Effect of Temperature of Electron Beam Evaporated CdSe Thin Films

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Abstract

CdSe thin films were deposited on a glass substrate by using electron beam evaporation technique. The as deposited films were annealed from 100°C to 300°C with an increment of 100°C. Morphological, structural and optical characterization of the films was carried out by using scanning electron microscope (SEM), X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy; and Fourier transform infrared spectroscopy. The X-ray diffraction pattern of the film has a cubic phase with preferred orientation (100), the grain size was found to be in the range of 29-46 nm. SEM results reveal that film grains are polycrystalline in nature covered the whole surface of the substrate.

Keywords: CdSe thinfilm; X-ray diffraction (XRD); Scanning electron microscope; FTIR

Introduction

Semiconductor nano crystallites prepared as powder or thin film form is of recent interest for many novel applications [1,2]. It is used as an n-type window layer material in thin film solar cells, and is a suitable candidate for photovoltaic applications [3]. The deposition of CdSe thin films was made using different deposition methods, EBE is one of the most promising methods for making high quality thin films for photovoltaic applications because it is an efficient and reasonably cost effective method [4]. Electron beam evaporation technique is very useful owing to low consumption of material, high deposition rate and low cost of operation. The reaction was carried out in open atmosphere with one-pot by using selenium dioxide to replace selenium or its other hazardous, expensive and unstable precursors. This new precursor of selenium has been successfully implemented to develop a new aqueous method to obtain fluorescent thin films. The diffraction patterns and other morphological characterization indicate that as deposited thin films have a pure cubic cadmium selenide structure with spherical shape. Small particle size in the range 29-46 nm was achieved. The main advantage of the present thin films are that it is low cost, greener, water soluble precursors; the capping molecule itself acts as reducing agent and is easily up-scalable for larger quantity synthesis. The optical properties and morphological analysis of the CdSe were evaluated. The crystalline semiconductors are being used in electronic, optoelectronic and solar energy conversion devices very often. Notably in the field of bio photonics, long excitation wavelength and high order nonlinear absorptions are strongly preferred. So far, a lot of researches has been carried out on controlling the size, shape and crystal structure as these affect their optical properties. The optical properties of the semiconductor nanomaterials can be tuned by the band gap engineering, which could be achieved by varying their shapes and size. The optical properties and morphological analysis of the CdSe were evaluated. The crystalline semiconductors are being used in electronic, optoelectronic and solar energy conversion devices very often. Notably in the field of bio photonics, long excitation wavelength and high order nonlinear absorptions are strongly preferred. So far, a lot of researches has been carried out on controlling the size, shape and crystal structure as these affect their optical properties. The optical properties of the semiconductor nanomaterials can be tuned by the band gap engineering, which could be achieved by varying their shapes and size.

Low dimensional semiconductor structures, usually called nanocrystals or quantum dots possess unique features having importance in the field of science and technology [5]. During the last two decades, optical properties of semiconductor nanoparticles have been extensively studied due to their unique size-dependent properties which originate mainly from quantum confinement effect [6-11]. The electronic properties of solids are determined by occupation of the bands and by the absolute values of the forbidden gap between the completely occupied and the partly unoccupied or the empty bands. If all the bands at T=0 are either occupied or completely free, material will show dielectric properties. The highest occupied band is called valence band and the lowest unoccupied band is called conduction band.

Optical nonlinearities in bulk semiconductors have been extensively investigated for potential applications in photonics. In recent years, there has been intense research on the nonlinear optical properties of nanometer-sized semiconductors and fabrication techniques for these small particles. A large enhancement of the nonlinear coefficient in the semiconductor crystallites is predicted by theoretical considerations that are based on the quantum size effects of the carriers in the crystallites. In the nano-regime, quantum confinement produces exciton resonances those are sharper than the corresponding ones in the bulk semiconductors, resulting in large optical nonlinearities.

Many studies were devoted to CdSe QDs due to their excellent optical properties, narrow band gap and a variety of optoelectronic conversion properties compared to bulk CdSe [12,13]. In light of this and UV-visible absorption has been one of the most important measurements to investigate the optical properties of CdSe QDs [14]. In addition, considerable progress has been made in the synthesis of CdSe QDs to produce CdSe QDs with excellent optical properties [5,15]. The process needs to be operated in nitrogen atmosphere. However, little...
knowledge has been obtained for the formation mechanism of CdSe QDs using this technique [6]. Furthermore, the cost of large-scale synthesis of CdSe QDs is very high for such expensive TOP solvents. Furthermore, TOP is hazardous, unstable and not environmentally friendly. Recently, a new method has been developed for the synthesis of CdSe QDs without TOP solvents [9]. Furthermore, the process can be operated in open atmosphere [10]. In this work, the CdSe films have been prepared by EB evaporation technique at room temperature and annealed at different temperatures. The structural, optical, electrical and surface morphological properties of the films were characterized by XRD, SEM, UV-visible and FTIR measurements. The results were tabulated and discussed in detail. The Stoichiometry, surface morphology and optical property changes with temperature were discussed elaborately.

**Experimental**

Thin films of CdSe were prepared by EBE technique using a HINDHI-VAC vacuum unit (model: 12A4D) fitted with electron beam power supply (model: EBG-PS-3K) on glass substrates at different substrate temperatures in the range of RT to 300ºC in steps of 100ºC. Well degreased microscopic glass plates have been employed as the substrates in the present work. 500 mg of spectroscopically pure Cadmium selenide (99.99%) was mixed well using a pestle and mortar. The mixture was pressed into pellets by hydraulic method to get pellet with a pressure of 500 kg/cm², which was used as the source material for evaporation. The pellet was taken in a graphite crucible and kept in water cooled copper hearth of the electron gun. The pelletized CdSe targets were heated by means of an electron beam collimated from the dc heated tungsten filament cathode. The surface of the CdSe pellet was bombarded by 180° deflected electron beam with an accelerating voltage of 5 kV and a power density of ~1.5 kW/cm². The evaporated species from CdSe pellet were deposited as thin films on the substrates in a pressure of about 1×10⁻⁵ mbar (or the films were deposited with 5 kV and 10 mA under a vacuum of 10⁻⁵ Torr). Each substrate was placed normal to the line of sight from the evaporation source at a polar angle to avoid shadow effects and also to obtain uniform deposition. The different preparation parameters such as source to substrate distance (15 cm) and partial pressure (0.5×10⁻³ millibar), have been varied and optimized for depositing uniform, well adherent and transparent films. The rate of evaporation (0.5 nm/s) was used to deposit all CdSe films. CdSe films were prepared at room temperature (RT), and annealed at different temperatures to study the effect of Oxygen Pressure on the structural, optical, and morphological properties. The films were characterized by X-ray diffraction (XRD) studies using CuKα radiation from an X’pert Pro PANanalytical XRD unit. Optical studies were made at room temperature using a Hitachi-330 UV-Visible spectrophotometer. The elemental composition was found using an energy-dispersive X-ray (EDX) spectrometer attached with the HITACHI Model S-3000H SEM instrument.

**Results and Discussion**

**XRD analysis**

The XRD analysis was carried out to study the temperature effect on the material properties of CdSe films. The thickness of the films was found to be in the range of 250-270 nm. The Grain sizes, dislocation density, strain and lattice constant of CdSe films have been calculated and their variations could be viewed from their graph. The Figure 1 showed the XRD patterns of CdSe thin films deposited at RT and that films were annealed at different temperatures. A strong peak was observed at 25.3° (2θ) corresponding to (100). Both the signals confirm the CdSe structure belongs to hexagonal lattice and also validated as per the JCPDS (08-0459) data. When the annealing temperature was increased from 100ºC to 300ºC, the peak intensity of (100) plane was increased further and attained maximum. Such results exposed the fact that, the hexagonal structure was stabilized at 300ºC. The same result has been observed in the CdSe films deposited by molecular beam epitaxy technique in the earlier work [11]. From the analysis, it was also observed that, in the room temperature the CdSe film was polycrystalline nature.

The Figure 2 showed the possible nanocrystals formation of the CdSe compound which was analysed by using the Gaussian software. As per the XRD spectral data at all noted temperatures, the title compound belongs to hexagonal lattice. In this hexagonal frame, it was observed that, the Cd and Se atoms were situated alternatively and formed the hexagonal ring. Thus the entire structure was constructed during the thin film coating. The possible formation of the hexagonal form was shown in Figure 2. Normally, the CdSe possess hexagonal primitive structure; in this case the Se was replaced by Se and making CdSe. So, the hexagonal structure was not changed by the replacement of the Se. Usually, the condition of the hexagonal structure is a=b=c (a=0.344 Å–b and c=0.699 Å), it can be concluded that the present compound possess hexagonal primitive structure. Further, the crystal structure of CdSe does not get altered after the annealing of thin films. Hence it is concluded that CdSe atoms are deposited on the surface of glass substrate loading stress causes the observed changes in the lattice parameters ‘a’ and ‘c’. The average crystallite size from (100) hexagonal peak is calculated using Scherer’s relation, which is found to be in the range of 29-46 nm.

**Lattice parameter analysis**

Figures 3a-3d showed the variation of crystal size, dislocation density and strain of CdSe film deposited at three different annealing temperatures. The crystal size was calculated using Scherrer’s equation.

\[
D = \frac{0.942}{\beta \cos \theta}
\]

(1)

Where, D is the grain size, λ is the wavelength of X-rays (Cu Kα radiation – 1.5406 Å), β is the full width at half maximum and θ is the Bragg angle. The crystal size of the film at RT, was found to be 29 nm.
increased to 300°C, the strain in the lattice utilized for the completion of hexagonal structure. The lattice parameters values of the hexagonal structure (planes) were calculated from the following equation:

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2}
\]  

(4)

Normally, the strain creates local deviation of lattice constants from its bulk value which is size dependent [17]. From the tabulated result of the lattice parameters, it was observed that the lattice parameter values were very close to the standard values and these values were fluctuated slightly due to the stress movement along the lattice. Generally the CdSe crystal has Zinc blende (Cubic) structure of space group F4-3m or Wurtzite (Hexagonal) structure of space group P6,mc. The XRD patterns of CdSe thin films on glass substrate at RT, 100, 200 and 300°C deposition temperature by electron beam evaporation technique with thickness in the range of 300 nm shown in Figure 1 clearly indicates the increase of crystallinity of the film with the increasing of deposition temperature. A sharp peak is observed mostly in all films close to 2θ at 25.3° corresponding to (100) plane of the hexagonal phase (JCPDS 08–0459). The CdSe films deposited by Electron Beam Evaporation (EBE) technique at various substrate temperatures ranging from room temperature to 300°C showed single peak corresponding to highly oriented hexagonal structure of polycrystalline nature. The effect of substrate temperature on the microstructure of CdSe films is summarized in Table 1. It is observed that the grain size of CdSe can be tuned between 29 nm to 46 nm by varying the substrate temperature.

Grain size was calculated using Debye-Scherrer’s equation (1).

\[
\text{Transmittance studies}
\]

The transmission spectra of CdSe thin films were recorded in the wavelength range 450 nm to 2500 nm at different substrate temperatures and were shown in Figure 4. Usually, the Transmittance spectra have given the information regarding the optical features, band structure and the result of deposition temperatures of semiconductor films. The absorption coefficient (α) and direct or in-direct band gap were estimated from the transmission spectra. In order to find out the nature of the band gap (direct or in-direct band gap) of the CdSe films, α and hν values were used to fit-in with the following equation for finding direct band gap,

\[
(\alpha h\nu) = A (h\nu-Eg)^{1/2}
\]  

(5)

whereas at 300°C, it was identified to be 46 nm. This view indicated that, the crystal size of CdSe was increased with respect to temperature. Thus, the crystal size of CdSe can be tuned by varying the substrate temperature. The values of dislocation density and lattice strain were calculated using the following relations,

\[
\text{Dislocation density (}\delta\text{)} = 15\beta\cos\theta/4aD \quad (2)
\]

\[
\text{lattice strain (}\epsilon\text{)} = \beta\cos\theta/4 \quad (3)
\]

The dislocation density and strain values are decreased when the temperature is increased which was tabulated. Generally, when the dislocation density of the film was decreased the crystal size increases with respect to annealing temperature [16].

The Strain is inherent and natural mechanism of annealed materials of thin films was obtained. Due to the large number of grain boundaries and the concomitant short distance between the grains, the intrinsic strain associated with interface of the lattice are always present in thin films. Moreover, the increasing surface energy contributes the variation of magnitude of strain. Similar results have been observed in this case and it was decreased with the increasing of annealing temperature. It was evident that, when the annealing temperature

![Figure 2: Absorbance variation of CdSe thin films with respect to annealing temperature (i) RT (ii) 100°C (iii) 200°C and (iii) 300°C.](image2)

![Figure 3: Transmittance curves of CdSe thin films with respect to annealing temperature (i) RT (ii) 100°C (iii) 200°C and (iii) 300°C.](image3)

![Figure 4: Bandgap variation of CdSe thin films with respect to annealing temperature (i) RT (ii) 100°C (iii) 200°C and (iii) 300°C.](image4)
Where, \( E_g \) is the band gap, \( \alpha \) is the absorption coefficient, \( A \) is the constant and \( h\nu \) is the photon energy. The plots of \((\alpha h\nu)^2\) versus \( h\nu \) were shown in Figures 5a-5d. The band gap values can be found on straight line portions which cut the \( h\nu \) axis (x-axis) on extrapolation. From the graph, it was observed that, the presence of straight line portions in the high energy region confirms the direct band gap nature of the CdSe films. The calculated \( E_g \) values were 2.33, 2.385, 2.50 and 2.564 eV of the CdSe films deposited on glass substrates at RT, 100, 200 and 300°C respectively. From these values order it was observed that, the \( E_g \) value decreases with increasing of substrate temperature.

For direct band gap, where \( E_g \) is the bandgap of the CdSe films, \( \alpha \) is the absorption coefficient, \( A \) is the constant and \( h\nu \) is the photon energy. The \((\alpha h\nu)^2\) versus \( h\nu \) plots Figure 5c, for all the films deposited on glass substrates, show straight line portions which cut the \( h\nu \) axis (x-axis) on extrapolation giving the band gap values. It is observed that all graphs for the films deposited at different substrate temperatures have straight line portions in the high energy region which confirms the direct band gap nature for all the CdSe films prepared by EB evaporation technique here. The values of \( E_g \) are listed in Table 1. It is observed that the \( E_g \) value increased with increasing substrate temperature. Which, in turn, depend on the increase of grain/particle size of the CdSe films with increasing substrate temperature, such observations have been reported for vacuum evaporated films. When the substrate temperature increases the band gap value of the CdSe films decreased. Such an observation has been reported for vacuum evaporated films [18]. When the substrate temperature was increased from RT to 200°C, a band gap variation in the range of 2.33-2.564 eV was observed for the vacuum evaporated CdSe films [19]. A decrement in band gap from 2.33 to 2.564 eV was observed when the substrate temperature was raised for the chemically deposited CdSe thin films [20,21]. After the deep screening of the literature, it was found that, the variation of the band gap is inversely proportional to the substrate temperature. The decrement of the band gap is also favour for the electrical conductivity of the CdSe film. Whenever the electrical conductivity of the material increases, the resistivity of the same is decreased. So it can be concluded that, the conductivity and resistivity of the material can be controlled by the substrate temperature [22-24].

The electrons are excited from the CdSe valence band to conduction band by absorbing the energy equal to or greater than their bandgap.
energy. Subsequent relaxation of these photo-excited electrons to some surface states or levels is followed by radiative decay enabling the luminescence invisible region [25,26].

FT-IR Analysis

The present compound was made up two atoms such as Cadmium and Selenide and its FTIR spectra are shown in Figures 6a-6d. Both the atoms were bonded and form CdSe molecule. In a crystal, there were number of molecules. When the energy was applied to the molecule whether in bulk or nano, the Cd-Se molecule executes the vibrational motion two three forms. Such as stretching and bending vibrations. The bending vibration was further can be divided in to two vibrations such as in plane and out of plane bending vibration. The entire molecule was vibrated according to their degrees of freedom. In this present case, the Cd-Se can execute only one Cd-Se stretching mode. Normally, the metal atoms stretching vibrations are observed in the region of 500-3000 cm⁻¹ [27,28]. The films thickness was in the range of 400-500 nm with a growing time of 1 hr. The material obtained was characterized by optical absorption, SEM (Scanning Electron microscope), Energy Dispersive X-ray analysis (EDAX) and X-ray diffraction (XRD). XRD analysis reveals that, as deposited films are polycrystalline in nature with the orientation in the (100) direction. The films revealed the homogeneous and uniform film growth in the RT & 300°C regions without pinholes. No perceptible cracks are there and the films are well covered all over the substrate [29]. At 300°C, the films show few discontinuities. The grains are of nano size and distributed all over the surface in all the films. The presence of Cd and Se are determined by EDAX spectrum [30].

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References