorbance values displayed in the figure, caused by the film annealed at 100°C. The immediate cause of this is not easily discernible and may have been caused by unforeseen deposition condition. The transmittance of the films against wavelength shown in figure 4 shows that the films deposited in this work have very low transmittance of both visible and infrared radiation. There is a slight red shift in the transmittance of the films with annealing temperature and with the peaks occurring at a wavelength of 625nm (as-grown), 655nm (annealed at 100°C) and 290nm (annealed at 150°C).

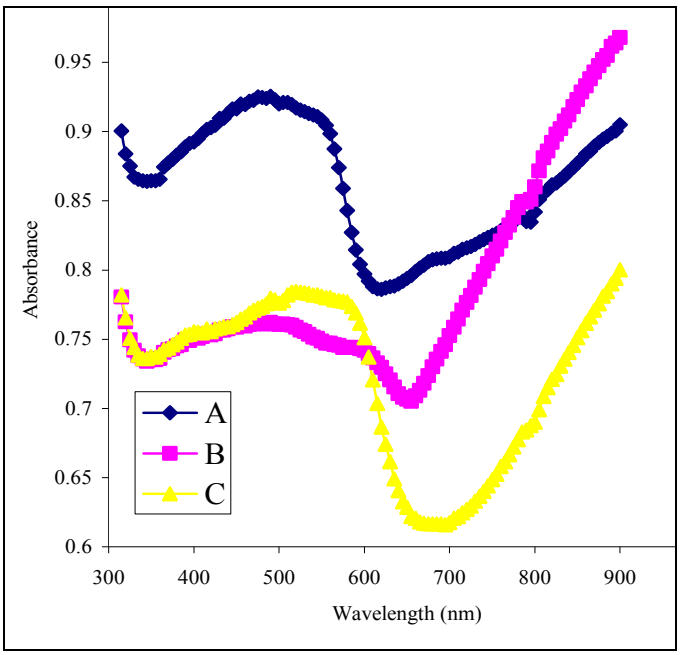

Fig.3. Absorbance vs. wavelength for CdSe nanoparticle thin films

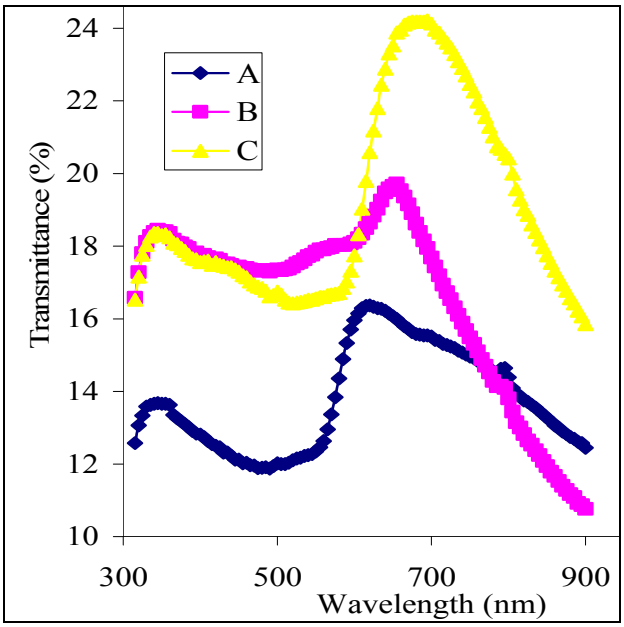

Fig.4. Transmittance vs. wavelength for CdSe nanoparticle thin films

3.4 Absorption coefficient and energy band gap

Figure 5 is a plot of the absorption coefficient against photon energy for CdSe nanoparticle thin films deposited in this work. Band to band transition in semiconductor thin films depends on the absorption coefficient α and photon energy by the relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g)^{1/2} \quad (2)$$

Where A is a constant, hν is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively. The usual difficulty in applying this concept to polycrystalline thin films with nanometer-scale crystalline grains is the size distribution of grains and consequent variation in the band gap due to quantum confinement effects. Thus the straight-line portion may not extend beyond a few tenths of an electronvolt, and hence value of the band gap could turn out to be very subjective [22]. The best fit of the experimental curve to a band gap semiconductor absorption function was obtained for n = ½.

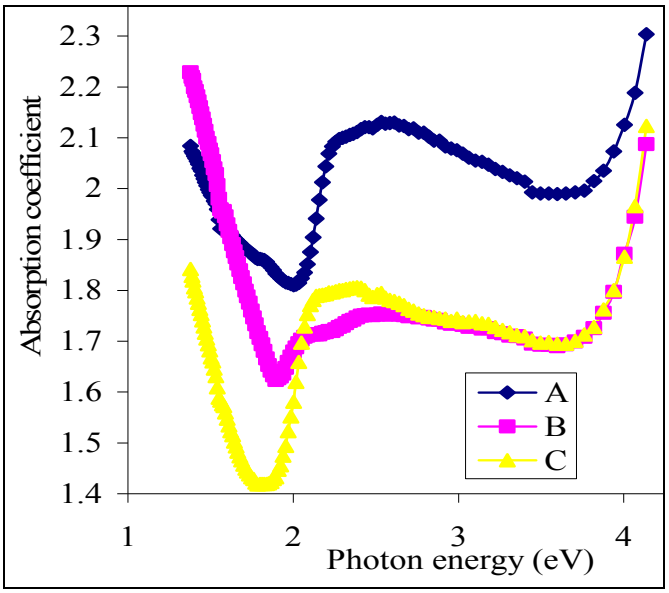

Fig.5: Absorption coefficient vs. photon energy for CdSe nanoparticle thin films

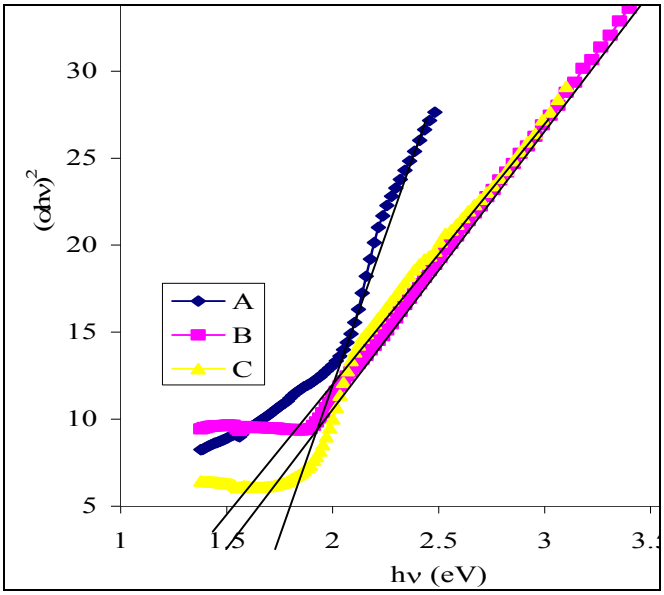

Fig.6: Plot of $(\alpha h\nu)^2$ vs. hν for CdSe nanoparticle thin films

The calculated values of the direct energy band gap, from figure 5 lie in the range of 1.50eV – 1.70eV. Annealing the sample in the oven reduced the value of band gap energy from 1.70eV for the as-grown to 1.50eV for the film annealed at 150°C. Other researchers have observed this trend too. However, the band gap energy obtained here are low when compared with the values in literature [19, 23]. A material with a direct band gap lower than 1.9eV and a high absorption coefficient of more than $10^4 cm^{-1}$ has been regarded as a promising absorber for thin film photovoltaic applications. The low band gap values exhibited by CdSe nanoparticle thin film together with high absorbance in the VIS make the film ideal for use as absorber material in solar cell application.

4. Conclusion

Nanocrystalline thin films of CdSe were successfully deposited on glass slide using chemical bath deposition technique. XRD studies reveal that the CdSe nanoparticle thin films have a preferred orientation in the (100) plane of a hexagonal structure. The average crystallite size was found to be 23.54nm. Optical studies and band gap analysis show that thermal annealing has significant effect on these properties. The values of band gap energy exhibited by the films are in the required range for the application of the films as absorber layer in solar cell fabrication.

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