Chapter No. VII

Effect of Electron Beam Irradiation on Cadmium Chalcogenide Thin Films
7.1 Introduction

7.1.1 Irradiation Process

Irradiation process deals with the exposure to ionizing radiation. Irradiation is the process by which an item is exposed to radiation. The exposure can be intentional, sometimes to serve a specific purpose, or it can be accidental. In common usage the term refers specifically to ionizing radiation, and to a level of radiation that will serve that specific purpose, rather than radiation exposure to normal levels of background radiation or abnormal levels of radiation due to accidental exposure[1].

Physical and chemical changes induced by absorption of radiation sufficiently high in energy to produce ionization have been the subject of both university and industrial research. Chemical effects of ionizing radiation utilized the natural radioisotopes radium and radon as radiation sources [2]. At this time, the most common commercial sources of ionizing radiation are $^{60}$Co and $^{137}$Cs for gamma irradiation, and electron accelerators for e-beam (beta) irradiation. When the electron-beam generated by an accelerator is directed at a target consisting of a high-atomic-number metal, such as tungsten or gold, X-rays with a broad spectrum of energies can also be produced. The amount of energy absorbed, also known as the dose, is measured in units of kilo Grays (kGy), where 1 kGy is equal to 1,000 Joules per kilogram[3,4].

As shown in Fig.7 radiation is classified into two main categories, nonionizing and ionizing, depending on its ability to ionize matter. The ionization potential of atoms (i.e. the minimum energy required to ionize an atom) ranges from a few electronvolts for alkali elements to 24.5 eV for helium (noble gas).

- Non-ionizing radiation (cannot ionize matter).
- Ionizing radiation (can ionize matter either directly or indirectly):
  - Directly ionizing radiation (charged particles): electrons, protons, a particles and heavy ions. Directly ionizing radiation deposits energy in the medium through
direct Coulomb interactions between the directly ionizing charged particle and orbital electrons of atoms in the medium.

ii. Indirectly ionizing radiation (neutral particles): photons (x-rays and γ-rays), neutrons. Indirectly ionizing radiation (photons or neutrons) deposits energy in the medium through a two step process:
1. In the first step a charged particle is released in the medium (photons release electrons or positrons, neutrons release protons or heavier ions);
2. In the second step the released charged particles deposit energy to the medium through direct Coulomb interactions with orbital electrons of the atoms in the medium[5].

Fig. 7 Classification of radiation.

7.2 Literature survey with Experimental details

Capacitance variation with frequency indicates that irradiation does not contribute significantly to the increase of deep level defects in the interface. And the CSS grown CdTe/CdS thin film solar cells are stable against electron irradiation and are better suited for space application has been reported by Sheeja Krishnan et al [5]. The effect of swift heavy ions on the structural, optical and electrical properties of nanocrystalline bismuth sulphide has been reported by Ahire et al [7]. Increase in grain size of the films due to both annealing and irradiation, leading to the decrease in resistivity and increase in thermoemf of the films has been observed. Effect of electron irradiation on electrophysical properties of CdSe and CdS thin films has been carried out by Spanulescu et al [8]. Optical absorption spectra and photoelectrical properties of CdSe and CdS layers
are influenced by ionizing radiation and activation of the sample in different media. Effects of irradiation of 1 MeV electrons or $^{60}$Co gamma-quantum and nanostructuring on CdS$_x$Se$_{1-x}$ solid solution layers, affecting their influence on the fluctuations of the potential relief, were studied by Saad et al [9].

Gigantic deformations were found for the copper sulfide (Cu$_{1.4}$S and Cu$_2$S) thin films irradiated with 100MeV Au$^{8+}$ swift heavy ions (SHI) for $10^{11}$ and $10^{12}$ ions cm$^{-2}$ fluencies [10].

Cadmium Sulfide and Cadmium Telluride thin films were irradiated with high energy heavy ion beam to study the irradiation induced effects in these films [11]. The X-ray diffraction patterns exhibit a reduction in peak intensities in both CdS and CdTe films. Effect of $\gamma$-irradiation on the optical properties of a- (Sb$_{0.1}$Ge$_{0.3}$Se$_{0.6}$) and Ag$_5$(Sb$_{0.1}$Ge$_{0.3}$Se$_{0.6}$)$_{95}$ thin film material was reported by Salem et al [12]. Systematic studies of the refractive index, extinction coefficient and optical band gap have been presented as a function of the $\gamma$-dose. The effect of electron beam irradiation on two partially fluorinated polymer films i.e. poly(vinylidene fluoride) (PVDF) and poly(ethylene-tetrafluoroethylene) copolymer (ETFE) were studied at does ranging from 100 to 1200kGy in air at room temperature [13]. The chemical structure, thermal and mechanical properties of irradiated films were investigated. Zenkiweicz [14] reported effect of electron-beam irradiation on the tensile strength at break, elongation at break, and tear resistance for packaging films made of low-density polyethylene (LDPE), biaxially oriented polypropylene (BOPP), and polyethylene terephthalate (PET).

Metal sulphides are fascinating the researchers continuously because of their interesting properties, which can be easily tailored by different deposition techniques and/or by different post-deposition treatments. Annealing at different temperatures and in various environments is one of the well-known techniques. Nowadays, swift heavy ions (SHI) are also getting popular to engineer the materials properties. They have been extensively used for ion implantation, ion
beam assisted self-assembled nonoparticles formation and template synthesis, etc. [15-18].

In chapters II, III and IV we have discussed how to prepare Cadmium chalcogenide thin films by electrodeposition. The films of different concentrations were prepared by electrodeposition. The irradiation experiments were carried out at the 6MeV linear electron accelerator set up at B.A.R.C. Mumbai and Department of Physics Pune University, Pune, India. The thin film samples are kept in front of the exit slit of the LINAC at a distance of 12 cm. The sample cell dimensions are 10 mm x 10 mm x 50 mm and are kept for the pulse radiolysis study. The dose absorbed by aqueous solutions per pulse was determined by using a chemical dosimeter, an aerated aqueous solution containing $5 \times 10^{-2}$ mol dm$^{-3}$ potassium thiocyanate (KSCN) [19]. This dose value was used to calculate the total dose delivered in a sample under a repetitive irradiation condition. Electron pulses of 2 µs time duration with a peak current, 70mA were used for the irradiation of the samples. The electron flux was about $3 \times 10^{12}$ electrons / 2µs / cm$^2$. The samples were irradiated by these electron pulses at a repetition rate of 12 pulses per second for about 5.5 seconds, accounting for a cumulative dose of about 10 kGy.

The as-deposited and irradiated films were characterized by X-ray diffraction, Scanning Electron Microscopy (SEM), UV-VIS-NIR spectrophotometer, the surface wettability of the films are determine by measuring contact angle with water using (Rame hart instrument) contact angle meter. The FT. Raman spectra recorded by model Raman II FT. Raman spectrometer.

7.3 Results and discussions

7.3.1 Structural analysis

i. Cadmium sulfide (CdS) thin films

The effects on the polycrystallinity of the as-deposited and irradiated films are analyzed using glancing angle X-ray diffraction. Fig. 7.1, 7.2 and 7.3 shows the XRD pattern of the as-deposited and electron irradiated CdS films for,
\((A_2) = 0.04 \text{ M CdSO}_4 + 0.4 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.06 \text{ M EDTA}, (B_2) = 0.06 \text{ M CdSO}_4 + 0.6 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.08 \text{ M EDTA}, \) and \((C_2) = 0.08 \text{ M CdSO}_4 + 0.8 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA}.\) It indicates polycrystalline with hexagonal crystal structure. Cds films were matched with database in JCPDS [20,21]. It is noteworthy to mention here that crystallite size of the films calculated from the Scherer’s formula for \((A_2), (B_2)\) and \((C_2)\) as-deposited it’s 32.95 nm to 65.97 nm and electron irradiated have exhibited the crystallite size varies from 34.31 to 67.03 nm. 67.03 nm respectively. The crystallite size increases after irradiation due to induced disorder in the structure. The peak intensity increases after electron beam irradiation [22].

![X-ray diffraction pattern of as-deposited CdS thin film onto stainless steel substrate for bath concentration, \((A_2) = 0.04 \text{ M CdSO}_4 + 0.4 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA}.\) for various deposition times, \(A_{12}, A_{22}\) and \(A_{32}\) as-deposited, \(a_{12}, a_{22}\) and \(a_{32}\) electron irradiated](image)

Fig.7.1 X-ray diffraction pattern of as-deposited CdS thin film onto stainless steel substrate for bath concentration, \((A_2) = 0.04 \text{ M CdSO}_4 + 0.4 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA}.\) for various deposition times, \(A_{12}, A_{22}\) and \(A_{32}\) as-deposited, \(a_{12}, a_{22}\) and \(a_{32}\) electron irradiated.
Fig. 7.2 X-ray diffraction pattern of as-deposited CdS thin film onto stainless steel substrate for bath concentration, (B₂)=0.06 M CdSO₄ + 0.6 M Na₂S₂O₃ + 0.1 M EDTA, for various deposition times, B¹₂, B²₂, and B³₂ as-deposited, b¹₂, b²₂, and b³₂ electron irradiated.

Fig. 7.3 X-ray diffraction pattern of as-deposited CdS thin film onto stainless steel substrate for bath concentration, (C₂)=0.08 M CdSO₄ + 0.8 M Na₂S₂O₃ + 0.1 M EDTA, for various deposition times, C¹₂, C²₂, and C³₂ as-deposited, c¹₂, c²₂, and c³₂ electron irradiated.
(ii) Structural analysis of Cadmium Selenide (CdSe) thin films.

The effects on the polycrystallinity of the as-deposited and irradiated films are analyzed using glancing angle X-ray diffraction. Fig. 7.4, 7.5 and 7.6 shows the XRD pattern of the as-deposited and electron irradiated CdSe films for \((A_3) = 0.04M \text{ CdSO}_4 + 0.06M \text{ SeO}_2 + 0.1M \text{ EDTA.}, (B_3) = 0.06M \text{ CdSO}_4 + 0.08M \text{ SeO}_2 + 0.1M \text{ EDTA.} \) and \((C_3) = 0.08M \text{ CdSO}_4 + 0.1M \text{ SeO}_2 + 0.1M \text{ EDTA.} \). It indicates polycrystalline with hexagonal crystal structure. CdSe films were matched with database in JCPDS [23,]. It is noteworthy to mention here that crystallite size of the films calculated from the Scherer’s formula for as-deposited have exhibited the crystallite size varies from 19.40 nm to 24.58 and electron irradiated from 21.22 nm to 26.08nm for \((A_3), (B_3)\) and \((C_3)\) bath concentration respectively. The crystallite size increases after irradiation due to induced disorder in the structure. The peak intensity increases after electron beam irradiation.

![X-ray diffraction pattern of as-deposited CdSe thin film onto stainless steel substrate for bath concentration, \((A_3)=0.04M \text{ CdSO}_4 + 0.06M \text{ SeO}_2 + 0.1M \text{ EDTA.} \) for various deposition times, \(A_1\), \(A_2\) and \(A_3\) as-deposited, \(a_1\), \(a_2\) and \(a_3\) electron irradiated](image-url)

Fig.7.4 X-ray diffraction pattern of as-deposited CdSe thin film onto stainless steel substrate for bath concentration, \((A_3)=0.04M \text{ CdSO}_4 + 0.06M \text{ SeO}_2 + 0.1M \text{ EDTA.} \). for various deposition times, \(A_1\), \(A_2\) and \(A_3\) as-deposited, \(a_1\), \(a_2\) and \(a_3\) electron irradiated.
Fig. 7.5 X-ray diffraction pattern of as-deposited CdSe thin film onto stainless steel substrate for bath concentration, \( (B_3) = 0.06 \text{M CdSO}_4 + 0.08 \text{M SeO}_2 + 0.1 \text{M EDTA} \) for various deposition times, \( B_1^3, B_2^3 \) and \( B_3^3 \) as-deposited, \( b_1^3, b_2^3 \) and \( b_3^3 \) electron irradiated.

Fig. 7.6 X-ray diffraction pattern of as-deposited CdSe thin film onto stainless steel substrate for bath concentration, \( (C_3) = 0.08 \text{M CdSO}_4 + 0.1 \text{M SeO}_2 + 0.1 \text{M EDTA} \) for various deposition times, \( C_1^3, C_2^3 \) and \( C_3^3 \) as-deposited, \( c_1^3, c_2^3 \) and \( c_3^3 \) electron irradiated.
(iii) Structural analysis of Cadmium Telluride thin films

The effects on the polycrystallinity of the as-deposited and irradiated films are analyzed using glancing angle X-ray diffraction. Fig. 7.7, 7.8 and 7.9 shows the XRD pattern of the as-deposited and electron irradiated CdTe films for \( A_4 = 0.04 \text{M CdSO}_4 + 0.01 \text{M Na}_2\text{TeO}_3 + 0.1 \text{M EDTA.} \), \( B_4 = 0.06 \text{M CdSO}_4 + 0.02 \text{M Na}_2\text{TeO}_3 + 0.1 \text{M EDTA.} \) and \( C_4 = 0.08 \text{M CdSO}_4 + 0.03 \text{M Na}_2\text{TeO}_3 + 0.1 \text{M EDTA.} \). It indicates polycrystalline with hexagonal crystal structure. CdTe films were matched with database in JCPDS [24]. It is noteworthy to mention here that crystallite size of the films calculated from the Scherer’s formula for as-deposited have exhibited the crystallite size varies from 21.97 nm to 29.20 nm and electron irradiated 23.46 nm to 31.08 nm for \( A_4 \), \( B_4 \) and \( C_4 \) bath concentration respectively. The crystallite size increases after irradiation due to induced disorder in the structure. The peak intensity increases after electron beam irradiation.

![X-ray diffraction pattern](image)

Fig.7.7 X-ray diffraction pattern of as-deposited CdTe thin film onto stainless steel substrate for bath concentration, \( A_4=0.04 \text{M CdSO}_4 + 0.01 \text{M Na}_2\text{TeO}_3 + 0.1 \text{M EDTA.} \) for various deposition times, \( A_4^1, A_4^2 \) and \( A_4^3 \) as-deposited, \( a_4^1, a_4^2 \) and \( a_4^3 \) electron irradiated.
Fig.7.8 X-ray diffraction pattern of as-deposited CdTe thin film onto stainless steel substrate for bath concentration, \((B_4) = 0.06\text{M CdSO}_4 + 0.02\text{M Na}_2\text{TeO}_3 + 0.1\text{M EDTA}\). for various deposition times, \(B_{14}, B_{24}\) and \(B_{34}\) as-deposited, \(b_{14}, b_{24}\) and \(b_{34}\) electron irradiated

Fig.7.9 X-ray diffraction pattern of as-deposited CdTe thin film onto stainless steel substrate for bath concentration, \((C_4) = 0.08\text{M CdSO}_4 + 0.03\text{M Na}_2\text{TeO}_3 + 0.1\text{M EDTA}\). for various deposition times, \(C_{14}, C_{24}\) and \(C_{34}\) as-deposited, \(c_{14}, c_{24}\) and \(c_{34}\) electron irradiated
7.3.2 Surface Morphology

(i) Cadmium Sulfide

The surface morphology of as-deposited and irradiated CdS films were determined using Scanning Electron Microscope (SEM). Fig. 7.10 [A₂, B₂ and C₂] and [a₂, a₂ and a₂] gives an idea about a SEM micrograph of as-deposited and irradiated CdS thin films for bath concentrations, (A₂)= 0.04 M CdSO₄ + 0.4 M Na₂S₂O₃ + 0.06 M EDTA, (B₂)= 0.06 M CdSO₄ + 0.6 M Na₂S₂O₃ + 0.08 M EDTA, (B₂)= 0.08 M CdSO₄ + 0.8 M Na₂S₂O₃ + 0.1 M EDTA. It is observed that the films are with spherical shaped grains, uniform and pinhole free. The average grain size was calculated to be 214.2 nm and 262 nm respectively. It is observed that electron irradiation resulted in the increase in grain size. This observation is also supported by XRD studies. The SEM images shown in Figs. 7.10 [A₂, B₂ and C₂] and [a₂, a₂ and a₂] clearly indicate that films have very good coverage with slight change in morphology.
Fig. 7.10 SEM images of CdS thin film for bath concentrations, \((A_2) = 0.04 \text{ M CdSO}_4 + 0.4 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.06 \text{ M EDTA}\), for different time, \((A_1, a_1) = 110 \text{ Sec.} \quad (A_2, a_2) = 120 \text{ Sec.} \quad (A_3, a_3) = 130 \text{ Sec.}\) \([A_2]\) as-deposited \([a_2]\) electron irradiated.

Fig. 7.10 SEM images of CdS thin film for bath concentrations, \((B_2) = 0.06 \text{ M CdSO}_4 + 0.6 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.08 \text{ M EDTA}\), for different time, \((B_1, b_1) = 110 \text{ Sec.} \quad (B_2, b_2) = 120 \text{ Sec.} \quad (B_3, b_3) = 130 \text{ Sec.}\) \([B_2]\) as-deposited \([b_2]\) electron irradiated.
Fig. 7.10 SEM images of CdS thin film for bath concentrations, $(C_2) = 0.08 \text{ M CdSO}_4 + 0.8 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA}$ for different time, $(C^{12}, c^{12}) = 110 \text{ Sec.} (C^{22}, c^{22}) = 120 \text{ Sec.} (C^{32}, c^{32}) = 130 \text{ Sec.}$ $[C_2]$ as-deposited $[c_2]$ electron irradiated

(ii) Cadmium Selenide

The surface morphology of as-deposited and irradiated CdSe films were determined using Scanning Electron Microscope (SEM). Fig. 7.11 $[A_3, B_3$ and $C_3]$ and $[a_3, b_3$ and $c_3]$ gives an idea about a SEM micrograph of as-deposited and irradiated CdSe thin films for different concentrations, $(A_3) 0.04\text{ M CdSO}_4 + 0.06\text{ M SeO}_2 + 0.1\text{ M EDTA}$, $(B_3) 0.06\text{ M CdSO}_4 + 0.08\text{ M SeO}_2 + 0.1\text{ M EDTA}$ and $(C_3) 0.08\text{ M CdSO}_4 + 0.1\text{ M SeO}_2 + 0.1\text{ M EDTA}$. It is observed that the films are with spherical shaped grains, uniform and pinhole free. The average grain size was calculated to be 230 nm and 428 nm respectively. It is observed that electron irradiation resulted in the increase in grain size.
Fig. 7.11 SEM images of CdSe thin film for bath concentrations, \((A_3) = 0.04\text{M CdSO}_4 + 0.06\text{M SeO}_2 + 0.1\text{M EDTA.}\) for different time, \((A_1^1, a_1^1) = 60 \text{ Sec.} \ (A_2^2, a_2^2) = 70 \text{ Sec.} \ (A_3^3, a_3^3) = 80 \text{ Sec.} \ [A_3] \) as-deposited \([a_3]\) electron irradiated

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Fig. 7.11 SEM images of CdSe thin film for bath concentrations, $(B_3)=0.06M \text{ CdSO}_4 + 0.08M \text{ SeO}_2 + 0.1M \text{ EDTA}$. for different time, $(B_1^3, b_1^3)=60$ Sec. $(B_2^3, b_2^3)=70$ Sec. $(B_3^3, b_3^3)=80$ Sec. $[B_3]$ as-deposited $[b_3]$ electron irradiated.

Fig. 7.11 SEM images of CdSe thin film for bath concentrations, $(C_3)=0.08M \text{ CdSO}_4 + 0.1M \text{ SeO}_2 + 0.1M \text{ EDTA}$ for different time, $(C_1^3, c_1^3)=60$ Sec. $(C_2^3, c_2^3)=70$ Sec. $(C_3^3, c_3^3)=80$ Sec. $[C_3]$ as-deposited $[c_3]$ electron irradiated.
(iii) Cadmium Telluride

The surface morphology of as-deposited and irradiated CdTe films were determined using Scanning Electron Microscope (SEM). Fig. 7.12[A<sub>4</sub>, B<sub>4</sub> and C<sub>4</sub>] and [a<sub>4</sub>, a<sub>4</sub> and a<sub>4</sub>] gives an idea about a SEM micrograph of as-deposited and irradiated CdTe thin films for different concentrations, (A<sub>4</sub>) = 0.04M CdSO<sub>4</sub> + 0.01M Na<sub>2</sub>TeO<sub>3</sub> + 0.1M EDTA., (B<sub>4</sub>) = 0.06M CdSO<sub>4</sub> + 0.02M Na<sub>2</sub>TeO<sub>3</sub> + 0.1M EDTA. and (C<sub>4</sub>) = 0.08M CdSO<sub>4</sub> + 0.03M Na<sub>2</sub>TeO<sub>3</sub> + 0.1M EDTA. It is observed that the films are with spherical shaped grains, uniform and pinhole free. The average grain size was calculated to be 263 nm and 365 nm respectively. It is observed that electron irradiation resulted in the increase in grain size.

Fig. 7.12 SEM images of CdTe thin film for bath concentrations, (A<sub>4</sub>)=0.04M CdSO<sub>4</sub> + 0.01M Na<sub>2</sub>TeO<sub>3</sub> + 0.1M EDTA. for different time (A<sup>1</sup> <sub>4</sub>, a<sup>1</sup> <sub>4</sub>)=120 Sec. (A<sup>2</sup> <sub>4</sub>, a<sup>2</sup> <sub>4</sub>)=180 Sec. (A<sup>3</sup> <sub>4</sub>, a<sup>3</sup> <sub>4</sub>)=240 Sec. [A<sub>4</sub>] as-deposited [a<sub>4</sub>] electron irradiated
Fig. 7.12 SEM images of CdTe thin film for bath concentrations, $(B_4) = 0.06M \text{CdSO}_4 + 0.02M \text{Na}_2\text{TeO}_3 + 0.1M \text{EDTA}$. for different time $(B_{14}, b_{14}) = 120$ Sec. $(B_{24}, b_{24}) = 180$ Sec. $(B_{34}, b_{34}) = 240$ Sec. $[B_4]$ as-deposited $[b_4]$ electron irradiated
Fig. 7.12 SEM images of CdTe thin film for bath concentrations, $(C_4) = 0.08M$ CdSO$_4$ + 0.03M Na$_2$TeO$_3$ + 0.1M EDTA. for different time $(C_1^4, c_1^4) = 120$ Sec. $(C_2^4, c_2^4) = 180$ Sec. $(C_3^4, c_3^4) = 240$ Sec. $[C_4]$ as-deposited $[c_4]$ electron irradiated

**7.3.3 Optical analysis**

(i) Cadmium Sulfide (CdS) thin films

The optical absorption of these films been studied in the wavelength range 350-1200 nm, without accounting for reflection and transmission losses. According to the theory of optical interband transition (direct and indirect) in solids, near the absorption edge, the absorption coefficient varies with photon energy $h\nu$ which is given by the following expression,

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$$  \hspace{1cm} (7.1)

Where,

- $A$ - constant
- $E_g$ - optical band gap energy.
- $n$ - depends on the kind of optical transition.

Fig. 7.13(A$_2$ as-deposited ) and (a$_2$ electron irradiated). Fig. 7.14(B$_2$) and (b$_2$) and Fig. 7.15(C$_2$) and (c$_2$) represents plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$ for as deposited and electron beam irradiated CdS thin films from a bath having composition for (A$_2$). Calculated optical band gap for as deposited decreases from 2.41eV to 2.29eV and radiation dose of 10Kgy caused band gap decreases from
1.38eV to 1.27eV. Similarly for (B₂) bath concentration the bandgap energy decreases from 2.40 to 2.31eV after electron beam irradiation it’s decreases from 2.39 to 2.26eV. For (C₂) bath concentrations the bandgap energy decreases from 2.34 to 2.24eV after electron beam irradiation bandgap energy decreases from 2.31 to 2.21eV. From this graph direct allowed transition energy was estimated by extrapolating the linear portion to intercept on the energy axis. The band gap was found to be 2.41eV to 2.24eV for different concentration. The optical absorption studies shows that the as deposited CdS thin films has decreasing band gap energy with increasing bath concentration. The band gap energies estimated from the graphs are found to be 2.39eV to 2.21eV for irradiated film. Similar decrease in band gap energy during irradiation was reported on other semiconductor thin films [26, 27]. The observed decrease in the band gap might be due to the creation of shallow defect levels near the conduction band as a result of irradiation [28,29].

![Graph showing optical absorption studies of CdS thin films](image)

Fig. 7.13 CdS thin film represent a plot of \((\alpha h\nu)^2\) versus \(h\nu\) for (A₂)=0.04 M CdSO₄ + 0.4 M Na₂S₂O₃ + 0.06 M EDTA concentrations, for different time (A₁, a₁) =110 Sec. (A₂, a₂)=120 Sec. (A₃, a₃)=130 Sec. [A₂] as-deposited [a₂] electron irradiated.
Fig. 7.14 CdS thin film represent a plot of \((\alpha hv)^2\) versus \(hv\) for \((B_2)=0.06\) M CdSO\(_4\) + 0.6 M Na\(_2\)S\(_2\)O\(_3\) + 0.08 M EDTA. concentrations, for different time \((B_1, b_1)=110\) Sec. \((B_2, b_2)=120\) Sec. \((B_3, b_3)=130\) Sec. \([B_2]\) as-deposited \([b_2]\) electron irradiated.

Fig. 7.15 CdS thin film represent a plot of \((\alpha hv)^2\) versus \(hv\) for \((C_2)=0.08\) M CdSO\(_4\) + 0.8 M Na\(_2\)S\(_2\)O\(_3\) + 0.1 M EDTA. concentrations, for different time \((C_1, c_1)=110\) Sec. \((C_2, c_2)=120\) Sec. \((C_3, c_3)=130\) Sec. \([C_2]\) as-deposited \([c_2]\) electron irradiated.
(ii) Cadmium Selenide (CdSe) thin films

Fig. 7.16 (A₃ as-deposited) and (a₃ electron irradiated). Fig. 7.17(B₃) and (b₃) and Fig. 7.18(C₃) and (c₃) represents plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$ for as deposited and electron beam irradiated CdSe thin films from a bath having composition for (A₃). Calculated optical band gap for as deposited decreases from 1.78 eV to 1.66 eV and radiation dose of 10Kgy caused band gap decreases from 1.75 eV to 1.63 eV. Similarly for (B₃) bath concentration the bandgap energy decreases from 1.74 eV to 1.65 eV after electron beam irradiation it’s decreases from 1.72 eV to 1.62 eV. For (C₃) bath concentrations the bandgap energy decreases from 1.73 eV to 1.64 eV after electron beam irradiation it’s decreases from 1.71 eV to 1.61 eV. From this graph direct allowed transition energy was estimated by extrapolating the linear portion to intercept on the energy axis. The band gap was found to be 1.78 eV to 1.64 eV for different concentration. The optical absorption studies shows that the as deposited CdSe thin films has decreasing band gap energy with increasing bath concentration. The band gap energies estimated from the graphs are found to be 1.75 eV to 1.61 eV for irradiated film. Thus it seen that as a result of irradiation, it is decrease in the band gap which might be due to the creation of shallow defect levels near the conduction band and due to increase in grain size[30].
Fig. 7.16 CdSe thin film represent a plot of $(\alpha h\nu)^2$ versus $h\nu$ for $(A_3)$ concentrations, for different time $(A_1^3, a_1^3)=60$ Sec. $(A_2^3, a_2^3)=70$ Sec. $(A_3^3, a_3^3)=80$ Sec. $[A_3]$ as-deposited $[a_3]$ electron irradiated.

Fig. 7.17 CdSe thin film represent a plot of $(\alpha h\nu)^2$ versus $h\nu$ for $(B_3)$ concentrations, for different time $(B_1^3, b_1^3)=60$ Sec. $(B_2^3, b_2^3)=70$ Sec. $(B_3^3, b_3^3)=80$ Sec. $[B_3]$ as-deposited $[b_3]$ electron irradiated.
Fig. 7.18 CdSe thin film represent a plot of $(\alpha h\nu)^2$ versus $h\nu$ for $(C_3)$ concentrations, for different time $(C_1^3, c_1^3)=60$ Sec. $(C_2^3, c_2^3)=70$ Sec. $(C_3^3, c_3^3)=80$ Sec. $[C_3]$ as-deposited $[c_3]$ electron irradiated.

(iii) Cadmium Telluride (CdTe) thin films

Fig. 7.19 (A$_4$ as-deposited ) and (a$_4$ electron irradiated). Fig. 7.20 (B$_4$) and (b$_4$) and Fig. 7.21 (C$_4$) and (c$_4$) represents plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$ for as deposited and electron beam irradiated CdTe thin films from a bath having composition for (A$_4$). Calculated optical band gap for as deposited decreases from 1.59 eV to 1.53 eV and radiation dose of 10Kgy caused band gap decreases from 1.58 eV to 1.52 eV. Similarly for (B$_4$) bath concentration the bandgap energy decreases from 1.57 eV to 1.51 eV after electron beam irradiation it’s decreases from 1.56 eV to 1.50 eV. and (C$_4$) bath concentrations the bandgap energy decreases from 1.56 eV to 1.52 eV after electron beam irradiation it’s decreases from 1.55 eV to 1.51 eV. From this graph direct allowed transition energy was estimated by extrapolating the linear portion to intercept on the energy axis. The band gap was found to be 1.59 eV to 1.51 eV. for different concentration. The optical absorption studies shows that the as deposited CdTe thin films has decreasing band gap energy with increasing bath concentration. The band gap energies estimated from the graphs are found to be 1.58 eV to 1.50 eV for irradiated film. Thus it seen that as a result of irradiation, it is decrease in the
band gap which might be due to the creation of shallow defect levels near the conduction band and due to increase in grain size.

Fig. 7.19 CdTe thin film represent a plot of \((\alpha h\nu)^2\) versus \(h\nu\) for \((A_4)\) concentrations, for different time \((A_1^4 , a_1^4)= 120\) Sec. \((A_2^4 , a_2^4)= 180\) Sec. \((A_3^4 , a_3^4)=240\) Sec. \([A_4]\) as-deposited [a₄] electron irradiated.

Fig. 7.20 CdTe thin film represent a plot of \((\alpha h\nu)^2\) versus \(h\nu\) for \((B_4)\) concentrations, for different time \((B_1^4 , b_1^4)= 120\) Sec. \((B_2^4 , b_2^4)= 180\) Sec. \((B_3^4 , b_3^4)=240\) Sec. \([B_4]\) as-deposited [b₄] electron irradiated.
7.3.4 Surface wettability

(i) Cadmium Sulfide (CdS) thin films

Wettability involves the interaction between a liquid and a solid in contact. The wetting behavior is characterized by the value of the contact angle, a microscopic parameter. If the wettability is high, contact angle ($\theta$), will be small and the surface is hydrophilic. On the contrary, if the wettability is low, $\theta$ will be large and the surface is hydrophobic. Observed values of contact angles of CdS material. It shows that surface of CdS thin films is Super hydrophilic material[31].

(ii) Cadmium Selenide (CdSe) thin films

Fig. 7.22 [A_3] and [a_3] shows the systematic presentation of measurement of contact angles for as deposited and electron beam irradiated CdSe thin films for (A_3=a_3)= 0.04M CdSO_4 + 0.06M SeO_2 + 0.1M EDTA. Contact angles as deposited 31°, 52° and 56° and electron beam irradiated 46°, 63° and 76° respectively, indicating that CdSe is a hydrophilic material. Fig. 7.23 [B_3] and [b_3] illustrate the schematic presentation of measurement of contact angles for as deposited 36°,67° and 84°and electron beam irradiated 58°,81° and 91° of CdSe thin films for (B_3=b_3) = 0.06M CdSO_4 + 0.08M SeO_2 +0.1M EDTA. Fig. 7.24
[C₃] and [c₃] illustrate the schematic presentation of measurement of contact angles for as deposited 75°,86° and 90° and electron beam irradiated 88°,91° and 97° of CdSe thin films for (C₃=c₃)= 0.08M CdSO₄ + 0.1M SeO₂ + 0.1M EDTA. It shows that surface of CdSe thin films is hydrophobic material after electron beam irradiated.

It shows that surface of CdSe thin films is highly compact and smooth as like surface of glass. Slight increase in contact angle after irradiation is attributed to little enhancement in grain size. All the films have as deposited hydrophilic nature but after electron beam irradiated for bath [b₃] and [c₃] its change hydrophilic to hydrophobic nature. Efforts are in progress to increase contact angle by modifying surface properties [32-34].

**Fig. 7.22** contact angle of CdSe thin films for bath concentration (A₃)=as deposited and (a₄)=irradiated for deposition time [A₁₃, a₁₃ =60 sec.], [A²₃,a²₃=70 sec.] and [A³₃,a³₃=80 sec] bath composition (A₃=a₃)= 0.04M CdSO₄ + 0.06M SeO₂ + 0.1M EDTA.
Fig. 7.23 contact angle of CdSe thin films for bath concentration \( (B_3) = \) as deposited and \( (b_3) = \) irradiated for deposition time \([B_3^1, b_3^1 = 60 \text{ sec.}], \ [B_3^2, b_3^2 = 70 \text{ sec.}] \) and \([B_3^3, b_3^3 = 80 \text{ sec.}] \) bath composition \((B_3 = b_3)= 0.06 \text{M CdSO}_4 + 0.08 \text{M SeO}_2 + 0.1 \text{M EDTA.}\)

Fig. 7.24 contact angle of CdSe thin films for bath concentration \( (C_3) = \) as deposited and \( (c_3) = \) irradiated for deposition time \([C_3^1, c_3^1 = 60 \text{ sec.}], \ [C_3^2, c_3^2 = 70 \text{ sec.}] \) and \([C_3^3, c_3^3 = 80 \text{ sec.}] \) bath composition \((C_3 = c_3)= 0.08 \text{M CdSO}_4 + 0.1 \text{M SeO}_2 + 0.1 \text{M EDTA.}\)
(iii) Cadmium Telluride (CdTe) thin films

Fig. 7.25 \([A_4]\) and \([a_4]\) shows the systematic presentation of measurement of contact angles for as deposited and electron beam irradiated CdTe thin films for \((A_4=a_4)= 0.04\text{M CdSO}_4 + 0.01\text{M Na}_2\text{TeO}_3 + 0.1\text{M EDTA}\). contact angles as deposited 37°, 41° and 50° and electron beam irradiated 37°, 49° and 62° respectively, indicating that CdTe is a hydrophilic material. Fig. 7.26 \([B_4]\) and \([b_4]\) illustrate the schematic presentation of measurement of contact angles for as deposited 43°, 63° and 70° and electron beam irradiated 47°, 68° and 84° of CdTe thin films for \((B_4=b_4) = 0.06\text{M CdSO}_4 + 0.02\text{M Na}_2\text{TeO}_3 + 0.1\text{M EDTA}\). Fig. 7.27 \([C_4]\) and \([c_4]\) illustrate the schematic presentation of measurement of contact angles for as deposited 48°, 82° and 95° and electron beam irradiated 72°, 93° and 102° of CdTe thin films for \((C_4=c_4) = 0.08\text{M CdSO}_4 + 0.04\text{M Na}_2\text{TeO}_3 + 0.1\text{M EDTA}\). It shows that surface of CdTe thin films is hydrophobic material after electron beam irradiated.

It shows that surface of CdTe thin films is highly compact and smooth as like surface of glass. Slight increase in contact angle after irradiation is attributed to little enhancement in grain size. The contact angle factor is known to affect the wettability of a solid surface. Efforts are in progress to increase contact angle by modifying surface properties.
Fig. 7.25 Photo image of contact angle for bath concentration ($A_4$)=as deposited and ($a_4$)=irradiated for deposition time [$A_4^1 , a_4^1 =$120 sec.], [$A_4^2 , a_4^2 =$180 sec.] and [$A_4^3 , a_4^3 =$240 sec.] bath composition ($A_4=a_4$) = 0.04M CdSO$_4$ + 0.01M Na$_2$TeO$_3$ + 0.1M EDTA,

Fig. 7.26 Photo image of contact angle for bath concentration ($B_4$)=as deposited and ($b_4$)=irradiated for deposition time [$B_4^1 , b_4^1 =$120 sec.], [$B_4^2 , b_4^2 =$180 sec.] and [$B_4^3 , b_4^3 =$240 sec.] bath composition ($B_4=b_4$) = 0.06M CdSO$_4$ + 0.02M Na$_2$TeO$_3$+ 0.1M EDTA.
Fig. 7.27 Photo image of contact angle for bath concentration \((C_4)\) as deposited and \((c_4)\) irradiated for deposition time \([C_4^1, c_4^1 = 120 \text{ sec.}], [C_4^2, c_4^2 = 180 \text{ sec.}]\) and \([C_4^3, c_4^3 = 240 \text{ sec.}]\) bath composition \((C_4 = C_4) = 0.08 \text{M CdSO}_4 + 0.04 \text{M Na}_2\text{TeO}_3 + 0.1 \text{M EDTA}.

7.3.5 Fourier Transform Raman Spectroscopy (FT Raman spectroscopy)

(i) Cadmium Sulfide

The FT-Raman spectra of as-deposited and irradiated CdS thin films for bath composition \((A_2) = 0.04 \text{ M CdSO}_4 + 0.4 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.06 \text{ M EDTA}, (B_2) = 0.06 \text{ M CdSO}_4 + 0.6 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.08 \text{ M EDTA} and (C_2) = 0.08 \text{ M CdSO}_4 + 0.8 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA}. The Raman bands of as-deposited and irradiated thin films are observed at around three bands at 169.62, 250.40 and 306.59 cm\(^{-1}\). The peak intensity and width increases after irradiation of electron beam. The ion bombardment increases the crystallinity of films due to induced defects and therefore the Raman bands whose intensity depends on the crystallinity also get increased shown in Fig. 7.28 \((A_3^3)\) as-deposited and \((a_3^3)\) irradiated films. FT-Raman spectra shows three bands at 168.52, 247.32 and 300.19 cm\(^{-1}\) and slight increase in intensity of peaks due to irradiation[35].
Fig. 7.28 FT Raman spectra of \((A^3_2), (B^3_2)\) and \((C^3_2)\) as deposited and \((a^3_2), (b^3_2)\) and \((c^3_2)\) irradiated CdS films for bath composition \((A_2, a_2) = 0.04\ M\ CdSO_4 + 0.4\ M\ Na_2S_2O_3 + 0.06\ M\ EDTA,\) \((B_2, b_2) = 0.06\ M\ CdSO_4 + 0.6\ M\ Na_2S_2O_3 + 0.08\ M\ EDTA,\) \((C_2, c_2) = 0.08\ M\ CdSO_4 + 0.8\ M\ Na_2S_2O_3 + 0.1\ M\ EDTA.\)

(ii) Cadmium Selenide

The FT-Raman spectra of as-deposited and irradiated CdSe thin films for bath composition \((A_3)=0.04M\ CdSO_4 + 0.06M\ SeO_2 + 0.1M\ EDTA,\) \((B_3) 0.06M\ CdSO_4 + 0.08M\ SeO_2 + 0.1M\ EDTA.\) \((C_3) 0.08M\ CdSO_4 + 0.1M\ SeO_2 + 0.1M\ EDTA.\) The Raman bands of as-deposited and irradiated thin films are observed at around three bands at 175.24, 263.70 and 317.89 cm\(^{-1}\). The peak intensity and width increases after irradiation of electron beam. The ion bombardment increases the crystallinity of films due to induced defects and therefore the Raman bands whose intensity depends on the crystallinity also get increased shown in Fig. 7.29 \((A^3_3)\) as-deposited and \((a^3_3)\) irradiated films.
Fig. 7.29 FT Raman spectra of (A₃), (B₃) and (C₃) as deposited and (a₃), (b₃) and (c₃) irradiated CdSe films for bath composition (A₃, a₃)=0.04M CdSO₄ + 0.06M SeO₂ + 0.1M EDTA., (B₃, b₃)=0.06M CdSO₄ + 0.08M SeO₂ + 0.1M EDTA. and (C₃, c₃)=0.08M CdSO₄ + 0.1M SeO₂ + 0.1M EDTA.

(iii) Cadmium Telluride

The FT-Raman spectra of as-deposited and irradiated CdTe thin films for bath composition (A₄) = 0.04M CdSO₄ + 0.01M Na₂TeO₃ + 0.1M EDTA., (B₄) = 0.06M CdSO₄ + 0.02M Na₂TeO₃ + 0.1M EDTA. and (C₄) = 0.08M CdSO₄ + 0.03M Na₂TeO₃ + 0.1M EDTA. The Raman bands of as-deposited and irradiated thin films are observed at around three bands at 155.24, 263.56 and 317.29 cm⁻¹. The peak intensity and width increases after irradiation of electron beam. The ion bombardment increases the crystallinity of films due to induced defects and therefore the Raman bands whose intensity depends on the crystallinity also get increased shown in Fig. 7.30 (A₄) as-deposited and (a₄) irradiated films.
7.3.6 FT-IR spectroscopy

(i) Cadmium Sulfide

FT-IR spectra were recorded on a spectrophotometer (Perkin Elmer FT-IR Spectrum-GX), at laser power 0-450 mW, the wave number ranging from 400-4000 cm\(^{-1}\). The FT-IR spectra of CdS films are shown in Fig. 7.31 for bath concentration \((A_2, a_2) = 0.04 \text{ M CdSO}_4 + 0.4 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.06 \text{ M EDTA}, \ (B_2, b_2) = 0.06 \text{ M CdSO}_4 + 0.6 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.08 \text{ M EDTA} , \ (C_2, c_2) = 0.08 \text{ M CdSO}_4 + 0.8 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA}. The FT-IR bands are at around 617.78, 858.06, 1116.43 cm\(^{-1}\) for bath concentration \((A_2, a_2)\), 663.17, 1006.41, 1129.33 cm\(^{-1}\) for bath concentration \((B_2, b_2)\) and 659.55, 1017.27, 1114.80 cm\(^{-1}\) for bath concentration \((C_2, c_2)\).
Fig. 7.31 FT-IR spectra of (A\textsuperscript{3} \textsubscript{2}), (B\textsuperscript{3} \textsubscript{2}) and (C\textsuperscript{3} \textsubscript{2}) as deposited and (a\textsuperscript{3} \textsubscript{2}), (b\textsuperscript{3} \textsubscript{2}) and (c\textsuperscript{3} \textsubscript{2}) irradiated CdS films for bath composition (A\textsubscript{2}, a\textsubscript{2}) = 0.04 M CdSO\textsubscript{4} + 0.4 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} + 0.06 M EDTA, (B\textsubscript{2}, b\textsubscript{2}) = 0.06 M CdSO\textsubscript{4} + 0.6 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} + 0.08 M EDTA, (C\textsubscript{2}, c\textsubscript{2}) = 0.08 M CdSO\textsubscript{4} + 0.8 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} + 0.1 M EDTA.

(ii) Cadmium Selenide

FT-IR spectra were recorded on a spectrophotometer (Perkin Elmer FT-IR Spectrum-GX), at laser power 0-450 mW, the wave number ranging from 400-4000 cm\textsuperscript{-1}. The FT-IR spectra of CdSe films are shown in Fig.7.32 for bath concentration (A\textsubscript{3}, a\textsubscript{3}) = 0.04 M CdSO\textsubscript{4} + 0.06 M SeO\textsubscript{2} + 0.1 M EDTA, (B\textsubscript{3}, b\textsubscript{3}) = 0.06 M CdSO\textsubscript{4} + 0.08 M SeO\textsubscript{2} + 0.1 M EDTA, (C\textsubscript{3}, c\textsubscript{3}) = 0.08 M CdSO\textsubscript{4} + 0.1 M SeO\textsubscript{2} + 0.1 M EDTA. The FT-IR bands are at around 617.64, 1019.45, 1118.91 cm\textsuperscript{-1} for bath concentration (A\textsubscript{3}, a\textsubscript{3}), 616.20, 908.85, 1113.72 cm\textsuperscript{-1} for bath concentration (B\textsubscript{3}, b\textsubscript{3}), and 612.58, 854.66, 1109.52 cm\textsuperscript{-1} for bath concentration (C\textsubscript{3}, c\textsubscript{3}).
Fig. 7.32 FT-IR spectra of (A\textsuperscript{3}), (B\textsuperscript{3}) and (C\textsuperscript{3}) as deposited and (a\textsuperscript{3}), (b\textsuperscript{3}) and (c\textsuperscript{3}) irradiated CdS films for bath composition (A\textsubscript{3}, a\textsubscript{3}) = 0.04M CdSO\textsubscript{4} + 0.06M SeO\textsubscript{2} + 0.1M EDTA., (B\textsubscript{3}, b\textsubscript{3}) = 0.06M CdSO\textsubscript{4} + 0.08M SeO\textsubscript{2} + 0.1M EDTA., (C\textsubscript{3}, c\textsubscript{3}) = 0.08M CdSO\textsubscript{4} + 0.1M SeO\textsubscript{2} + 0.1M EDTA.

(iii) Cadmium Telluride

FT-IR spectra were recorded on a spectrophotometer (Perkin Elmer FT-IR Spectrum-GX), at laser power 0-450 mW, the wave number ranging from 400-4000 cm\textsuperscript{-1}. The FT-IR spectra of CdTe films are shown in Fig.7.33 for bath concentration (A\textsubscript{4}, a\textsubscript{4}) = 0.04M CdSO\textsubscript{4} + 0.01M Na\textsubscript{2}TeO\textsubscript{3} + 0.1M EDTA., (B\textsubscript{4}, b\textsubscript{4}) = 0.06M CdSO\textsubscript{4} + 0.02M Na\textsubscript{2}TeO\textsubscript{3} + 0.1M EDTA., (C\textsubscript{4}, c\textsubscript{4}) = 0.08M CdSO\textsubscript{4} + 0.03M Na\textsubscript{2}TeO\textsubscript{3} + 0.1M EDTA. The FT-IR bands are at around 739.94, 861.88 cm\textsuperscript{-1} for bath concentration (A\textsubscript{4}, a\textsubscript{4}), 618.94, 771.83, 867.29 cm\textsuperscript{-1} for bath concentration (B\textsubscript{4}, b\textsubscript{4}), and 620.84, 768.79, 869.77 cm\textsuperscript{-1} for bath concentration (C\textsubscript{4}, c\textsubscript{4}).
Fig. 7.33 FT-IR spectra of (A\(^3\)\(^4\)), (B\(^3\)\(^4\)) and (C\(^3\)\(^4\)) as deposited and (a\(^3\)\(^4\)), (b\(^3\)\(^4\)) and (c\(^3\)\(^4\)) irradiated CdS films for bath composition (A\(_4\), a\(_4\)) = 0.04M CdSO\(_4\) + 0.01M Na\(_2\)TeO\(_3\) + 0.1M EDTA., (B\(_4\), b\(_4\)) = 0.06M CdSO\(_4\) + 0.02M Na\(_2\)TeO\(_3\) + 0.1M EDTA., (C\(_4\), c\(_4\)) = 0.08M CdSO\(_4\) + 0.03M Na\(_2\)TeO\(_3\) + 0.1M EDTA.
References


20. JCPDS data file No- 00-041-1049.
21. JCPDS data file No. 43-1471.
23. JCPDS data file No- 77-2307.
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