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A variable electron beam and its irradiation effect on optical and electrical properties of CdS thin films

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Abstract. A low energy electron accelerator has been constructed and tested. The electron beam can operate in low energy mode (100 eV to 10 keV) having a beam diameter of 8–10 mm. Thin films of CdS having thickness of 100 nm deposited on ITO-coated glass substrate by thermal evaporation method have been irradiated by electron beam in the above instrument. The *I–V* characteristic is found to be nonlinear before electron irradiation and linear after electron irradiation. The TEP measurement confirms the n-type nature of the material. The TEP and *I–V* measurements also confirm the modification of ITO/CdS interface with electron irradiation.

Keywords. Electron irradiation; semiconductor; optical energy band gap and absorption characteristics; thermo-electric power and conductivity.

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1. Introduction

The electron irradiation is a method for introducing simple intrinsic defects in a sample in a controlled manner and also for inducing regrowth and crystallization of materials. Electron irradiation creates mainly monovacancies, divacancies and Frenkel defects [1]. CdS thin films are of considerable interest as they can be used in fabrication of solar cells and other opto-electronic devices [2–4]. In particular, heterojunction solar cells with a narrow band gap base and wide band gap window have been investigated in an attempt to develop efficient, stable and low-cost solar cells. The technology which promises highly efficient CdS/CdTe solar cells requires conductor substrates for improving efficiency [4]. Indium tin oxide (ITO) film deposited on glass substrate is used both as a conductor and as an electrode to support the CdS thin film into the heterostructure CdTe/CdS/ITO/glass solar cells [5]. The CdS/ITO interface quality plays an important role in facilitating the free electron flow through the solar cell. The lattice mismatch between ITO/CdS is one of these attractive topics because of the influence of defect induced during the relaxation process on the material properties. It is well-known that these intrinsic strains develop during the film growth process from the accumulation of the thermal expansion coefficient mismatch between the film and the substrate as observed by Castro-Rodringer *et al* [7]. Castro-Rodringer *et al* suggested that misfit between the CdS film and ITO substrate and other effects such as the roughness of ITO substrate and grain size of CdS films induce this strain. The optical transmission and absorbance spectra are used to find the optical band gap of CdS thin film (see [8–12]). The shifting of an absorbance spectrum towards lower energies or higher wavelength was due to self-absorption at glass/CdS interface as observed by Ullrich and Schroeder [15]. CdS film has been used in solar devices with CdTe as a hetero-junction material and the efficiency was found to be about 11.7% [13]. When CdS film is deposited on a transparent conductive oxide (TCO)/glass substrate by the metal oxide chemical vapour deposition (MOCVD) technique and CdTe film is deposited on it in atmospheric pressure by a close-spaced sublimation (CSS) technique, CdS/CdTe solar cell shows maximum efficiency of 10.5% [14]. Controlled changes in the properties of this interface can produce variations in the conductive properties of the semiconductor. Annealing processes are normally attempted to reduce the intrinsic stress improving lattice mismatch and to produce larger trajectory for the free electrons for better electrical conductivity [6]. Ion beams and electron beams are also used for modifications of surfaces and interfaces of semiconductors.

The J–V characteristics were studied by Mahmoud *et al* [18] for an Al/CdS/Al sandwich structure to test the rectification effects. It was found that no rectifying behaviour was noticed when polarity of applied voltage was reversed. A similar behaviour was also observed by [17] for Au/CdS/Au structure but after the electron irradiation (5 to 7 MeV) it is found that barriers associated with stacking faults increased (columnar structure that grew perpendicular to the glass substrate) and the number of traps in the band of the semiconductor also increased. These defects could be identified as Cd vacancies induced by electron irradiation. A low energy electron beam-induced regrowth of isolated amorphous zones in Si and Ge has been observed by Jencic and Robertson [19]. According to these authors the faster regrowth rate at low electron beam energies could be attributed to electronic excitation rather than displacement caused directly by collision stimulating the defect responsible for the regrowth process. However, the effect of such a low energy electron irradiation on the optical properties of CdS thin films for interface and surface modification is not reported in literature.

In this paper we are presenting the effect of low energy electron beam irradiation on the absorbance edge, optical band gap, V–I characteristics, TEP and conductivity measurements of CdS thin films. We are suggesting that electron beam irradiation may be used to modify the lattice mismatch to increase the efficiency of solar cells.

2. Experimental

The vacuum system has been designed and developed in our laboratory for production of low energy electron beam with a beam target chamber. It consists of an ultra-high vacuum system with a turbo-molecular pump and ion pump to provide a quick recyclable vacuum system of 10^{-7} Torr. The beam can operate in low energy mode (100 eV to 10 KeV) with a beam diameter of 8–10 mm. The transmission coefficient is found to be $1.4 * 10^{-2}$ from electron emission source to target position through 2.5 m long U-tube at a pressure of 10^{-7} Torr. The beam was generated using electron-emitting filament kept at −300 V with respect to ground. An electrostatic lens system with three elements kept at −150 V, −100 V and −40 V provides a stable electron beam up to 50 nA through an aperture of 8 mm on target samples. The beam trajectory as estimated using SIMION-6 software [20] has been found to give satisfactory focusing action at the voltages within +5 V and −5 V accuracy [21].

CdS thin films were prepared using vacuum thermal evaporation method at a pressure of 10^{-5} Torr. CdS powder (99.99%) obtained from BDH Chemicals Ltd., England was placed in a tantalum boat in a vacuum chamber for thermal evaporation. The films were deposited on glass substrate and glass substrate coated with indium tin oxide (ITO). The thickness of the thin films was found to be 100 nm as measured using a quartz crystal thickness monitor. An electron beam of 10 keV energy was used to irradiate the as-deposited films. The optical absorbance spectra were recorded for thin films, before and after electron irradiation, using Hitachi spectrophotometer model 330 in the wavelength range 350–850 nm. The TEP measurements were carried out on CdS thin films before and after electron irradiation. In this method temperature at one end of the film was varied and temperature of other end was kept constant. The conductivity and I–V characteristic of thin film were also carried out using Keithley-238, high current source measurement unit before and after electron irradiation.

3. Results and discussion

3.1 *Absorbance spectra of CdS thin film*

Figure 1a shows the absorbance spectra of a CdS film deposited on a glass substrate. The absorbance edge is found in the green region at wavelength ∼540 nm. However, for films deposited on conducting glass substrates (shown in figure 1b), the absorbance edge is found in the near red region of wavelength (590 nm). This variation of absorbance edge may be due to the combined effect of ITO and CdS film or strain mismatch between ITO and CdS films. A similar effect is observed also by Ullrich and Schroeder [15]. They have suggested that the absorbance spectrum was shifted to lower energies or higher wavelength due to self-absorption at glass/CdS interface. We also believe that this shift occurs due to self-absorption at glass/ITO/CdS interface. Figure 1c shows the absorbance spectra of electron-irradiated CdS film, which was deposited on a conducting glass substrate. It was observed that the absorbance edge move into the green region of wavelength (540 nm). This may be due to two effects taking place simultaneously: (1) due to the strain mismatch between ITO and CdS thin films and (2) owing to the electronic excitation [12] reducing self-absorption. The reduced efficiency of a CdTe/CdS/ITO solar cell may be due to the substrate conducting oxide layer, which is consistent with our study of ITO/CdS film, as it also shows a reduction in absorbance spectra. But after electron irradiation strain mismatch seems to be modified and absorbance spectra move towards its original position as deposited on glass substrate.

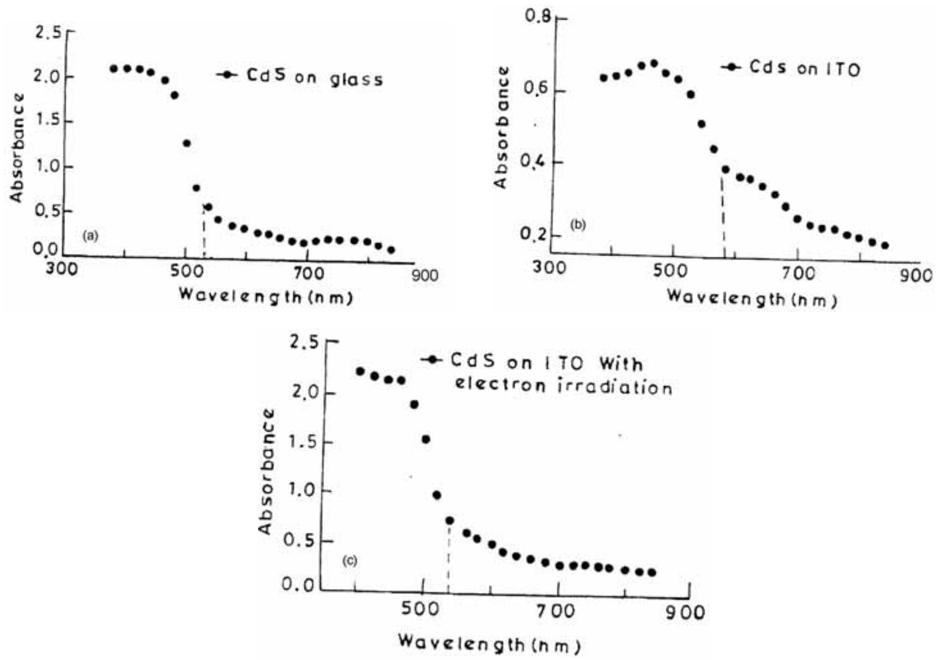

Figure 1. Absorbance spectra of CdS thin films with photon wavelength. (**a**) CdS film on glass, (**b**) CdS film on ITO conducting surface, (**c**) CdS film on ITO conducting surface with electron irradiation.

3.2 *Optical band gap of CdS thin films*

The optical band gap was calculated using the Tauc [22] relation given by the formula

$$\alpha h\nu = A(h\nu - E_g)^n.$$

Here $h\nu$ is the photon energy, α is the absorption coefficient, E_g is the optical band gap, A is a constant and $n = 1/2$ for direct band gap material. Figures 2a–2c show a plot of $(\alpha h\nu)^2$ vs. photon energy in the wavelength range 350–850 nm. The values of the optical band gap are determined by extrapolating the linear part of $(\alpha h\nu)^2$ vs. energy axis, where α is the absorption coefficient. The plots show different band gaps for samples prepared under different deposition conditions. As shown in figure 2a the optical band gap is found to be 2.26 eV for CdS film deposited on glass substrate. The value of optical band gap agrees well with the value of vacuum-evaporated CdS thin films reported in [8]. However, as shown in figure 2b band gap of CdS films deposited on ITO-coated glass is found to be 1.95 eV, which is slightly less than the reported value of band gap (2.22 eV). This may be attributed to lattice strain mismatch between CdS and ITO thin films. After electron irradiation the optical band gap is found to increase from 1.95 to 2.26 eV as shown in figure 2c. It appears that the strains have been modified by electron irradiation possibly due to the elimination of defect accumulation in ITO and CdS films. As mentioned

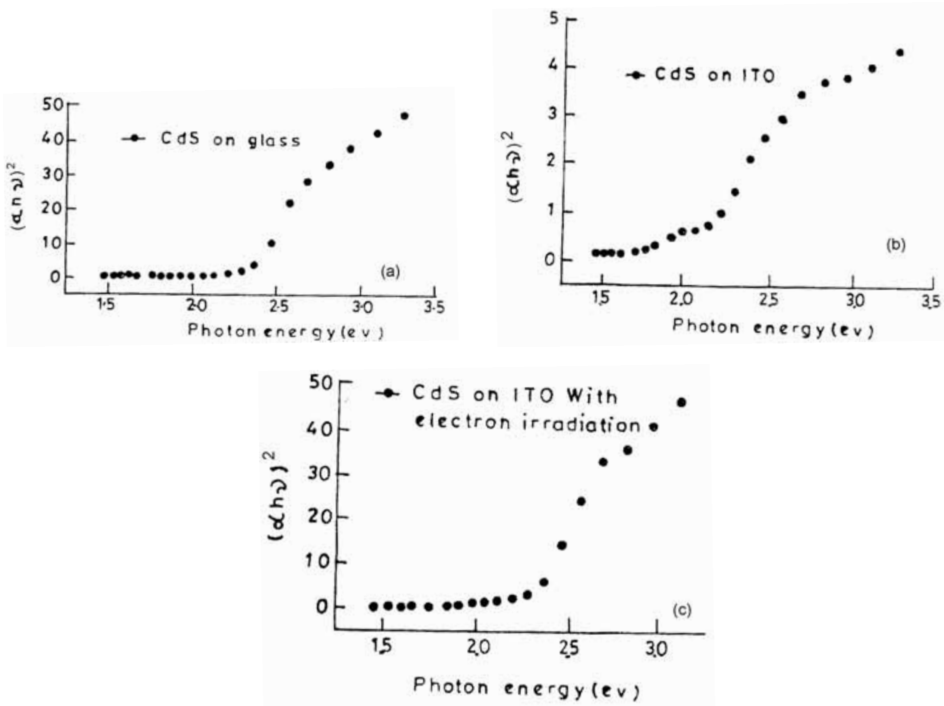

Figure 2. The graph showing photon energy (eV) vs. $(\alpha h\nu)^2$ for CdS thin films. (**a**) CdS film on glass, (**b**) CdS film on ITO conducting surface, (**c**) CdS film on ITO conducting surface with electron irradiation.

earlier, similar behaviour was also observed by Jencic and Robertson [19] who have also observed regrowth for both axial and tilted illumination for low energy electron beam irradiation.

3.3 *The I–V characteristic of thin films*

The *I–V* characteristics measured with and without electron beam irradiation for ITO/CdS thin films are shown in figure 3. It is observed that *I–V* characteristic behaviour is nonlinear before irradiation and becomes linear after electron irradiation. This is due to mismatch modification between the interfaces of films. However, in our case the thin film structure (glass/ITO/CdS) was found to be rectifying or nonlinear due to mismatching of interface of ITO/CdS film without electron irradiation. This nonlinear behaviour would be eliminated after an electron irradiation which is useful in modifying the interface.

3.4 *The conductivity measurement of CdS thin films*

Figure 4 shows the variation of conductivity with temperature for CdS films deposited on ITO-coated glass. The conductivity is initially found to increase with

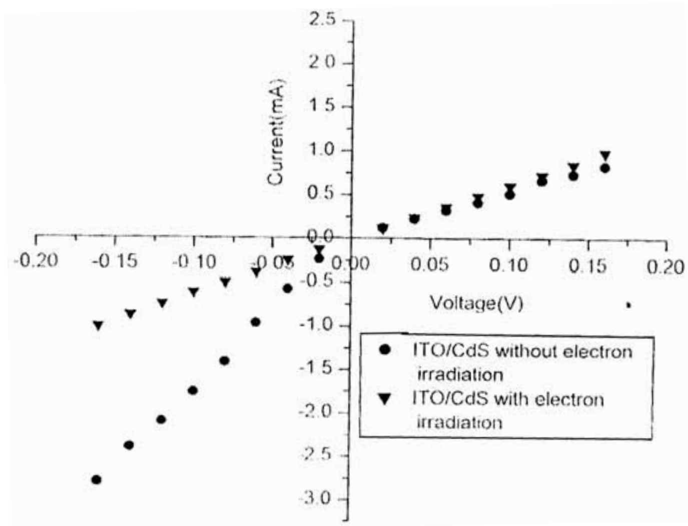

Figure 3. The V–I characteristics of ITO/CdS film with and without electron irradiation.

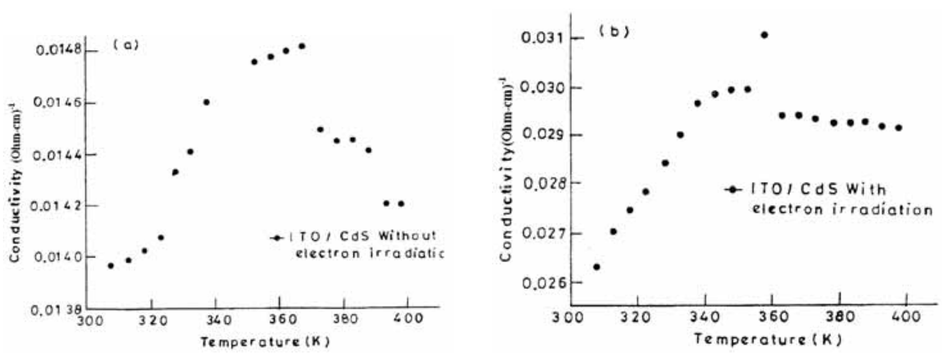

Figure 4. The conductivity vs. temperature. (**a**) ITO/CdS without electron irradiation, (**b**) ITO/CdS with electron irradiation.

temperature but at higher temperatures, it was found to decrease sharply. This may be due to reduction of mobility of charge carriers by strain produced defects. This behaviour is also observed after electron irradiation. However, the slope of reduction of conductivity at high temperature is significantly reduced, which confirms the modification of misfit between ITO/CdS thin films. The value of conductivity after electron irradiation is larger than that of an unirradiated sample. Similar results have been reported by other workers also [6] where annealing process is found to reduce the intrinsic stress, improving lattice mismatch and producing larger trajectory for the free electrons for better electrical conductivity. The increase in conductivity after electron irradiation might also be due to some more charge creation by heat generation during irradiation process. However, in the case of Si and Ge semiconductors, it was observed [19] that low energy electrons were unable to

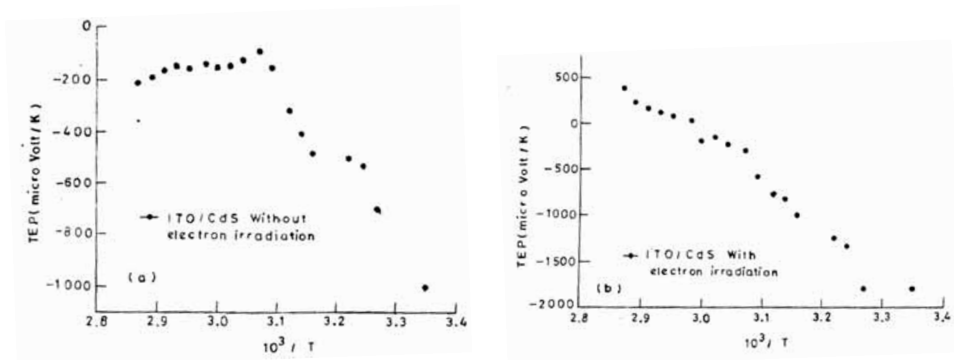

Figure 5. The thermoelectric power vs. $10^3/T$. (**a**) ITO/CdS without electron irradiation, (**b**) ITO/CdS with electron irradiation.

produce heat and displacement of ions because they require high energy for this purpose. Low energy electrons are only able to break and rearrange the incorrect bonds at the interface.

3.5 *The thermo-electric power measurement*

The thermo-electric power (TEP) measurements carried out on CdS with and without electron irradiation are shown in figures 5a and 5b. In this method the temperature of one end was varied and temperature of the other was kept constant. Thermoelectric power was calculated as

$$S = \Delta V/\Delta T,$$

where ΔV is the thermo EMF and ΔT is the temperature gradient.

It was observed that sign of thermoelectric power is negative before electron irradiation which confirms the n-type nature of samples. The complicated nature of variation of TEP with temperature and irradiation is yet to be completely understood and the increase in TEP with increasing temperature may be due to elimination of grain boundaries and defects. It was also observed that TEP changes sign after electron irradiation at higher temperature, which suggests the variation of Fermi level with irradiation and temperature.

4. Conclusion

1. The optical band gap of thin film was found to vary with electron irradiation and this may be due to misfit parameter modification by electron irradiation for ITO/CdS films.
2. The V–I curves are found to be nonlinear before irradiation and linear after irradiation.
3. The conductivity measurements confirm the modification of the CdS/ITO interface after electron irradiation.
4. The TEP measurements confirm the n-type nature of CdS films.

5. Low energy electron beam can be used to modify optical properties of semiconducting materials.

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