

Preparation and characterization of $\text{ZnS}_x\text{CdSe}_{1-x}/\text{ZnTe}$ heterojunctions

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Thin films of ZnTe, ZnTe:Cu have been grown on glass substrates by vacuum evaporation. Doping increases the conductivity by three orders of magnitude. The optical band gap and structure were also determined. Heterojunctions of ZnTe/ $\text{ZnS}_x\text{CdSe}_{1-x}$ were prepared and characterized by dark J-V, C-V and Photovoltaic studies. The dark conductivity studies with temperature shows the dominance of tunneling mechanism in these heterojunctions. The open circuit voltages obtained for ZnTe/ $\text{ZnS}_x\text{CdSe}_{1-x}$ were in the range 0.42 – 0.50 V. The short circuit current densities are in the range 5.55 – 7.05 mA/cm² and efficiencies varied in the range 1.35 – 2.05 %.

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1. Introduction

The usefulness of any semiconductor depends on its multifaceted responses to various fields and its interaction with other materials. ZnTe is a consistently p-type material which offers wide applicability in devices with n-type materials. The energy gap is in the range of 2.102 to 2.28 eV. Because of this band gap, the material is used as window/absorber material in tandem solar cells. A material which promises broad application in optoelectronics is ZnTe especially in case of electroluminescence diodes. ZnTe has received much attention not only for having properties suitable for optoelectronic devices but also for its potential applications to strained layers [1, 2]. Kimmerle et al [3, 4] reported the suitability of different semiconductor compounds for applications in tandem solar cells. The heteroaxial deposition of ZnTe layers has been investigated for substrates of GaAs [5] and CdS [6] by the molecular beam epitaxy technique.

Demand for optoelectronic devices is ever increasing and material scientists efforts are not in phase with the demand. Some of the demands are met by tailoring the properties through alloying the materials of known properties. Some of the properties such as structure, lattice parameter and energy gap seem to be controllable in thin film form. II-VI compounds with energy gaps covering the visible range are compatible candidates for optoelectronic devices and extensively studied. ZnS and CdSe are excellent luminescent materials and operated in the visible spectral region. Hence these materials utilized for the fabrication of heterojunction solar cells. CdSe is the most photosensitive [7, 8] of all semiconductors. The properties of CdSe make it suitable for application in photodetection, optoelectronics, rectifiers and solar cells. Earlier, we reported [9, 10] properties of $\text{ZnS}_x\text{CdSe}_{1-x}$

alloy films formed by thermal evaporation. In this work preparation and characterization of $\text{ZnS}_x\text{CdSe}_{1-x}/\text{ZnTe}$ ($x \leq 0.5$) heterojunctions are reported here.

2. Preparation of ZnTe and Cu doped ZnTe films

p-ZnTe was used in preparing the heterojunctions of n- $\text{ZnS}_x\text{CdSe}_{1-x}$ films. The preparation conditions used for ZnTe and ZnTe:Cu films were identical to $\text{ZnS}_x\text{CdSe}_{1-x}$ films. Vacuum evaporated ZnTe and ZnTe:Cu films were found to be homogeneous and strongly adherent to the glass substrates. The thickness of the films was in the range 1 - 2 μm . Nearly stoichiometric films are obtained at temperature of 470 K with Cu doping of 1.5 wt%. The films were characterized by optical, structural and electrical studies.

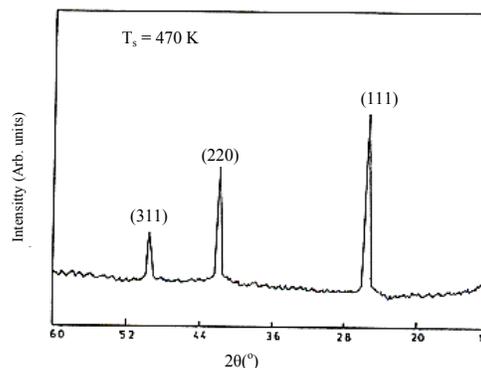


Fig.1. X-ray diffractogram of ZnTe films.

Fig.1 shows X-ray diffractograms for ZnTe at 470 K. The films are polycrystalline in nature with zincblende ($a=6.10 \text{ \AA}$). The same zincblende structure was reported by Mondal et al [11] in ZnTe films formed by hotwall evaporation in the substrate temperature range 470-570 K. Ciorasu et al [12] investigated the electrophysical properties of ZnTe films with varying stoichiometric defects. They reported a cubic structure in ZnTe films grown in the presence of Te excess and a hexagonal structure when metallic Zn was evaporated together with ZnTe. Zincblende structure of ZnTe ($a=6.10 \text{ \AA}$) was reported by Pal et al [13] at room temperature. Raju et al [14] reported cubic structure in vacuum evaporated ZnTe films formed at 303 and 523K without much deviation in stoichiometry. The grain size was calculated and it is increased with deposition temperature. Similar increase in grain size with substrate temperature was reported by Pal et al [13] and Raju et al [14].

The optical transmission spectra of ZnTe, ZnTe:Cu films were recorded in the wavelength range 500 – 2000 nm. The films prepared at higher substrate temperature have more transmittance than those prepared at room temperature. This is consists with the better crystallinity as revealed in the structural studies. The optical transparency of doped films is less than that of undoped films. From transmittance spectra the absorption coefficient (α) was calculated and plots of $(\alpha h\nu)^2$ vs $h\nu$ are shown in Fig.2. The direct band gaps are found to be 2.15, 2.26 and 2.24 eV for films formed at 300 K and 470 K, ZnTe:Cu formed at 470 K. The results are in good agreement with the reported value of Mondal et al [11]. The fundamental band gap is not affected by the microstructure of the films.

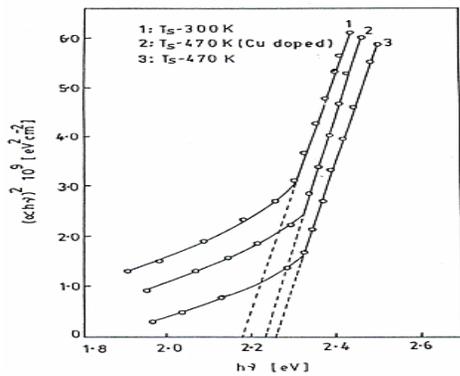


Fig. 2. Variation of $(\alpha h\nu)^2$ vs. $h\nu$ for ZnTe films (a) 300 K (b) 470 k and (c) 470 K: Cu doped.

Hot probe test [15] showed that all the films were p-type irrespective of substrate temperature. Different dopant concentrations of Cu were tried and better conductivity films were obtained with 1.5 wt% Cu. The conductivity, carrier concentration and mobility are higher in films formed at 470 K. The conductivity, carrier concentration, mobility increases with increase of

temperature for all the films. Mondal et al [14] reported decrease of conductivity in ZnTe films with deposition temperature and increase of conductivity in Cu doped films with deposition temperature. The Hall mobilities observed in the present work are in agreement with the values reported by Mondal et al [14]. The Hall mobilities observed in the present work ($6.10\text{cm}^2/\text{V}\cdot\text{Sec}$) are in good agreement with the values reported by Mondal et al [14]. The increase of mobility with temperature may be due to the grain boundary scattering. In conclusion polycrystalline, cubic and nearly stoichiometric conducting films were obtained by co-evaporation of Cu with ZnTe at a substrate temperature of 470 K. The conductivity of ZnTe films improved by three orders of magnitude from $\sim 10^{-4}$ to $0.5 (\Omega\text{cm})^{-1}$ on doping with Cu. Romeo et al [16] tried to increase the conductivity by doping ZnTe ZnTe films with antimony. The dopants were incorporated during the film growth. The films exhibited good optical properties with a low resistivity (about $4 \times 10^{-2} \Omega\text{cm}$). They identified three acceptor levels which were related to the substitutional position of antimony with tellurium atoms and native defects due to zinc vacancies. Copper doped ZnTe films were studied by Kobayashi et al [17] and Kimmerle et al [4]. Kobayashi et al [17] indicated that films deposited below 125°C were grayish black and highly resistive. The films exhibited increasing conductivity with increase in deposition temperature.

3. Deposition of alloy $\text{ZnS}_x\text{CdSe}_{1-x}$ films

Thin films of $\text{ZnS}_x\text{CdSe}_{1-x}$ with $x=0, 0.2, 0.4$ and 0.5 were deposited on glass substrates by thermal vacuum evaporation. The source materials for all the compositions were prepared by first physically mixing desired quantities of 99.99% pure ZnS and CdSe and then sintering at 1100°C in vacuum sealed quartz tubes for about 40 hours. The sintering charge was slowly cooled to room temperature in about 6 hours and used as a source material for $\text{ZnS}_x\text{CdSe}_{1-x}$ films. The films preparation condition and characterization results are already reported [10]. These films are used as absorber/window material depending on the band gap.

4. Experimental details of heterojunctions

In the present investigation heterojunctions of ZnTe/ $\text{ZnS}_x\text{CdSe}_{1-x}$ ($x \leq 0.5$) were prepared by vacuum evaporation. Back wall configuration heterojunction photovoltaic devices were prepared on 7059 corning glass substrates. In this configuration, one of the ohmic contact materials In/Ni was deposited on the glass substrates. The material having lower band gap among $\text{ZnS}_x\text{CdSe}_{1-x}$ and ZnTe were then evaporated which acted as absorber. The higher band gap material (ZnTe/ $\text{ZnS}_x\text{CdSe}_{1-x}$) was deposited on the absorber layer to a thickness about 1-2 μm . After deposition of window material the ohmic contact was given in the form of grid structure using mica masks. All junctions were annealed in H_2 atmosphere at

500 K for 10 mts for better stabilization. Two pressure contacts provided on evaporated ohmic contacts served as leads to the devices. In J-V measurements a Heathkit USA regulated power supply with 1 mV resolution was used as a voltage source for biasing the junctions. Current through the junctions were measured using a Keathley 614 USA digital electrometer. The C-V measurements were carried out on all heterojunctions at 1 MHz using a Boonton 72 B USA analogue capacitance meter.

5. Results and discussion

The forward dark current densities vs. voltage (J-V) plots at room temperature for different compositions of heterojunctions are shown in Fig.3. It is clear that the J-V characteristics deviate considerably from the ideal diode behaviour in tow ways. Firstly the forward current is not tending to zero for zero bias and secondly there are two distinct regions with different slopes instead of single slope. These deviations are attributed to different transport mechanisms other than the diffusion mechanism. By fitting the forward J-V data to the emission-recombination transport equation

$$J = J_0 [\exp (eV/AKT-1)] \tag{1}$$

to the two different linear region, J_0 and A were calculated. The quality factor in the low bias region is greater than unity and it is about 2 in the higher bias region. In both the cases the quality factor is higher and indicates the presence of other transport mechanism like tunneling or tunneling-recombination.

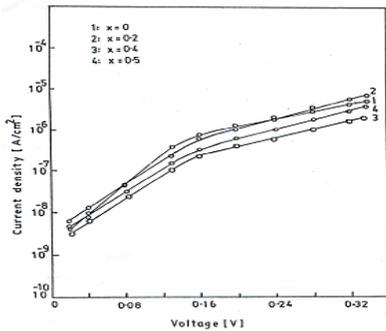


Fig. 3. Dark current-voltage characteristics of $ZnS_xCdSe_{1-x}/ZnTe$ heterojunctions.

The forward current characteristics in the temperature region 150-375 K are shown in Fig. 4. It is clear that the forward current is also sensitive to temperature indicating an appreciable contribution from tunneling mechanism. In such a case then forward current is given by

$$J = J_0 [\exp (A'V)] \exp (BT) \tag{2}$$

Here A' and B are constants which are independent of temperature and bias condition. The above equation

explains the current transport controlled by tunneling through the energy barrier at the junction. The insets in the figures show plots of $\ln J$ vs. T for a forward bias of 0.2 V. The linearity of these plots indicates an appreciable role of tunneling transport mechanism. A' and B are calculated from the slopes of $\ln J$ vs. V and $\ln J$ vs. T plots at constant temperature and voltage respectively. The values of A' is almost constant and B varies regularly with composition. Bockharyova and Simashkevich [18] reported similar type of J-V curves for different temperatures for $ZnSe/ZnTe$ heterojunctions.

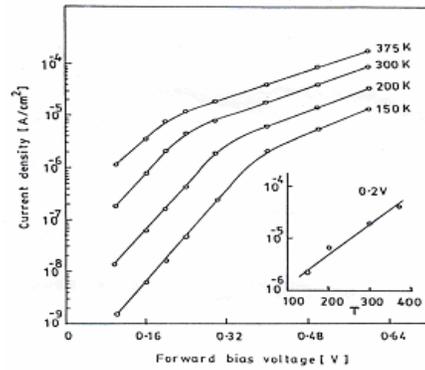


Fig. 4. A typical forward J-V characteristics of $ZnS_{0.2}CdSe_{0.8}/ZnTe$ heterojunctions.

Raju et al [19] also observed similar J-V dependence in heterojunctions of CdSe-ZnTe system in the entire range of composition. The tunneling mechanism often controls the transport in a heterojunction such as ITO/CdTe [20] ZnO/CdTe [21], CdS/CdTe [22-24] and CdTe/CdS_xZnSe_{1-x} [25]

6. Capacitance-Voltage (C-V) characteristics

The C-V measurements give information about the junction interface states built-in-voltage and acceptor/donor density of states in the junctions.

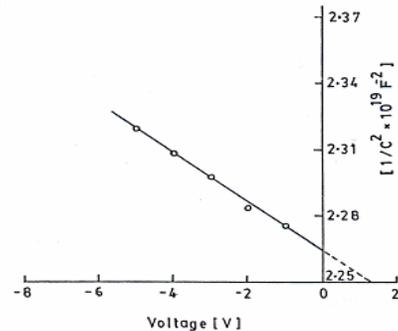


Fig.5. Variation of $1/C^2$ with reverse bias of $ZnS_{0.2}CdSe_{0.8}/ZnTe$ heterojunctions.

Fig. 5 shows plots of $1/C^2$ vs V . It is obvious that these plots are linear indicating that the junctions are abrupt in nature. The intercepts on the V -axis obtained by extrapolating the plots give the built-in potentials (V_b) of the heterojunctions. The built-in potentials lie in the range 0.8 – 1.3 V. Pal et al [26] also reported a built-in voltage of 2V in the surface modified CdSe/ZnTe heterojunctions. From the slopes of the C-V plots, the approximate impurity concentrations in the junctions have also been calculated

7. Photovoltaic studies

The J-V curves of all heterojunctions of n- $\text{ZnS}_x\text{CdSe}_{1-x}/\text{ZnTe}$ obtained by illuminating with 85 mW/cm^2 intensity are shown in Fig.6. The short circuit current (J_{sc}) open circuit voltage (V_{oc}) fill factor (FF) and efficiency (η) of the heterojunctions deduced [28] from these curves.

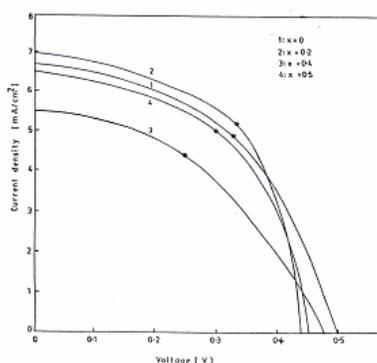


Fig. 6. J-V characteristics under illumination for different compositions (x) of $\text{ZnS}_x\text{CdSe}_{1-x}/\text{ZnTe}$ heterojunctions.

It is clear that all the junction parameters do not vary regularly with composition (x) of n- $\text{ZnS}_x\text{CdSe}_{1-x}/\text{p-ZnTe}$ heterojunctions. Shunt resistance is not very high and the series resistance is also appreciable. The efficiencies varied in the range 1.35 – 2.05 %. In the case of $\text{ZnS}_{0.4}\text{CdSe}_{0.6}/\text{ZnTe}$ heterojunction a low efficiency ~1.35% was observed. This might be due to the loss arising as a result of absorption in the window material ZnTe whose band gap is close to that of the absorber $\text{ZnS}_{0.4}\text{CdSe}_{0.6}$. The low efficiency of the present junctions may be due to the mismatch of the lattice, the electron and hole affinities of the junction materials. The lattice mismatch establishes a strain field in the interface which in many cases is relieved by accommodating dislocations. These dislocations normally act as recombination centers and hence reduce the junction efficiency. The number of dislocations that arise due to the lattice mismatch is established by $\Delta a/a^3$ [29]. Here Δa is the difference between the lattice parameters of the junction materials and 'a' is the average of the two lattice parameters.

The lattice mismatch is given by $\Delta a/a$ (~8 to 15 %) and the corresponding dislocation densities for all the heterojunctions are calculated and are in the range 1.98×10^{13} to $3.35 \times 10^{13} \text{ cm}^{-2}$. These dislocations normally act as recombination centers and hence reduce

the open circuit voltage and significantly lower the efficiency of the cell. These lie in the range 0.9 – 1.42 which are quite high and hence significantly reduce the open circuit voltage. Further the discontinuity in the valence band edge ΔE_v lie in the range 0.86 – 1.01 eV in the present heterojunction which may also reduce the transport efficiency of holes appreciably. All these factors along with the surface states might be responsible for the low efficiency observed in the $\text{ZnS}_x\text{CdSe}_{1-x}/\text{p-ZnTe}$ junctions. Pal et al [26] also reported low efficiencies of about 1.3 % in CdSe-ZnTe heterojunctions. Some other workers also reported low efficiency in II-VI junctions [30].

8. Conclusions

As deposited p-type films show high resistivity. The conductivity of films increased by three orders of magnitude on doping with 1.5 % Cu. ZnTe films crystallize in zincblende structure with a lattice parameter $a=6.10 \text{ \AA}$ and the conductivity was consistently p-type. The dark forward J-V studies of the prepared heterojunctions $\text{ZnS}_x\text{CdSe}_{1-x}/\text{ZnTe}$ showed two distinct linear regions with different slopes. These are attributed to different transport mechanism than the diffusion mechanism. The temperature dependence of the dark J-V characteristics conformed the dominance of tunneling mechanism in these heterojunctions. The $1/C^2$ vs. V plots was found to be linear showing that the junctions were abrupt in nature. The built-in-voltages of the present heterojunctions were in the range 0.8 – 1.3 V. The efficiencies of the junctions varied in the range 1.35 – 2.10 %. The low efficiency observed was attributed to shunt resistance, dislocation densities, lattice mismatch, electron, hole affinity differences.

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