ROLE OF THERMAL ANNEALING ON THE OPTICAL AND SOLID STATE PROPERTIES OF CHEMICALLY DEPOSITED CADMIUM SULPHIDE NANOCRYSTALLINE THIN FILM GROWN IN A POLYMER MATRIX

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Nanocrystalline thin films of CdS are deposited on glass substrates by chemical bath deposition technique using polyvinyl alcohol (PVA) matrix solution. The crystallite size of the nanocrystalline films are determined from broadening of X-ray diffraction lines and are found to be 16.39nm. Optical properties such as absorbance and transmittance were determined using Unico UV-2102 PC Spectrophotometer, at normal incidence of light in the wavelength range of 200-1000nm. From the absorbance and transmittance spectra, the band gap energy was determined. The band gap energy was found in the 2.25 to 2.65 eV range. The result shows that thermal annealing influences both the optical properties and band gap energy of the nanocrystalline thin films.

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1. Introduction

Energy conversion in solar cell consists of generation of electron-hole pairs in semiconductors by the absorption of light and separation of electrons and holes by an internal electric field. Charge carriers collected by two electrodes give rise to a photocurrent when the two terminals are connected externally. The spectrum of solar light energy spreads from the ultraviolet region (300nm) to the infrared region (3000nm). When the photon energy is less than band gap of the semiconductor, the light is transmitted through the material, that is, the semiconductor is transparent to the light. When the photon energy is larger than band gap, the electrons in the valence band are excited to the conduction band. It means that a photon is absorbed to create an electron-hole pair. This process is called intrinsic transition or band-to-band transition. The cutoff wavelength λ_o is very important to choose the solar cell material because the light with wavelength longer than cutoff wavelength cannot be used for solar energy conversion [1].

Cadmium sulphide (CdS) is one of the most promising II-IV compound materials because of its wide range of application in various optoelectronic, piezo-electronic and semiconducting devices [2, 3]. High efficiency thin film solar cells have been achieved using two types of structures: SnO_2:F/CdS/CdTe and ZnO/CdS/$CuInSe_2$ [4]. In these devices, the systems SnO_2:F/CdS and ZnO/CdS act as optical windows and the CdTe and $CuInS_2$ act as absorbent layers. The highest efficiency in CdTe and Cu(InGa)Se_2-based solar cells has been archived using CdS films deposited by chemical bath deposition process[5, 6]. However, poor conductivity as low as 10^{-8} $(\Omega m)^{-1}$ have been reported [7]. In order to overcome this problem, annealing and doping are used [7- 9].

In this study, result of chemical bath deposition of CdS nanocrystalline thin films and the role of thermal annealing on the films' optical and solid state properties are presented.

2. Material and method

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 30^{o}C above room temperature. The bath constituents for deposition of cadmium sulphide (CdS) thin films were cadmium chloride ($CdCl_2$) as a source of Cd^{2+}, thiourea [$(NH_2)_2CS$] as a source of sulphide ions (S^{2-}) in the presence of ammonia (NH_3) as the complexing agent. PVA solution was added to raise the volume of the bath solution to a certain level. The PVA solution used in this work was prepared by dissolving 0.9g of solid polyvinyl alcohol (PVA) in 450ml of distilled water at 90^{o}C. The homogenous solution was aged until the temperature drops to room temperature value. In a typical deposition bath, the solution was composed of 3ml of 1M $CdCl_2$, 5ml of NH_3, 5ml of 1M thiourea and 27ml of PVA solution put in that order. The deposition was allowed to proceed at room temperature for 6hours after which the coated substrate was removed, washed well with distilled water and allowed to dry. Two of the glass-CdS systems were annealed at 100^{o}C and 400^{o}C for one hour.

For optical absorption measurement of the films deposited on glass slides, a similar blank slide was used as reference in a Unico UV-2102 PC spectrophotometer at a scan step of 3nm. Optical band gaps were calculated knowing their absorption edge extrapolated from the absorption spectra. The XRD patterns for the samples were recorded using D/max-2000 Rigaku powder X-ray diffractometer in the 2θ range 20^0 - 80^0 using CuK_α radiation of wavelength λ = 1.5408 Å. The grain size of the deposited films was viewed by using scanning electron microscopy (SEM) technique.

3. Results and discussion

3.1 XRD spectra

Fig. 1 shows the XRD patterns of CdS thin films deposited in this work and annealed at 100^{o}C. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of tiny crystalline mixed with amorphous thin films. The most prominent peaks extend from 21.2^o to 26.5^o in 2θ angular units. The 26.540^o peak corresponds to (111) plane which agrees with JCPDS (:#80-0019). The peak at (111) is attributed to cubic CdS having lattice parameters a=b=c= 5.811Å. The average crystallite size was calculated from the recorded XRD patterns using Scherrer formula:

$D = 0.89\ \lambda/\beta \cos\theta$

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. From the calculation, the grain size was found to be of the order of 16.39nm.

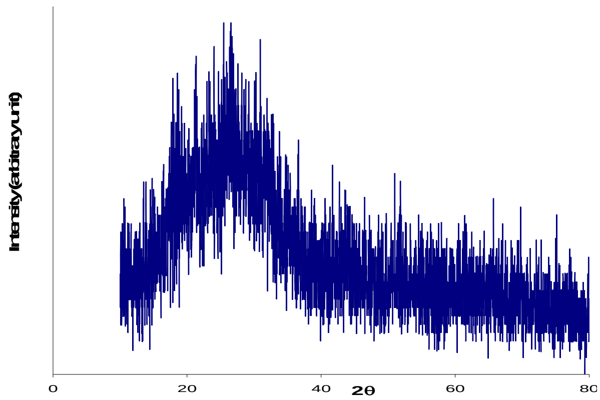

Fig.1. XRD of CdS nanocrystalline thin film.

3.2 SEM Images

Scanning electron microscopy (SEM) is a convenient method for studying the microstructure of thin films. Figure 2 shows the surface morphology of CdS thin films deposited at room temperature and annealed at 373K at different magnifications. From the micrographs, it is observed that the films are uniform throughout all the regions: the films are without pinhole or cracks. From the figure, we clearly observe the small nanosized grains engaged in a fibrous-like porous structure, which indicates the nanocrystalline nature of CdS thin films deposited in this work.

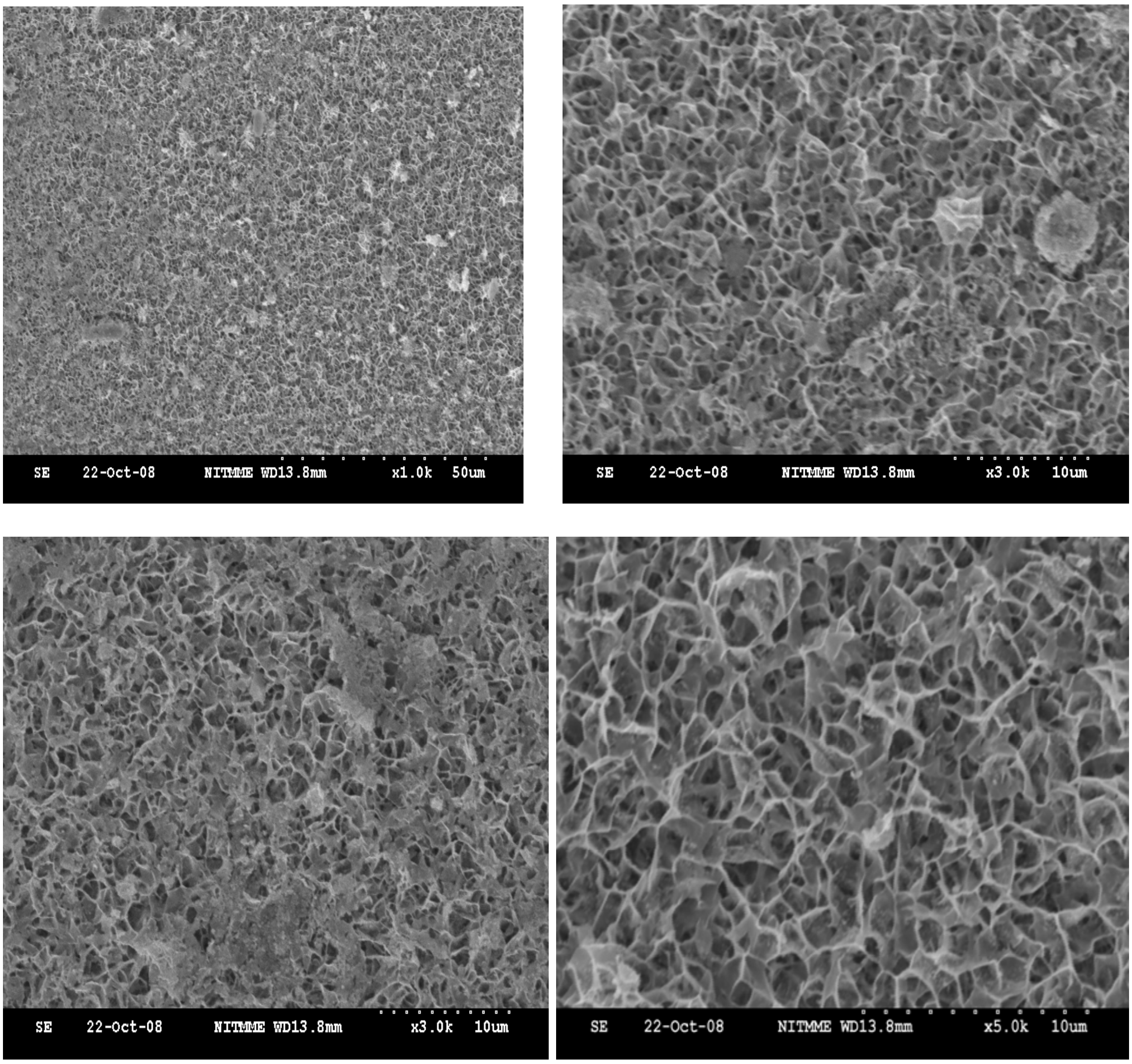

Fig.2: SEM picture for CdS thin films deposited at room temperature & annealed at 373K

3.3 Optical studies

Figs. 3 and 4 are plots of absorbance vs. wavelength and transmittance vs. wavelength for CdS nanocrystalline tin films grown in this work. From the absorbance spectra displayed in fig. 3, we observe that the absorption edge of the films shift towards longer wavelength (red shift) with increasing annealing temperature.

The films' absorbance is mainly in the VIS region of the solar radiation spectrum. The film annealed in air at 400 ^{o}C has the highest absorbance of 23% in the NIR region. A close observation of Fig. 4 shows that transmittance generally increases with wavelength and decreases with annealing temperature.

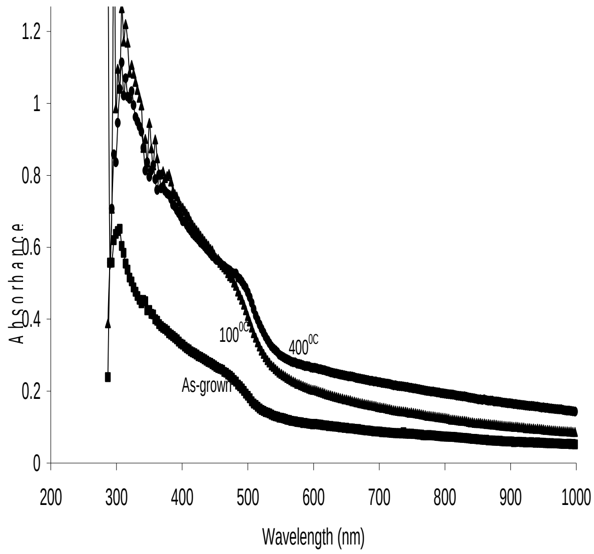

Fig.3. Absorbance vs wavelength for nanocrystalline CdS thin films.

The figure also shows that the films have high transmittance in the NIR region of the solar spectrum. In general, high thermal annealing tends to reduce transmittance in all the spectrum of solar light energy. This is attributable to formation of denser films because of water evaporation.

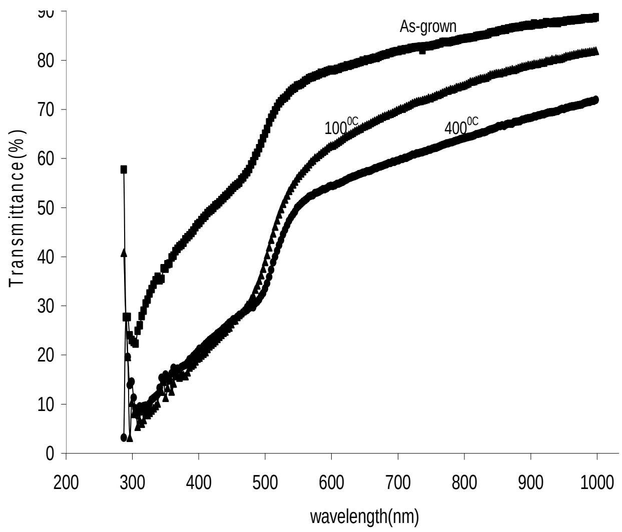

Fig.4. Transmittance vs wavelength for nanocrystalline CdS thin films.

Fig 5 shows that the refractive index of the annealed films increased uniformly to a maximum value at about 2.3 eV, corresponding to the VIS region of the solar spectrum. However, the as-grown film showed a gradual increase in refractive index up to NIR region. The highest observed refractive index of 2.28 was observed at photon energy of 2.37 eV for the film annealed in air at 400 ^{o}C. This trend in the behavior of refractive index with annealing temperature has also been observed and was attributed to denser films, arising from evaporation of water molecules off the film [14].

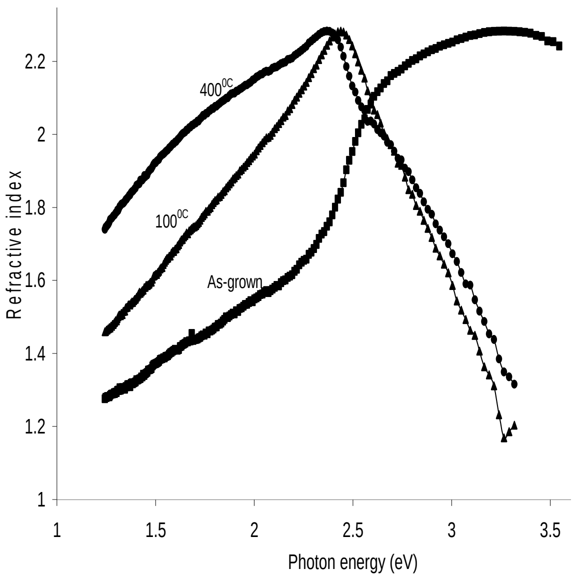

Fig.5: Refractive index vs photon energy for nanocrystalline CdS thin films

3.4 Band gap energy

CdS is a typical direct band gap semiconductor. According to Tauc relation, the absorption coefficient for direct band gap material is given by
$\alpha = c(h\nu - E_g)^{1/2}/ h\nu$, [10,11] where α is the absorption coefficient, c is a constant, hν is the photon energy and E_g the band gap. The direct band gap of the films were obtained from the linear portion of $(\alpha h\nu)^2$ versus hν plot as shown in figure 6. The values obtained for nanocrystalline CdS thin film lie in the range of 2.25 - 2.65 eV. Observation of figure 6 shows that the energy gap decreases with increasing annealing temperature. This is possibly due to the evaporation of water molecules off the film and reorganization of the films.

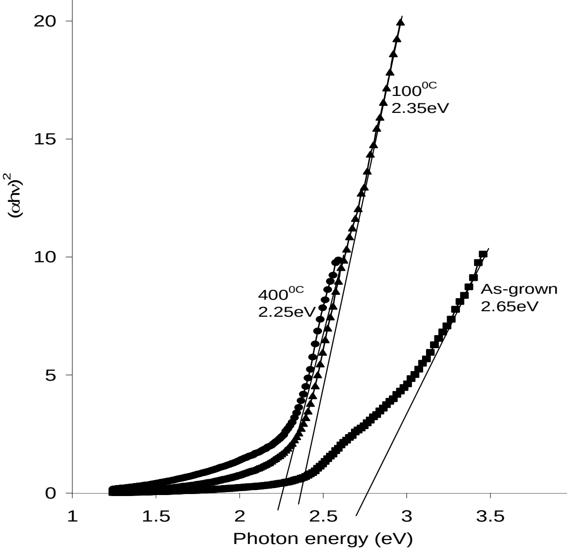

Fig. 6. Plot of $(\alpha h\nu)^2$ vs hν for nanocrystalline CdS thin films

The temperature dependence parameters that affect the band gap are reorganization of the film and self oxidation [8, 12]. The reorganization of the film should occur at all annealing temperature. By filling the voids in the film one expect denser film and lower energy gap. Both the range of values of band gap energy and their variation with thermal annealing obtained in this work are in close agreement with other reports [13 – 17].

4. Conclusions

Nanocrystalline thin films of CdS were successfully deposited on glass slide using chemical bath deposition technique. XRD studies reveal that the CdS nanocrystalline thin films have a preferred orientation in the (111) plane of a cubic structure. The average crystallite size was found to be 16.39 nm. Optical studies and band gap analysis show that high 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 window layer in solar cell fabrication. Duo to their low transmittance in the VIS, the films could also be applied as anti-dazzling coatings in car windscreen and driving mirrors to reduce the dazzling effect of light at night.

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