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Synthesis Of Polymer-Cdse Nanocomposite By Heat Induced Thermolysis Process And Its Photovoltaic Applications

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Abstract:

In the present study we report the development of a new route for the synthesis of polymer-CdSe nanocomposite thin film by heat induced thermolysis reaction which is completely free from any complexing agents and toxic chemicals. The as synthesized polymer-CdSe thin films were characterized by X-ray diffraction (XRD), Transmission electron microscopy(TEM), UV–Vis and PL spectroscopy. The optical studies showed a direct allowed band gap of 2.5 eV . XRD and SAED pattern shows the polycrystalline nature of CdSe thin film with cubic structure. TEM and HRTEM images indicated the small sized nanoparticles of CdSe(~ 10 nm) with a good crystalline structure in the CdSe nanoparticles. A proto-type thin film solar cell of CdSe/CdTe was fabricated (1cm x 1 cm) on glass substrates by using this deposition technique for CdSe. The CdTe layer was deposited by vacuum evaporation technique. The current voltage (I-V) characteristics of the cells were measured with a keithley Source Meter(Model No:2400). The efficiency of the solar cell was found as 1.7 %.

Keywords: *CdSe–polymer nanocomposite, Thin film, Solar cell, Thermolysis*

Introduction

Cadmium Selenide (CdSe) is an important II-VI semiconducting compound with a direct band gap energy of 1.74 eV [1-2]. Due to high absorption coefficient and favourable optical properties, CdSe thin films find application in photo-electrochemical solar cell (PEC), optoelectronic devices, gamma ray detectors [3-5], light emitting diodes, solar cells, photodetectors, electrophotography and in laser [6-8]. There are various methods for depositions of CdSe thin films such as vacuum evaporation [9], chemical bath deposition [10], chemical vapour deposition[11], molecular beam epitaxy [12], spray pyrolysis [13-14], electrodeposition[15], successive ionic layer adsorption and reaction (SILAR) [16-17]. Compared to other deposition techniques, CBD is one of the simplest and cost effective technique to grow CdSe thin films, as it does not require any sophisticated instrument. It is easy to handle, convenient for large area deposition and capable of yielding good quality uniform thin films [18, 19].

In recent years, synthesis of nanostructured CdSe thin film has been a rapidly growing area of research and CBD technique is generally adopted for deposition of CdSe thin film. The synthesis of CdSe thin film by CBD technique utilises triethanalomine (TEA) [N(CH2CH2OH)3], ammonia(NH3) etc. as complexing agent[20-22]. The synthesis of CdSe thin film from a complexing agent free system is still a potential area of research. K. Girija et al. [20] studied the structural, morphological and optical properties of CdSe thin films prepared under different bath temperatures using ammonia as a complexing agent. The effects of deposition times, pH and annealing temperature on the semiconducting optical band gap and structure of CBD deposited CdSe thin films were investigated by R. Moradian et al. [21]. They observed that the deposited samples at low pH values possess a large band gap and are composed of very small amorphous grains. In higher pHs, the grain size was increased so that the energy band gap diminished and approached to the bulk band gap. Structural, morphological and optical properties of CdSe nanocrystalline thin films were investigated by R.S. Singh et al using TEA as a complexing agent [22]. S.M.U. Ishiwu et al studied the optical and solid state properties of CdSe thin film grown by CBD technique [23].

The purpose of the present work is to study the structural, morphological and optical properties of CdSe thin film prepared by dip coating technique followed by heat

treatment. A solar cell with the structure CdSe/CdTe has been fabricated and its photovoltaic parameters were measured.

Experimental

Chemicals

All reagents were of analytical grade, obtained from Merk(India) Ltd. and used as received without further purification. Deionized water was used throughout the experiments.

Synthesis Of Cdse Thin Films

CdSe thin films were deposited on glass substrates by dip coating technique followed by heat treatment at 200^{o}C for 15-20 min. Cadmium acetate [$(CH_3COO)_2$ $Cd.2H_2O$] were used as Cd^{++} ion source , sodiumselenosulphite (Na_2SeSO_3) as Se^{--} ion source and polyvinyl alcohol(PVA) as the polymer matrix. Sodiumselenosulphite (Na_2SeSO_3) was prepared by refluxing 4 gms of selenium powder with 12gms of anhydrous sodium sulphite (Na_2SO_3) in 50 ml of double distilled deionized water for 4 hours at 80^{o}C. The technique used here for the synthesis of CdSe thin film is similar to that of our earlier work for the deposition of CdS/PVA nanocomposite thin film [24].

In a typical reaction a matrix solution was prepared by adding 0.1M cadmium acetate into 5% (w/v) aqueous solution of polyvinyl alcohol(PVA) and stirred continuously at 70^{0}C. The solution was left overnight to get transparent solution indicating complete dissolution of cadmium acetate. An amount of diluted sodiumselenosulphite was added drop by drop into the matrix solution and the reactants was stirred continuous for 15 minutes. Then the resulting precursor becomes just milky and gradually it changes from milky to yellow and within an hour the colour of the precursor was found to turn into red. The final precursor solution containing Cd^{2+} and Se^{2-} ions in the polymeric matrix and were then coated onto a chemically clean glass substrate by dip coating technique using a single dip coater (Model N0.-SDC 2007C, Apex Instruments Co.) resulting into a transparent film. The substrate was held vertically with the help of a substrate holder, dried and heated in a furnace to the desired temperature and thereby allowing the thermolysis reaction to take place between

Cd^{2+} and Se^{-2} ions. CdSe nanoparticles were formed at this stage, the colour of the film changes from transparent to brown within 15-20 minutes indicating the formation of CdSe nanoparticles in PVA matrix. The thickness of the films were found to be within the range 150-200Å.

The crystallographic structures of the films were analyzed with a Rigaku Ultima-IV X-ray diffractometer using CuKα radiations operated at 40 kV and 30 mA. For optical studies, absorption and transmission spectra were recorded with a Scinco (S 3100) PD UV-Vis spectrophotometer. Photoluminescence spectra were recorded with a HORIBA JOBIN-YVON Fluoromax-4 spectrofluorometer.. The High resolution transmission electron microscopy (HRTEM) images were taken by a TECNAI-T 30 model instrument operated at an accelerating voltage of 300 kV. Samples for HRTEM imaging were prepared by placing a drop of the solution sample in deionized water onto a carbon-coated Cu grid (3 nm thick, deposited on a commercial copper grid for electron microscope), dried in air and loaded into the electron microscopic chamber. The thickness of the films was determined by the multiple beam interferometry technique.

Results And Discussion

Structural Characteristics Of The Films

The crystalline structure of CdSe thin film prepared by CBD technique on glass substrate is shown in Fig.1. The XRD pattern shows diffraction peaks at $2\theta = 25.70^0$, 43.25^0 and 51.40^0 and can be ascribed due to reflections from (111), (220) and (311) planes respectively. It has been concluded that the as deposited CdSe thin films are polycrystalline in nature with cubic structure. The broad and low intense peaks may be attributed due to the formation of small size nanoparticles in CdSe thin film. The TEM analysis also supports the nanocrystalline structure of CdSe thin film.

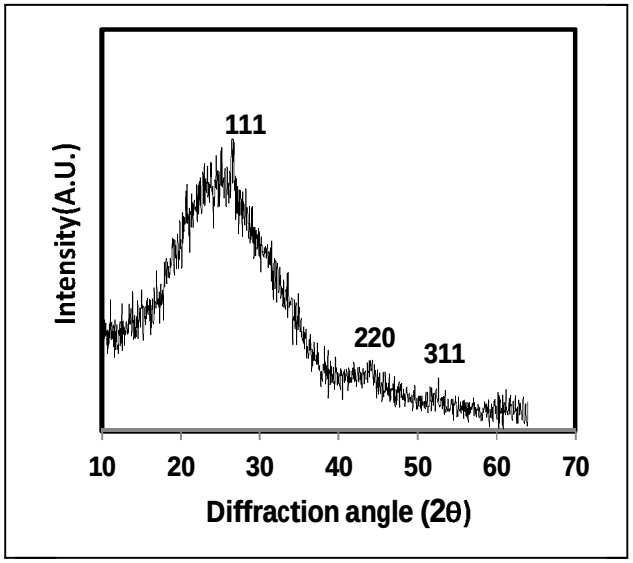

Figure 1: XRD Of Cdse Thin Flim

Optical Studies

The optical absorption spectrum of the as synthesized CdSe thin films is shown in fig.2 (a) The spectrum shows that the absorbance edges are blue shifted with respect to the bulk CdSe, indicating quantum confinement effect in nanoparticles. The absorption edge lies at about 580 nm, which is a pronounced blue shift from 712 nm of the bulk CdSe absorption edge.

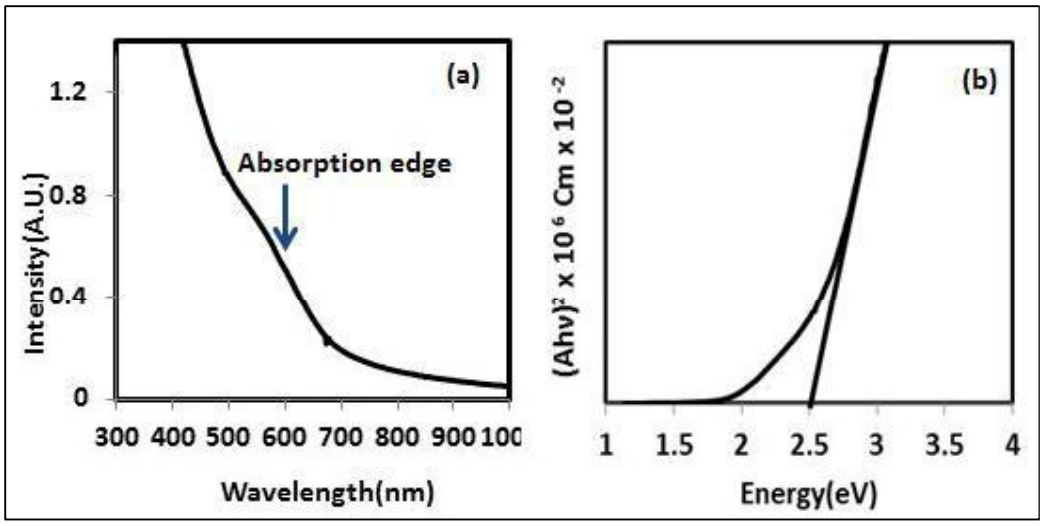

Figure 2(a): UV-Vis absorption spectrum of CdSe thin film ;
Figure 2(b): Band gap calculation of CdSe thin film from absorption spectra

The optical band gap of the CdSe/PVA thin film was obtained by using the following equation [25] for a semiconductor.

$$A = \frac{K (h\nu - Eg)^{m/2}}{h\nu} \qquad (1)$$

where 'A' is the absorbance, 'K' is a constant and 'm' is equal to '1' for direct transition and '2' for indirect transition. Linearity of the plots of $(Ah\nu)^2$ versus photon energy $h\nu$ for the CdSe thin film indicates that the material are of direct band gap type. The extrapolation of the straight line to $(Ah\nu)^2 = 0$ axis (Fig.2b) gives the energy band gap of the film material. The band gap of the CdSe/PVA film was found to be 2.5 eV .

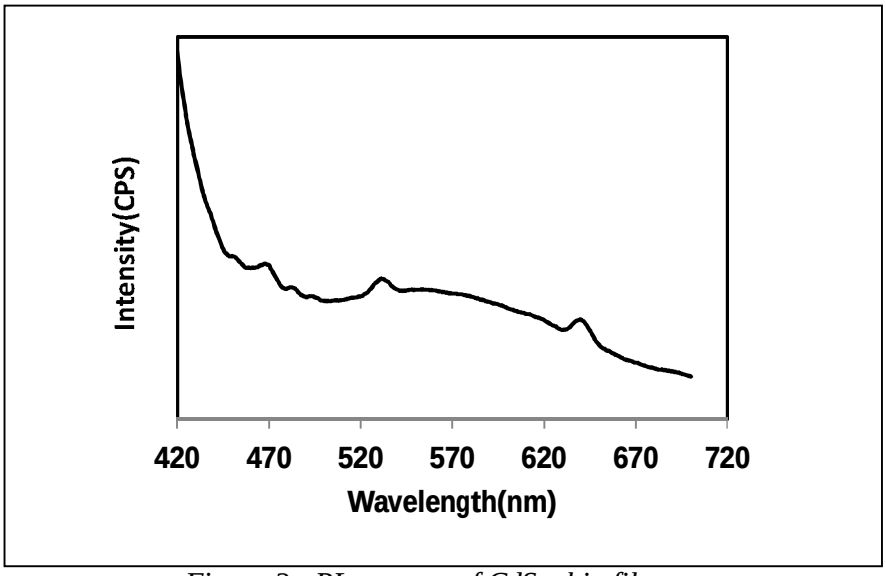

Figure 3: PL-spectra of CdSe thin film

The photoluminescence spectra of the as-prepared CdSe nanoparticles are shown in the fig.(3). Peaks are observed at 468, 527 and 635 nm. Peaks at 468nm and 527 nm correspond to red and green emission respectively and the prominent peak at 635nm is due to band edge transition.

TEM Analysis

The transmission electron microscopy (TEM) image of CdSe/PVA nanocomposite thin film deposited at 200^{o}C is shown in Fig. 4(a). From the TEM image, it can be revealed that the morphology of the CdSe NPs(nanoparticles) is almost uniform and contains many small NPs with the average size ranging from 8-10 nm, Fig. 4(b)shows

selected area electron diffraction (SAED) pattern of as synthesized CdSe NPs. The appearance of spot like rings is indicative of the polycrystalline nature of the material. Fig. 4(b) shows the high resolution transmission electron microscopy (HRTEM) image of CdSe/PVA nanocomposite thin film. The HRTEM image of the film shows the lattice fringes indicating the formation of good nanocrystalline structure in the CdSe NPs. The HRTEM gives a grain size of ≈ 10 nm. This confirms the formation of a nanocrystalline CdSe/PVA composite thin film with particle size in the quantum dot range.

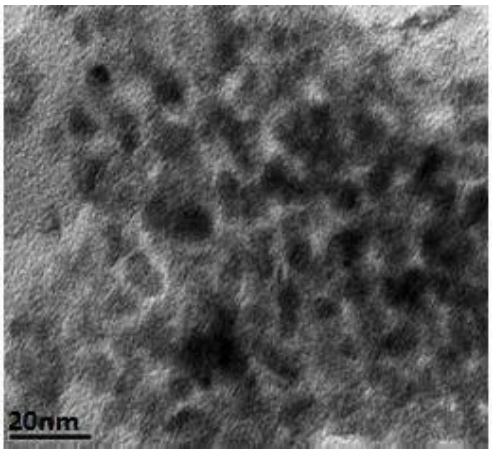

Figure 4(a): TEM images of CdSe thin film

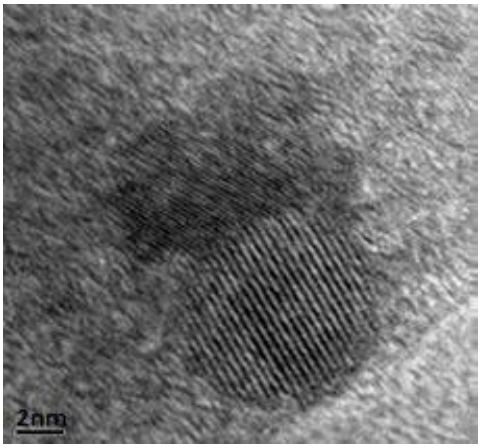

Figure 4(b):HRTEM images of CdSe thin film

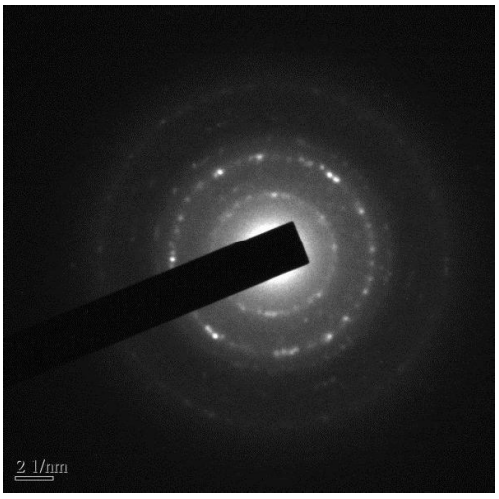

Figure 4(c): SAED images of CdSe thin film

Characterization Of The Cell

The current-voltage(I-V) characteristics of the as fabricated CdSe/CdTe solar cell was measured with Keithley Source Meter(Model No:2400)and is shown in Fig. 5(a). The intensity of illumination was measured with a Lutron LX-101 lux meter. The solar cell parameters were measured under illumination with a 50 mW Cm^{-2} (0.5 SUN) tungsten lamp. The experimental set-up for the measurement of photovoltaic parameters of the CdSe/CdTe solar cell is shown in fig.5(b).The observed photovoltaic parameters of the cells are tabulated in Table 1. A conversion efficiency of 1.70% (*Voc* = 0.380 V, *Jsc* = 53µA/cm^2, FF = 0.64) has been achieved for the cell.

Solar Cell	Thickness of CdSe layer (nm)	Thickness of CdTe layer (nm)	Short-circuit current, µA	Open-circuit voltage (mV)	Efficiency of the cell, η (%)	Fill-factor of the cell, FF (%)
CdSe/CdTe	165	830	53	380	1.7	64

Table 1: Photovoltaic parameters of CdSe/CdTe solar cell

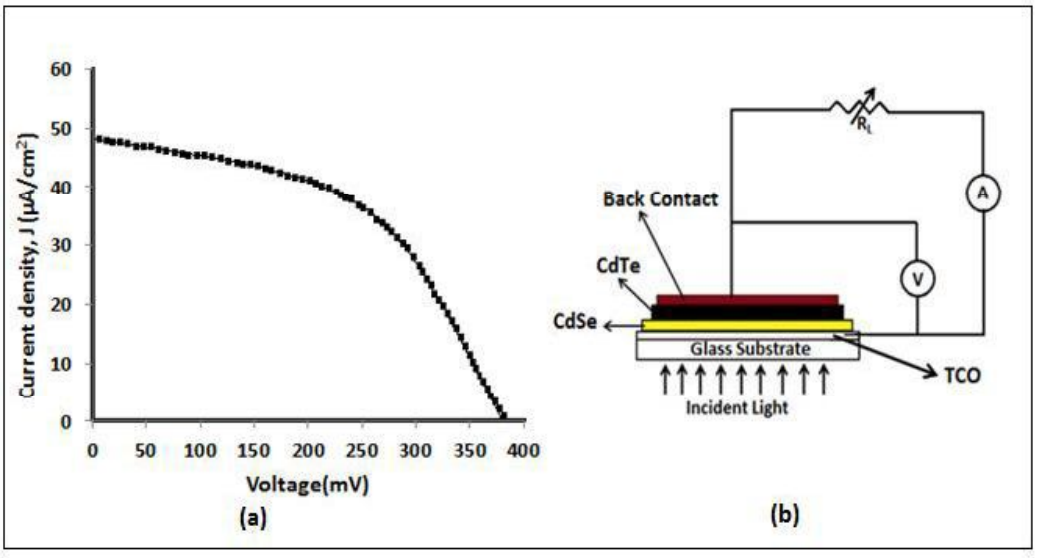

Figure 5(a): I-V characteristics of the as fabricated CdSe/CdTe Solar cell
Figure5(b): Experimental setup for measuring the current– voltage characteristics

Conclusion

CdSe/PVA nanocomposite thin films were prepared by dip coating technique followed by thermolysis at 200^{o} C. The blue shifting of the absorption edge of CdSe thin film indicated that as prepared films are composed of nanocrystals of CdSe. A band gap of 2.5 eV were calculated for CdSe thin film from the shift in absorption edge as a consequence of quantum confinement effect. The XRD & SAED results indicated the polycrystalline nature of the CdSe thin film. The HRTEM analysis provided the information about particle size as well as lattice fringes in the CdSe/PVA thin film. The efficiency of as fabricated solar cell with CdSe thin film deposited by the present technique was found to be 1.7%.

Acknowledgement

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