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Thermal and doping effect on photovoltaic behaviour of H-treated (*n*)ZnO/(*p*)CdTe heterojunctions

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The thin film (*n*)ZnO/(*p*)CdTe heterojuctions with different doping concentrations were prepared by vacuum evaporation and their electrical and optical properties, both in dark and under illumination at room temperature as well as at elevated temperatures were studied. The structures showed change of photovoltaic (PV) effect, giving fill factor 0.59 for H-treated sample with open-circuit voltage 368 mV and short-circuit current density 76.38×10^{-4} mA/cm^2 and for untreated sample 0.46 with open-circuit voltage 250mV and short-circuit current density 57.11x10^4 mA/cm^2 for doping concentration N_a=1.30×10^{17}/cm^3 (4.90% Sb doped CdTe) and N_d=3.33×10^{17}/cm^3(4.25% Al doped ZnO). The variations of PV efficiency at room temperature with respect to these doping concentrations were shown to be the optimal value of this typical (*n*)ZnO/(*p*)CdTe junction. The fill factor has been found to increase with temperatures showing a maximum value around 343K for H-treated and 335K for untreated samples. The proper doping, annealing and hydrogenation are necessary to reduce the series resistance so as to achieve an ideal and high efficiency PV converter.

Keywords: Heterojunction, Doping, Hydrogenation, Dangling bond, Photovoltaic effect
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1 Introduction

A particular class of heterojunction diodes, namely, the oxide semiconductor/semiconductor (base) solar cells have received wide attention[1]. One of them is ZnO/CdTe anisotype heterojunction. This paper describes recent work on thin film heterojunction in which one of the semiconductors is (*n*)ZnO and the other is (*p*)CdTe. The compound ZnO is a wide band gap (3.20 eV) II-VI group semiconductor[2] with remarkably large exciton and biexciton bonding energies (~60 and ~15meV), respectively[3]. It is found as a good candidate of transparent conducting oxides (TCO) and therefore, can substitute indium tin oxide (In_2O_3 : Sn) and tin oxide (SnO_2) in conductive electrodes of other semiconductor solar cells. Due to its high stability in hydrogen plasma, non-toxicity, controllable resistivity and low cost of the constituent elements, ZnO has become very attractive for photovoltaic applications[4]. ZnO is widely used in piezoelectric transducers, varistors, gas sensors and luminescent phosphors[5]. It has also extensive applications in energy efficient windows, liquid crystal displays, optoelectronic devices etc. On the other hand CdTe, (energy gap = 1.5 eV) a II-VI group is a direct band gap semiconductor and has a high absorption co-efficient which is required for a good conversion efficiency. This has led to the investigation of CdTe based heterojunctions and Schottky barrier junctions for using as photovoltaic (PV) devices. The formation mechanism of Zn_2SiO_4 and amorphous SiO_2 in a deep range from the surface to the interface of the ZnO/Si system was carried out[6]. The *I-V* characteristics under illumination of the ZnO/CdTe/Ag junction is reported without PV efficiency calculation[7]. A thin film ZnO/p-CdTe photovoltaic device, which showed an efficiency of 3.7% was reported[8]. One of the applications is the use of ZnO as substrate for growth of GaN based materials since the lattice mismatch between GaN and ZnO is relatively small[9]. The benefits of ZnO include higher resistance to H_2 plasma damage but studies show that hydrogen atoms can neutralize the excess Zn formed at the surface. Since hydrogen atoms can passivate dangling or defective bonds, the effects of hydrogenation on ZnO material is also very attractive, because its injection produces a significant improvement in the quality of ZnO crystal. Similarly, hydrogen atoms can neutralize the Cd vacancies in CdTe film. The hydrogen atoms which

act as impurities can be separated by the thermal energy[10].

2 Experimental Details

The thin films of equal effective area ($0.16cm^2$) of (*n*)ZnO/(*p*)CdTe heterojuctions with different doping concentrations such as (1.30% Al, ZnO : 1.40% Sb, CdTe), (2.70% Al, ZnO : 2.53% Sb, CdTe); (4.08% Al, ZnO : 4.90% Sb, CdTe) etc. were deposited by thermal vacuum evaporation at a pressure of 10^{-5} torr. The (*n*)ZnO films were first annealed for 5 h at temperature of 528 K and treated with hydrogen gas under vacuum condition for 15 min at constant temperature 363 K maintaining the pressure at 10^{-4} torr before making the junctions. The thickness of both (*n*)ZnO and (*p*)CdTe films was measured outside the vacuum chamber by multiple beam interference technique and the same was verified from the transmittance measurement[11]. For electrical measurement, Ag film deposited on the glass substrate was used as the lower electrodes and Sn film was used as upper electrode, making the junction structure as Ag-(*n*)ZnO/(*p*)CdTe-Sn. The junction, mounted on a specially designed sample holder, was put inside a vacuum chamber for measurement of *l-V* characteristics under pressure 10^{-2} torr. The experiment was performed at room temperature as well as at elevated temperature using a specially designed electronic temperature controller. For *l-V* measurement under illumination, the junction in the chamber was illuminated through glass window using a white light from a tungsten halogen lamp (500 watts). The light radiation was incident from the ZnO side. The input intensity of the light was measured with lux meter (luxmat-300ED; Research Ins ND-110028, India) and converted it into power (watt) by laser power meter (LPM-20). For transmittance, absorbance and reflectance measurement, Carry-300 Scan UV-visible spectrophotometer (Varian, Victoria-3170, Australia) was used. The type and carrier concentrations were determined by Hall effect measurement.

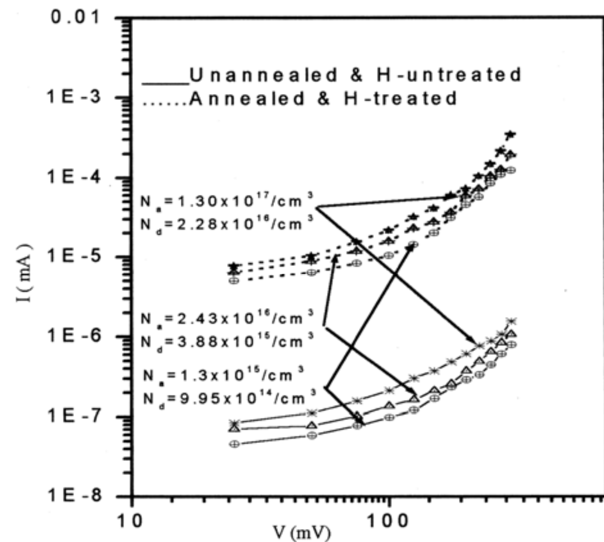

Fig. 1 — *I* versus *V* plots at room temperature in dark for different doping concentrations in forward bias (both for H-treated and untreated structures)

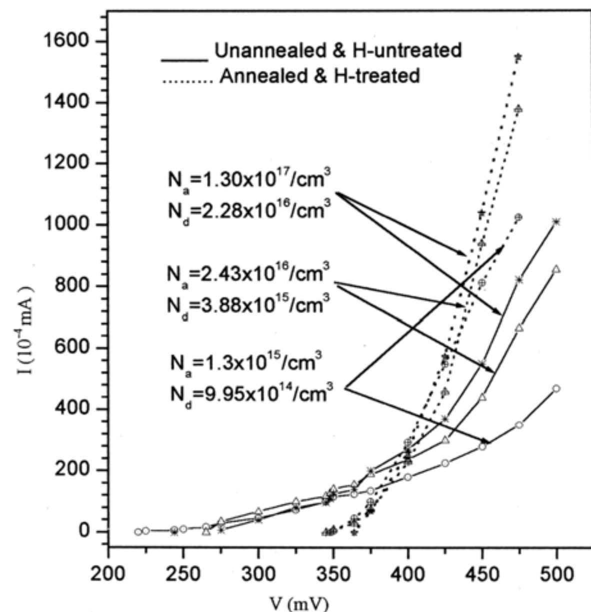

Fig. 2 — *I* versus *V* plots at room temperature under illumination for different doping concentrations in forward bias (both for H-treated and untreated structures)

3 Results and Discussion

The contact of the lower electrode[12] Ag (work function = 4.44 eV) with (*n*)ZnO and the upper electrode Sn (work function 4.43 eV) with (*p*) CdTe (electron affinity = 4.28 eV) were found ohmic[13]. The *I-V* characteristics of (*n*)ZnO/(*p*)CdTe junctions in dark and under illumination respectively under forward bias both for hydrogen untreated and hydrogen treated at room temperature (304K) have been shown in Figs 1 and 2. The junctions showed rectifying characteristics both in dark and under illumination. The characteristics under illumination showed photovoltaic effect and are more rectifying in nature for both H- treated and untreated junctions. However, the characteristics under illumination for H-treated junction showed more significant

photovoltaic effect than untreated junction. The current density is calculated by the well known expression,

$$J = qA^{*}TV_{bi}/k\{\exp(-qV_{bi}/kT)\}[\exp(qV_a/nkT)-1]$$
$$= J_s[\exp(qV_a/nkT)-1 \quad \ldots(1)$$
$$\cong J_s[\exp(qV_a/nkT)]$$
$$(\text{for } V_a \geq 3kT/q)$$

Using Eq. (1), diode ideality factor n and reverse saturation current density J_s can be obtained from the $\ln J$ versus V_a plots. The ideality factor of the junctions studied in the present case was found to vary from 3.98 to 2.08 (untreated) and 3.33 to 1.65 (H-treated) at different temperatures within 298 to 423K. The reverse saturation current density of a typical junction was found to be 1.22×10^{-10} A/cm^2 (untreated) and 9.11×10^{-9} A/cm^2 (H-treated) in dark. The same was found to increase with rise in temperature (Table 1). The effective Richardson constant A^* and built-in potential (V_{bi}) of the junctions were found to be 117 Acm^{-2}K^{-2} and 0.79 eV respectively for H-untreated and 118.5 Acm^{-2}K^{-2} and 0.92 eV respectively for H-treated structure. The value of A*, and that of V_{bi} have been observed to increase in H-treated junction but did not show significant change with change of temperature from 298 to 423K in both the cases. It has been observed that J-V curves are functions of doping concentration and electrode area. The presence of interfacial layer, image force lowering of built-in potential, recombination of electrons and holes in the depletion region and tunneling effect are the main reasons for ideality factor to be greater than unity. Figure 3 shows the temperature dependence short circuit current density and fill factor (FF) of a typical (n)ZnO/(p)CdTe heterojunction for the 298-423K temperature range under constant light intensity 8800 lux. The peaks in the fill factors are seen to be 59.67% for H-treated and 48.39% for untreated structures at temperatures 343 and 335K, respectively. Higher fill factors observed in H-treated structure is due to passivation of dangling bonds or defective bonds of ZnO film surface and the neutralization of excess Zn atoms due to application of hydrogen atoms before making the junction. Exactly same is the case for short circuit current density versus temperature curves. The increase of short circuit current density up to 78.21×10^{-4} mA/cm^2 for H-treated and 60.66×10^{-4} mA/cm^2 for untreated samples at temperatures 343 and 335K, respectively, is a result of the carrier diffusion length increase in higher temperatures and also a result of the absorption edge shift to the lower energies[14]. The decrease of short circuit current density as well as fill factor at higher temperatures both for H-treated and untreated at 343 and 335K, respectively are believed to be due to oxide formation film between the junction at higher temperatures which results in high series resistance. However, open circuit voltage, V_{oc} is found to be increased both for H-treated and untreated in the same set of structures.

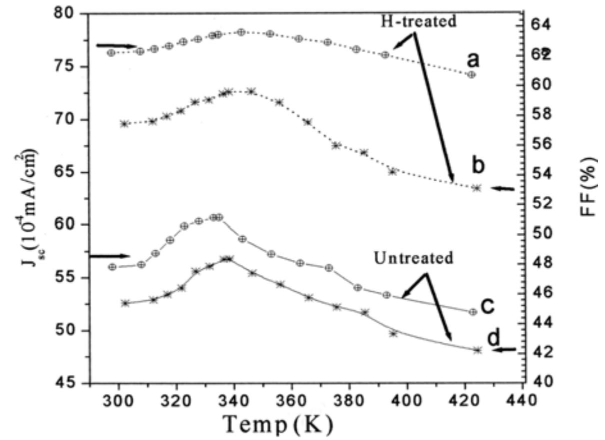

Fig. 3 — Variation of short circuit current density and fill factor with temperature both for H-treated and untreated structures

There is a close relationship between the limitations in PV efficiency and the doping concentration to improve heterojunction devices. The efficiency of PV cell is proportional to the power density that it generates. This in turn can be expressed as a product of three factors: J_{sc}, V_{oc} and FF with respect to input power. Figure 4 shows the variation of efficiency with respect to doping concentration N_d (donor) for fixed acceptor concentration N_a=1.30×10^{17} cm^{-3} of base semiconductor (p)CdTe under constant illumination of 8800 lux at room temperature both for H-treated and untreated (n)ZnO/(p)Cd structures. Since the power loss increases due to the series resistance increase when the doping concentration is decreased, and since the photo current decreases due to dependence of mobility, diffusion length and lifetime on the doping concentration, efficiency decreases on both sides of the optimal value of doping concentration. The nature of the curves is well agreed with the reported nature of Au-SiO_2-nSi solar cell[15].

Table 1 — Variation of some parameters of two typical junctions at different temperatures in dark

Temp. (K)	Untreated sample				H-treated sample			
	J_s (A/cm^2)	IF (n)	V_{bi} (eV)	A^* ($Acm^{-2}K^{-2}$)	J_s (A/cm^2)	IF (n)	V_{bi} (eV)	A^* ($Acm^{-2}K^{-2}$)
298	1.22×10^{-10}	3.98			9.11×10^{-9}	3.33		
304	3.32×10^{-10}	3.81			3.02×10^{-8}	3.24		
333	5.56×10^{-9}	2.98			2.75×10^{-7}	2.41		
363	4.38×10^{-8}	2.59	0.79	117	1.51×10^{-6}	2.18	0.92	118.5
393	2.84×10^{-7}	2.27			7.55×10^{-5}	1.58		
423	1.18×10^{-6}	2.08			2.76×10^{-5}	1.65		

Table 2 — Variation of some parameters of four different junctions under illumination at room temperature (both for H-treated and untreated)

Sample No.	Doping concentration		Unannealed & untreated			Annealed & H- treated		
	N_a (cm^{-3})	N_d (cm^{-3})	I_{sc} (10^{-4} mA/cm^2)	V_{oc} (mV)	FF (%)	I_{sc} (10^{-4} mA/cm^2)	V_{oc} (mV)	FF (%)
24w	1.03×10^{15}	9.95×10^{14}	51.04	220	39.37	74.00	348	56.48
25w	2.43×10^{16}	3.88×10^{15}	52.00	265	41.69	75.72	345	56.82
26w	1.30×10^{17}	2.28×10^{16}	56.00	244	45.42	76.30	364	57.51
27w	1.30×10^{17}	3.33×10^{17}	57.11	250	46.42	76.38	368	58.50

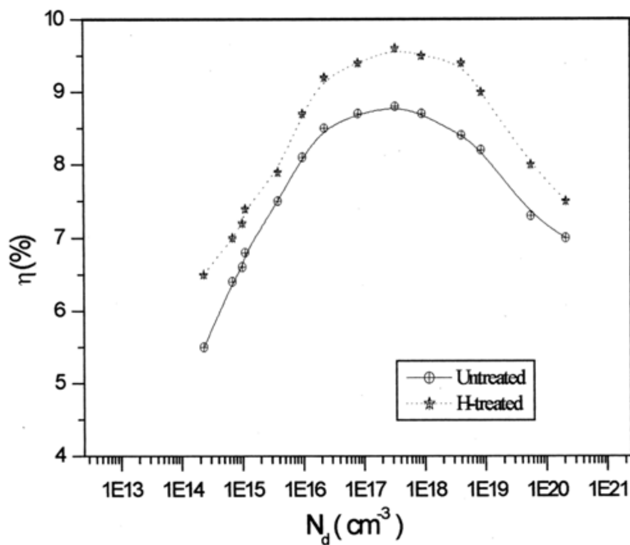

Fig. 4 — Effect of doping concentration (N_d) on efficiency of (n)ZnO/(p)CdTe heterojunction (for fix N_a=1.30×0^{17} cm^{-3})

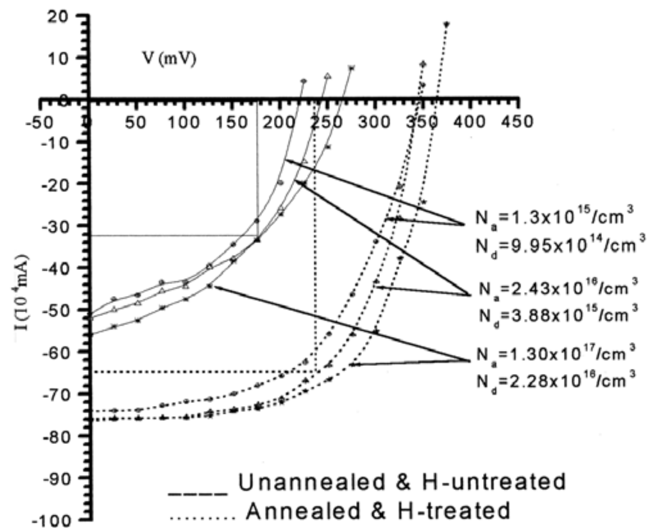

Fig. 5 — V versus I (revered current) plots under illumination for H-treated and untreated structures at room temperature

The junctions were studied for their PV performance at room temperature. The structures exhibited PV effect characterized by high series resistance in their I-V characteristics (Fig. 5). The open-circuit voltage of different junctions were found to increase from 220 to 265mV and short-circuit current from 51.04×10^{-7}A/cm^2 to 57.11×10^{-7}A/cm^2 with fill factor from 0.39 to 0.46 for untreated junction and that of H-treated junction the corresponding variation of quantities are 348-364mV, 74.00×10^{-7}-76.38×10^{-7}A/cm^2 and 0.56-0.59, respectively (Table 2). Results show that devices possess series resistance as high as 437 Ω (untreated) and 91 Ω (H-treated) under illumination. In both the cases R_s has been found to decrease with increasing doping concentrations up to the optimal value N_d=3.33×10^{17}cm^{-3}.

4 Conclusion

The junction parameters such as barrier height, diode ideality factor, Richardson constant, fill factor of vacuum deposited (*n*)ZnO-(*p*)CdTe structure were determined from its *I*-*V* characteristics. They are found to change under illumination and with change in temperature. Optimal values obtained for I_{sc}, FF and η due to variation of temperature and doping concentration are encouraging to fabricate more (*n*)ZnO/(*p*)CdTe heterojunctions. The junction, though rectifying, is characterized by high series resistance. Proper doping, annealing and hydrogenation are necessary to reduce the series resistance in order to achieve high performance solar cell.

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