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Studies on current-voltage characteristics of ITO/(n)CdSe-Al heterojunctions

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ITO/(n)CdSe heterojunction was fabricated by depositing Indium Tin Oxide (ITO) thin films onto n-type CdSe thin film by thermal evaporation method from pure ITO powder. The different diode parameters were calculated from the current-voltage characteristics of the junctions. The diode ideality factor was found to be greater than unity with high series resistance. The *J-V* characteristics under illumination showed poor photovoltaic effect of the junction. Large series resistance, high defect density and presence of interfacial layer are thought to be the main causes for higher value of diode ideality factor and poor photovoltaic conversion efficiency.

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Keywords: Indium Tin Oxide, thermal evaporation, diode ideality factor, photovoltaic effect

1. Introduction

Indium Tin Oxide (ITO) is a degenerate semiconductor having wide band gap of about 3.4 eV [1]. This high conducting material with high transparency in visible region with infrared reflectance [2] is a good transparent electrical conductor. ITO has been used as a transparent electrode in advanced optoelectronic devices such as solar cells, light emitting and photo diodes, photo transistors and liquid crystal displays. Thin films of Indium Tin Oxide have been reported to be prepared by variety of techniques such as spray pyrolysis [3], sputtering [4], reactive evaporation [5], pulsed laser deposition [6], thermal evaporation method [7] etc. The properties of a film depend on the method of preparation. From the literature it has been found that many investigations are made on the individual films of CdSe and ITO also their Schottky barriers with metals [8-15]. Earlier we have reported electrical and optical properties of thin film (n)CdSe/(p)CdTe heterojunction [16], a study of current-voltage characteristics of ITO/(p)Si heterojunction [17]. In the present work an effort has been made to investigate the heterojunction formed between polycrystalline CdSe film and ITO prepared by thermal evaporation. Various electrical parameters, effect of doping, annealing and photovoltaic performance of the junction have been discussed.

2. Experimental details

High purity CdSe powder (99.996%, Sigma Aldric, USA) and ITO powder (99.99%, Testbourne, UK) were used for the preparation of the films and junctions by thermal evaporation. The junctions were fabricated in the same vacuum chamber under the pressure better than 10^{-5} torr. Chemically cleaned glass substrates were used in the chamber separately for the films and the junctions using suitable musk and source shutter. Ag metal was used for doping of CdSe. For fabrication of a heterojunction, the sequential process is as follows; initially, Al strips each of 0.1cm width and length 2.5 cm as base electrodes were vacuum deposited on glass substrate (3×3 cm^2 size). Above these, Ag-doped CdSe film of area 1.5×1.5 cm^2 was thermally deposited by co-evaporation of CdSe powder from electrically heated molybdenum boat and Ag metal (99.99% purity) from tungsten spiral filament as reported in our earlier study [18]. The substrate temperature during deposition of CdSe film was kept at about 473K. The CdSe film was then annealed at about 573K in high vacuum for 30 minutes in order to ensure crystallization of the film. In the second step, strips of ITO film (each of 0.35cm width and length 2 cm) (as shown in Fig. 1) were deposited onto CdSe film at substrate temperature 573K making crosses with Al strips. The junctions were annealed in air at 583K for 30 minutes in order to improve the transparency of the ITO films as reported in our earlier study [19] and to ensure rectifying nature of the structure [20]. Finally a second set of Al strips were vacuum evaporated over ITO films as upper electrodes, having the same geometry as the base electrodes but being placed in a perpendicular direction with respect to them. The effective area, formed by the overlap of two perpendicular electrodes was 0.01 cm^2. Thus on a single substrate nine Al-ITO/(n)CdSe-Al structures of area of 0.01 cm^2 each could be obtained as shown in Fig.1.

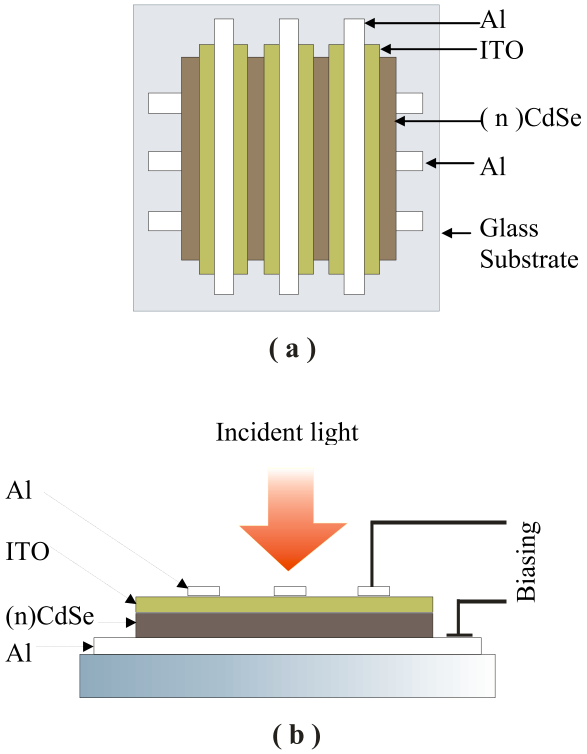

Fig.1. Al-ITO/(n)CdSe-Al structure: (a) top view and (b) side view (not to scale).

For measurement of conductivity type, thickness and other studies, separate films were deposited simultaneously at the same cycle by placing additional substrates. For electrical study of the films, gap type structures were formed by depositing Al electrodes on two ends of strips of ITO and CdSe films keeping the gaps between the electrodes. The thicknesses of the films were measured by multiple interference technique [21]. The optical transmittance was studied with the help of a UV-visible spectrophotometer (Cary 300, Varian, Australia). The conductivity type and carrier concentration of the films were determined by Hall effect measurement of the films and capacitance-voltage study [18] of the Schottky barriers. For films of lower doping concentration, the hot probe method [22] was also used to confirm the type of conductivity of the film.

To avoid effect of humidity, noise and light etc., all electrical and photovoltaic measurements were done by mounting the sample inside a specially assembled metal chamber evacuated up to 10^{-2} Torr. The details of this experimental arrangement have been reported elsewhere [23, 24]. For measurement of current in dark and under illumination, a Kiethley system Electrometer (model 6514) was used. The current (*I*)-voltage (*V*) characteristics of the junctions were recorded at room temperature as well as at elevated temperatures using heating arrangement with a temperature controller in the vacuum chamber. For *I-V* measurements under illumination, the samples in the chamber were illuminated through a glass window using a white light from a tungsten-halogen lamp. The *C-V* measurements were performed at room temperature on the junctions at 1kHz, using a digital Autocompute LCR-Q meter (Aplab-4910).

3. Results and discussion

3.1 Current–voltage characteristics

The electrical conductivity of ITO films forming the junctions was found to be $1.5\times10^{-2}\ \Omega^{-1}\text{cm}^{-1}$. The optical transmittance of the same ITO film in the wavelength from 300nm to 600nm is shown in figure 2. It is seen that the optical transmittance of the film is about 75% beyond 550nm of wave length. The Ag doped CdSe films used for fabrication of the junction showed conductivity of about $8\times10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$.

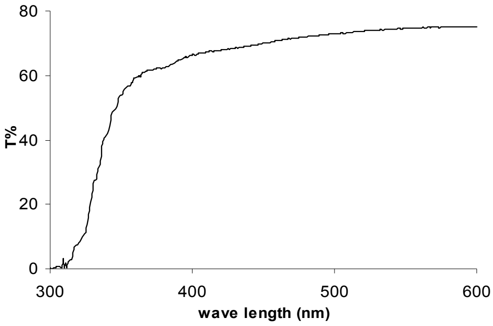

Fig.2 Transmittance vs wavelength of ITO films of thickness 2050Å.

Fig. 3 shows the current density (*J*)-voltage (*V*) characteristics of two typical heat treated ITO/(n)CdSe junctions in dark at room temperature (295K). However, after heat treatment at 583K in air for 30 minutes, the dark *J-V* characteristics became rectifying with low reverse current. As the contact between Al and CdSe layer is ohmic as tested, the rectifying effect appeared after heat treatment would seem to be due to the contact between the ITO and CdSe.

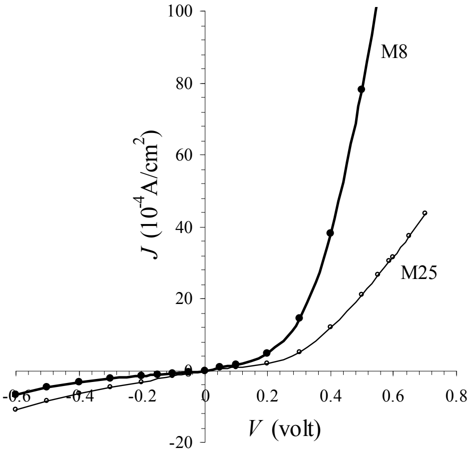

Fig.3 J-V characteristics of two different ITO/(n)CdSe junctions (M8, M25, electrode area $1\times10^{-2}cm^2$) in dark at room temperature (295K) for different doping concentrations (N_d): $5.03\times10^{15}\ cm^{-3}$ (M25), $7.23\times10^{16}\ cm^{-3}$(M8).

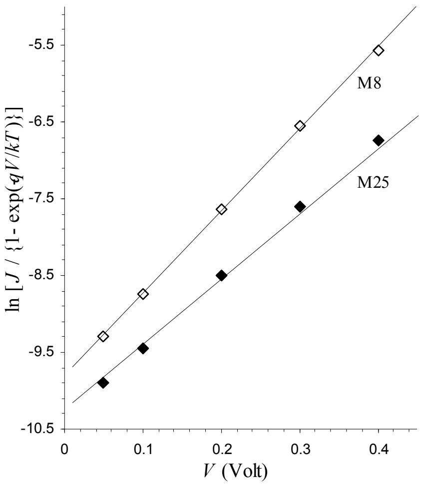

Fig.4. ln [J/(1-e$^{-qV/kT}$)] vs V plots of two typical ITO/(n)CdSe junctions in dark at room Temperature (295K).

Alamri *et al* [20] have observed that the heat treatment in air changes the ITO from an ohmic to rectifying (Schottky barrier) contact by raising the ITO work function through surface oxidation. In the present study, the rectifying nature of the structure after heat treatment in air may be due to increase of electron affinity of ITO. The high work function of ITO makes it suitable in principle as a rectifying contact to (n)CdSe. The increase of doping concentration of the (n)CdSe films was found to improve the diode quality by decreasing ideality factor.

Thus the rectifying nature of *J-V* characteristics of Al-ITO/(n)CdSe-Al structure indicated the formation of a barrier at the junction. The reverse current does not saturate and shows bias dependence of barrier height. The current density *J* of a diode is written [25]

$$J = J_0 \exp\left(\frac{qV}{nkT}\right)\left[1-\exp\left(-\frac{qV}{kT}\right)\right] \tag{1}$$

where J_0 is the reverse saturation current density, *n* the diode ideality factor, *V* is the biasing voltage, *k* the Boltzman constant, and *T* the absolute temperature.

The ideality factor (*n*) and the saturation current density (J_0) of different junctions after heat treatment (*T*) were calculated from the slopes and intercepts of the linear regions of respective ln[$J/(1-e^{-qV/kT})$] vs *V* plots (Fig. 4). The electrical parameters are shown in table 1. The diode ideality factors for these junctions were found to be greater than 2 and were decreased on heat treatment of the structures. However, the structures fabricated with CdSe films of higher doping concentration showed improvement in diode quality with reduced diode ideality factor.

A plot of ln*I* versus *V* (Fig.5) of these junctions shows the deviation from linearity at higher voltages (> 0.4V) indicating the presence of a series resistance (R_s) in the neutral region of the semiconductor CdSe. At large forward current (*I*), the voltage drop across the series resistance causes the actual voltage drop across the barrier to be less than the applied voltage to the terminals. In this case the current is proportional to $[e^{q(V-IR_s)/kT} -1]$ and deviate from the ideal condition of the diode [26].

A plot of horizontal displacement ΔV and extrapolation of the linear region of the ln*I-V* curve for two junctions are shown in Fig. 6. The series resistance have been calculated from the slope of the curves and are found to be high (Table 1).

The series resistance determined from *I* vs ΔV plots (Fig. 6) is of the order of KΩ and found to be in the range of 1.1 KΩ to 11.0 KΩ (Table. 1).The series resistance of the junctions was found to decrease with increase of doping concentration. Formation of any insulating layer between electrodes and semiconductors also contributes to the series resistance. In the present method of preparation of the devices, some interfacial layer is developed due to breaking of vacuum for deposition of every layer of film. Heat treatment of the devices reduces the defects of the films and also makes more ohmic contact between the electrodes and semiconductors. Thus heat treatment of the junctions reduces effect of series resistance, thereby enhancing diode quality.

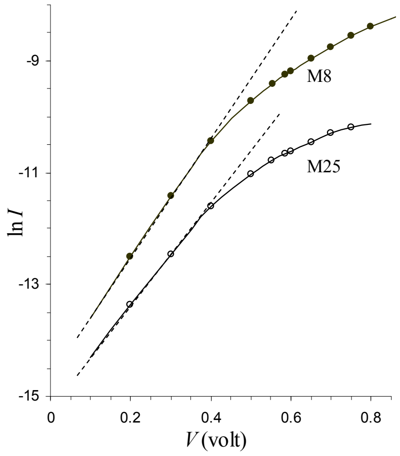

Fig.5. lnI vs V plots of two typical ITO/(n)CdSe junctions (M8, M25, in dark at room temperature (295K).

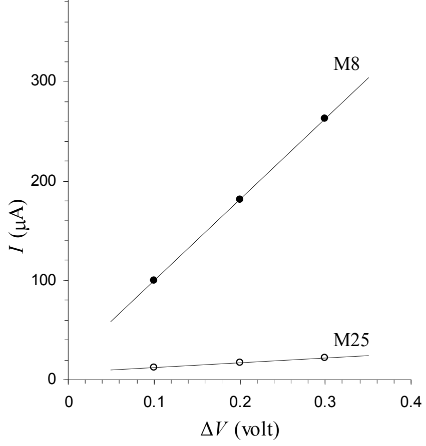

Fig.6. I vs ΔV plots of two typical ITO/(n)CdSe junctions (M8, M25) in dark at room temperature (295K).

The temperature dependence of *J-V* characteristics of ITO/(n)CdSe junction has been studied within the temperature range 295K to 343K (Fig. 7). It has been observed that above room temperature, thermal generation of extra carriers causes a gradual increase of current with forward voltage.

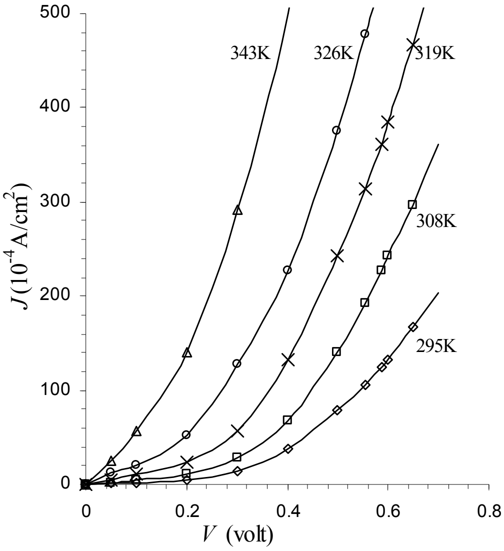

Fig.7. J-V plots of a typical ITO/(n)CdSe junction (M8) at different temperatures.

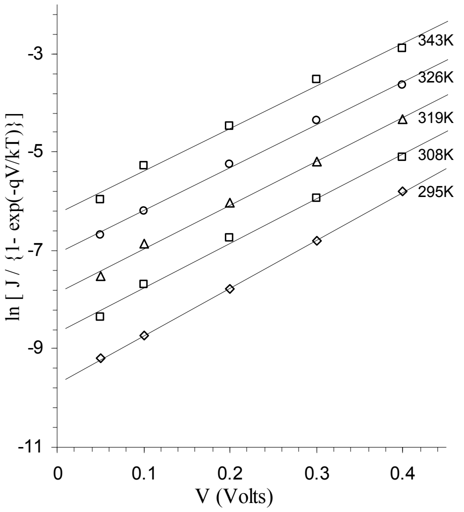

Fig.8. ln [$J/(1-e^{-qV/kT})$] vs V plots of a typical ITO/(n)CdSe junction (M8) in dark at different temperatures.

Fig. 8 shows *ln*[$J/(1-e^{-qV/kT})$] vs V plots for a typical ITO/(n)CdSe junction at different temperatures from which the values of saturation current density J_0 at different temperatures were calculated. The ideality factor (n) was found to be of nearly same and the saturation current density was found to increase from 5×10^{-5}A/cm^2 to 22×10^{-4}A/cm^2 within temperature range 295K to 343K.

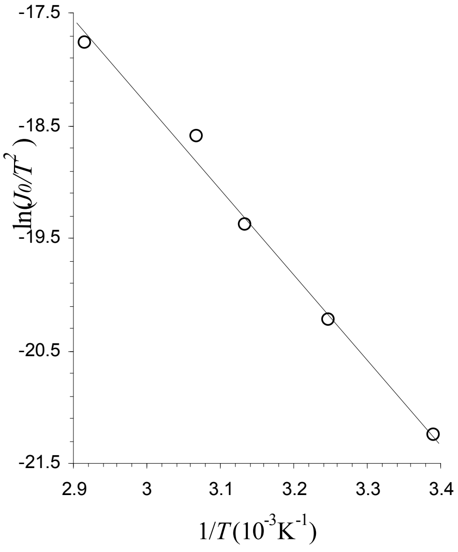

Fig.9. ln(J_0/T^2) vs T^1 plots of ITO/(n)CdSe junction (M8).

A plot of ln(J_0/T^2) vs T^{1} (Fig.9) shows a straight line and intercept on the vertical axis gives the Richardson's constant A^* to be around 80 (Table 2). Hence at this moderate doping the current transport is believed to be dominated by thermoionic emission process [27]. The ideal equation for the current can be written as

$$J_0 = A^* T^2 \exp\left(-\frac{q\phi}{kT}\right) \tag{2}$$

where, ϕ is the barrier height of the junction. The value of barrier height calculated for the junction is around 0.64eV and is not affected significantly by slight increase of doping concentration (Table 1). The polycrystalline films are endowed with defects that may arise from the incomplete atomic bonding (dangling bond). This leads to the surface states [28]. In this case barrier height is less dependent on work function and deviate from ideal Schottky barrier [29].

Table 1. Junction parameters for two typical ITO/(n)CdSe heterojunctions (M8, M25) in dark at room temperature for different doping concentrations concentrations (N_d): 7.23×10^{16} cm^{-3} (M8) and 5.03×10^{15} cm^{-3} (M25) for CdSe.

Smple no.	Thickness of CdSe layer (nm)	n	J_0 (μAcm^{-2})	R_s (KΩ)	Barrier height ϕ (eV)	
					From *J-V* study	From *C-V* study
M8	320	3.6	26	1.1	0.64	0.67
M25	470	5.1	12	11.0	0.62	0.65

Table 2. Variation of some junction parameters of a typical ITO/(n)CdSe heterojunction (Sample no. M8) with temperature in dark.

Temp (K)	J_0 (10^{-5}A.cm^{-2})	n	ϕ (eV)	A^* (Acm^{-2}K^{-2})
295	5	3.73	0.64	80
308	15	3.91	0.64	
319	39	4.07	0.64	
326	90	4.22	0.63	
343	220	4.13	0.64	

3.2 Capacitance-Voltage Characteristics:

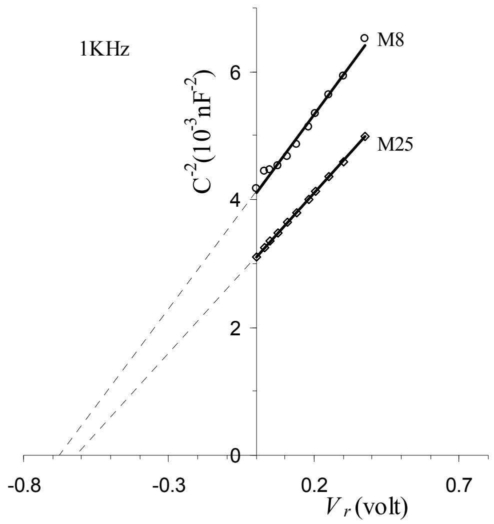

Fig. 10. C^{-2} vs V (reverse) plots for a typical ITO-(n)CdSe junction (M8) at room temperature in dark.

The C^{-2}-V plots at reverse bias for typical junctions were drawn at frequency 1 KHz (Fig. 10). The carrier concentration and the built-in potential at the junction were estimated from the slope and intercept of the plot using the following relation [30]

$$C^{-2} = \{2(V_{bi} - V - kT/q)/q\varepsilon N_d\} \qquad (3)$$

Here V_{bi} is the built in potential at zero bias which is equal to V_i+kT/q, where V_i is the negative intercept on the V_r axis and ε is the permittivity of CdSe. The carrier concentration evaluated from the slopes of the graph is of the order of 10^{16} cm^{-3} which is similar to the values obtained from the Hall effect measurement. The barrier height ϕ of the junction is calculated from the equation; $\phi = V_{bi}+V_n$, where V_n is the potential difference between the Fermi level and the bottom of the conduction band edge in CdSe, and depends upon the density of states (N_c) in the following way,

$$V_n = (kT/q)\ \ln(N_c/N_d) \qquad (4)$$

where $N_c=2(2\pi m_e kT/h^2)^{3/2}$ is the effective density of states in the conduction band of CdSe, where h is the Plank's constant and m_e is effective mass. Taking $m_e = 0.13m_0$ for CdSe [31] where m_0 is the free-electron mass, the value of N_c is found to be 1.17×10^{24} m^{-3} at room temperature. Thus the barrier height obtained for a typical junction junction (M8) is around 0.67 eV.

3.3. Photovoltaic effect

J-V characteristics under illumination

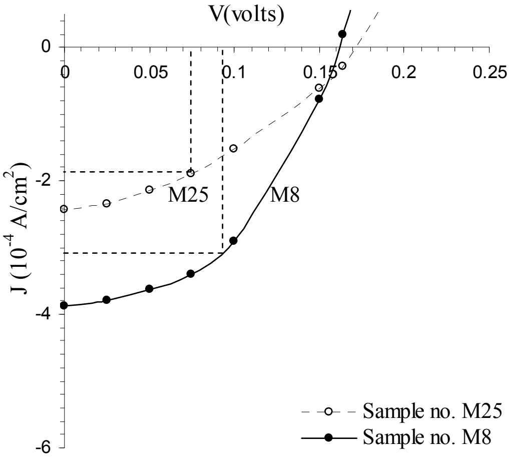

Fig.11. Photovoltaic plots of two typical heat treated ITO-(n)CdSe junctions of different doping concentrations [N_d = 7.32×10^{16}cm^{-3} (M8); N_d=3.03×10^{15} cm^{-3} (M25)] at room temperature.

The ITO-(n)CdSe junctions after heat treatment were studied under illumination for their photovoltaic performance. Fig. 11 shows the photovoltaic effect of two typical junctions of different doping concentrations under white light of intensity 5500 lux. At these moderate doping concentrations, the nearly linear nature of the J-V curve implies the existence of large series resistance in the junctions. The open-circuit voltage and short-circuit current are strongly dependent on the series resistance (R_s) as well as on diode ideality factor (n) as per the well known equations [32]

$$I_{SC} = I_0\left[\exp\left(\frac{q(V - IR_S)}{kT}\right) - 1\right] - I \qquad (5)$$

$$V_{OC} = \frac{nkT}{q}\ln\left(\frac{I_{SC}}{I_0} + 1\right) \qquad (6)$$

where, I is the total output current and I_0 the saturation current. The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor of these junctions are tabulated in Table 3. Low photovoltage has been observed in these junctions with maximum fill factor 0.44. In the polycrystalline films, the grain boundary potential may affect the series resistance and open-circuit voltage of solar cell [33]. Recombination of photo generated carriers takes place at grain boundary and hence the short-circuit current is reduced [33, 34]. Besides there are various factors responsible for the poor photovoltaic performance, such as high defect density present with thermally evaporated layers, low conductivity of ITO layer, presence of very thin interfacial layer and low doping concentration. The increase of doping concentration of the films of CdSe was found to improve the photovoltaic performance of the device (Table 3).

Table 3. Some photovoltaic parameters of two typical ITO/(n)CdSe junctions (M8, M25) at room temperature.

Smple no.	N_d (cm^{-3})	Open circuit voltage V_{oc} (Volt)	Short circuit current density J_{sc} (10^{-4} Acm^{-2})	Maximum power output (10^{-3} mW)	Fill factor ff
M8	7.23×10^{16}	0.163	3.87	22	0.44
M25	5.03×10^{15}	0.172	2.41	10	0.34

4. Conclusions

The study showed that rectifying ITO-(p)CdSe heterojunction diode can be fabricated by thermally depositing ITO films on CdSe thin films. The diodes have high series resistance. The low thermal conductivity of thermally evaporated ITO film contributes to the series resistance. The recombination of photogenerated carriers, surface states, low doping concentration also contributes to the quality of the diode. These causes are thought to affect the *J-V* characteristics as well as PV effect of the junctions. There are immense probabilities for improving the junction performance by controlling and optimizing the deposition parameters. The works are on progress to improve the diode quality and PV conversion by controlling the deposition parameters of the ITO layer and post deposition annealing for suitable conductivity, transmittivity and best quality CdSe polycrystalline film.

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