Int J Thermophys (2010) 31:2040–2049
DOI 10.1007/s10765-009-0556-8

Thermal and Doping Effect on Sn/(n)ZnO Schottky Junction and Its Performance as a *PV* Effect

G. Wary · A. Rahman

Abstract Thin film Sn/(n)ZnO Schottky junctions with different doping concentrations were prepared by vacuum evaporation. Different junction parameters such as ideality factor, barrier height, Richardson's constant, short-circuit current, etc. were determined from *I*–*V* characteristics. These parameters were found to change significantly with variations of doping concentration and temperature. The structures showed the change of the *PV* effect, giving a fill factor of 0.42 (efficiency of 0.39 %) with an open-circuit voltage of 124 mV and a short-circuit current density of $113\times10^{-5}\,\mathrm{A\cdot cm^{-2}}$ for a doping concentration, $N_\mathrm{d} = 3.88 \times 10^{15}\,\mathrm{cm^{-3}}$(2.74 % Al-doped ZnO). However, by increasing the doping concentration, the efficiency was found to increase by up to 4.54 % for doping concentration, $N_\mathrm{d} = 2.28 \times 10^{17}\,\mathrm{cm^{-3}}$. The conversion efficiencies varied with temperature and were observed to have an overall improvement up to 343 K. Proper doping, annealing, and hydrogenation are necessary to reduce the series resistance so as to achieve an ideal and high efficiency *PV* converter.

Keywords Barrier height · Fill factor · Ideality factor · *PV* efficiency · Schottky junction

1 Introduction

A particular class of Schottky junctions and heterojunction diodes, namely, the metal/oxide semiconductor and oxide semiconductor/semiconductor (base) solar cells have

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received wide attention [1]. One of them is the Sn/(n)ZnO Schottky junction. This paper describes recent work on thin-film Sn/(n)ZnO Schottky junctions in which its counter electrode is tin (Sn) and the base semiconductor is (n)ZnO. It is found as a good candidate for transparent conducting oxides (TCO) and, therefore, can substitute for 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 [2]. The formation mechanism of Zn_2SiO_4 and amorphous SiO_2 over a deep range from the surface to the interface of the ZnO/Si system was carried out [3]. The *I*–*V* characteristics under illumination of the ZnO/CdTe/Ag junction is reported without a *PV* efficiency calculation [4]. Sputter-deposited (n)ZnO on (p)Zn_3P_2 devices have been reported [5] with *PV* efficiencies of only 2.0 %. A thin-film ZnO/p-CdTe photovoltaic device, which showed an efficiency of 3.7 % was reported [6]. One of the main applications is the use of ZnO as a substrate for growth of GaN-based materials since the lattice mismatch between GaN and ZnO is relatively small [7]. Recently, the *PV* efficiency of a vacuum-deposited (p)CdTe/(n)ZnO heteorojunction has been reported [8,9] to be 4.01 % using hydrogenation for $N_a = 1.03 \times 10^{15}\,cm^{-3}$ and $N_d = 9.95 \times 10^{14}\,cm^{-3}$.

2 Experiment

Five thick films of silver, each with a width of 1 mm and a length of 25 mm, were first deposited by vacuum evaporation on a chemically cleaned glass substrate (each of $3 \times 3\,cm^2$ size) at a pressure of 10^{-5} Torr. Above these films, a 1.30 % Al-doped ZnO film of $1.5 \times 1.5\,cm^2$ area was deposited by thermal evaporation from a molybdenum boat. The film was then annealed for 5 h at a temperature of 528 K. Above the ZnO film, five film strips of tin (Sn), each of width of 1 mm and length of 25 mm, were vacuum deposited horizontally making crosses with the silver films. Thus, 25 Sn/(n)ZnO junctions, each of equal area (1 mm^2), were obtained on the same substrate. Similarly, a number of Sn/(n)ZnO structures of different doping proportions (2.7 % Al-doped ZnO, 4.08 % Al-doped ZnO), etc. were prepared. The substrate temperature and pressure were maintained at 350 K and 10^{-5} Torr, respectively, in all cases at the time of film deposition.

For electrical measurements, the Ag film deposited on the glass substrate was used as the lower electrode (ohmic contact) and the Sn film deposited over the ZnO film was used as the upper electrode (counter electrode), making the junction structure as Sn/(n)ZnO–Ag.

The experiment was performed at room temperature as well as at elevated temperatures using a specially designed electronic temperature controller. The junction, mounted on a specially designed sample holder, was put inside a vacuum chamber for measurement of *I*–*V* characteristics under a pressure of 10^{-2} Torr. For *I*–*V* measurements under illumination, the junction in the chamber was illuminated through a glass window using a white light from a tungsten halogen lamp (500 W). The light radiation was incident from the ZnO side. The input intensity of the light was measured with a lux meter (Luxmat-300ED; Research Ins ND-110028, India) and converted into power (W) by a laser power meter (LPM-20). The type and carrier concentrations were determined by a Hall effect measurement.

3 Results and Discussion

The *I*–*V* characteristics of Sn/(n)ZnO junctions in dark and under illumination (5500 lux) at room temperature (303 K) are shown in Fig. 1. The junctions exhibited rectifying characteristics both in dark and under illumination. The characteristics under illumination showed a photovoltaic effect and are more rectifying in nature. A significant rectification has been observed from the temperature dependent *I*–*V* characteristics (Fig. 2). The current density–voltage (*J*–*V*) relationship of the junction was calculated using [10]

$$J = J_\mathrm{o} \exp\left(qV/nkT\right)\left\{1 - \exp\left(-qV/kT\right)\right\} \tag{1}$$

where n is the ideality factor, V is the applied voltage, k is Boltzmann's constant, T is the absolute temperature, and J_o is the saturation current density given by

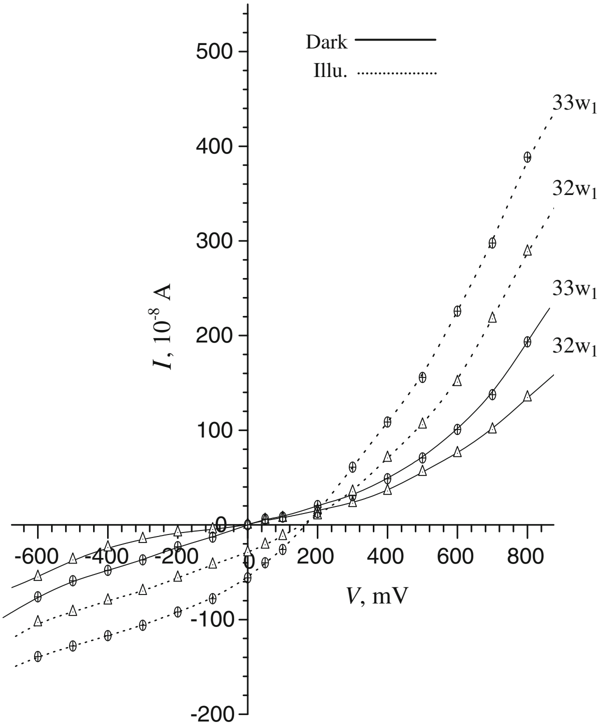

Fig. 1 Current (*I*) versus voltage (*V*) plots of Sn/(n)ZnO junctions in dark and under illumination (5500 lux) at room temperature (303 K)

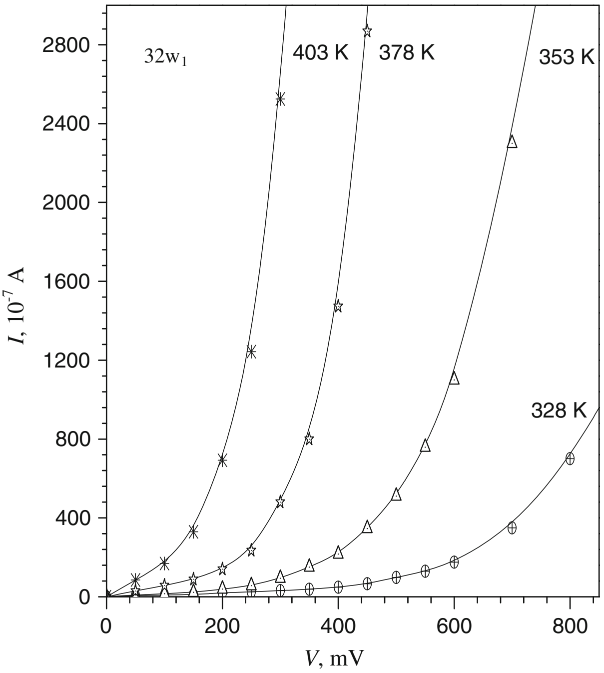

Fig. 2 Current *(I)* versus voltage *(V)* plots of a typical Sn/(n)ZnO junction in dark at different temperatures

$$J_o = A^* T^2 \exp(-q\Phi_b/kT) \quad (2)$$

here, Φ_b is the barrier height.

The ideality factor of the junctions studied in the present case at room temperature was found to vary from 6.09 (in dark) to 3.84 (under illumination) for a doping concentration of $3.88 \times 10^{15}\,\text{cm}^{-3}$and 5.01 (in dark) to 3.34 (under illumination) for a doping concentration of $2.28 \times 10^{17}\,\text{cm}^{-3}$. The reverse saturation current density of a typical junction (Sample No. $32w_1$) was found to be $4.45 \times 10^{-5}\,\text{A} \cdot \text{cm}^{-2}$ in dark and $5.57 \times 10^{-5}\,\text{A} \cdot \text{cm}^{-2}$ under illumination (Table 1). The same was found to increase with a rise in temperature. The effective Richardson's constant A^* and barrier height of the junctions were calculated from $\ln(J_o/T^2)$ versus T^{-1} plots (Fig. 3) and were found to be $115\,\text{A} \cdot \text{cm}^{-2} \cdot K^{-2}$ and 0.70 eV respectively, in dark and $114\,\text{A} \cdot \text{cm}^{-2} \cdot K^{-2}$ and 0.69 eV, respectively, under illumination. The effective Richardson's constant A^* did not show a significant change with a change of temperature but the value of the barrier height has been observed to decrease with a rise of temperature from 303 K to 478 K (Table 2). The decrease of barrier height is due mainly to the shifts of Femi levels E_F towards the center of the bandgap with an increase in T [11]. A reduction of the barrier height helps to transport majority electrons from the semiconductor (ZnO) to metal (counter electrode Sn).

Figure 4 represents the temperature dependences of *PV* parameters, short-circuit current density, and fill factor (FF), of a typical Sn/(n)ZnO junction for the 303 K to

Table 1 Values of saturation current density, ideality factor, doping concentration, and barrier height at room temperature for a typical Sn/(n)ZnO junction of electrode area of 1 mm^2

Condition	Sample No.	Thickness (Å)	Doping concentration (cm^{-3})	Ideality factor (n)	Saturation current density (10^{-5} A $\cdot$ cm^{-2})	Barrier height (eV)
In dark	32w$_1$	3486	3.88×10^{15}	6.09	4.45	0.70
	33w$_1$	4543	2.28×10^{17}	5.01	5.07	0.72
Under illum.	32w$_1$	3486	3.88×10^{15}	3.84	5.77	0.69
	33w$_1$	4543	2.28×10^{17}	3.34	7.01	0.71

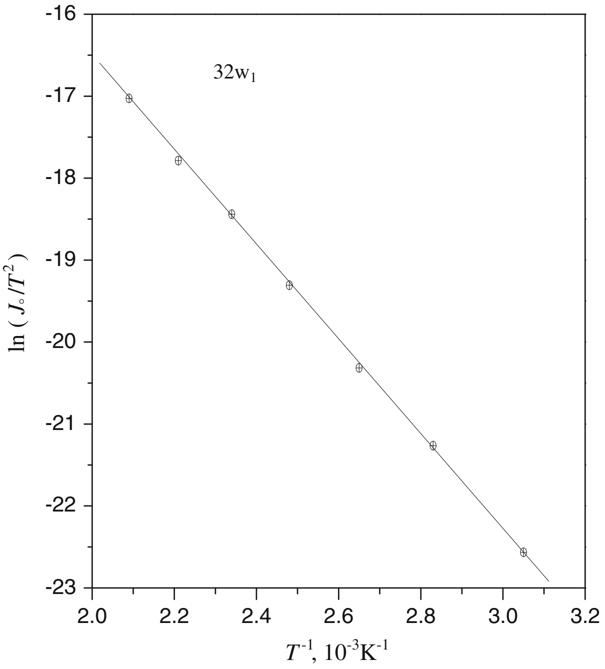

Fig. 3 ln ($J_{\rm o}/T^2$) versus T^{-1} plot of a typical Sn/(n)ZnO junction

478 K temperature range under a constant light intensity of 7508 lux. The characteristic peculiarities of a number of Sn/(n)ZnO junctions involved the existence of peaks in the fill factors and, therefore in the efficiencies versus temperature. The peak in the fill factors is seen to be 45.76 % at a temperature of 343 K. Exactly the same is the case for the short-circuit current density versus temperature curves. It is found that the open-circuit voltage ($V_{\rm oc}$) of the junction Sn/(n)ZnO exhibits a linear decrease with the temperature rise and with a decrease of the voltage temperature coefficient, $K_T(V_{\rm oc})$, using the expression [12],

$$K_T(V_{\rm oc}) = (\partial V_{\rm oc}/\partial T)\,(100/V_{\rm oc})\,\% \approx -\left[\left(\Delta E_{\rm g} - qV_{\rm oc}\right)/V_{\rm oc}qT\right]100\% \qquad (3)$$

Table 2 Values of short-circuit current density, barrier height, and fill factor at different temperatures for a typical Sn/(n)ZnO junction of electrode area of 1 mm^2

Sample No.	Thickness (Å)	Temperature (K)	Short-circuit current density ($10^{-5}\,\text{A}\cdot\text{cm}^{-2}$)	Barrier height (eV)	Fill factor (%)
32w_1	3486	303	113	0.70	42.00
		343	125	0.69	45.76
		353	123	0.67	45.38
		378	106	0.64	44.82
		403	81	0.62	43.92
		428	60	0.59	42.96
		453	48	0.58	42.67
		478	46	0.56	41.00

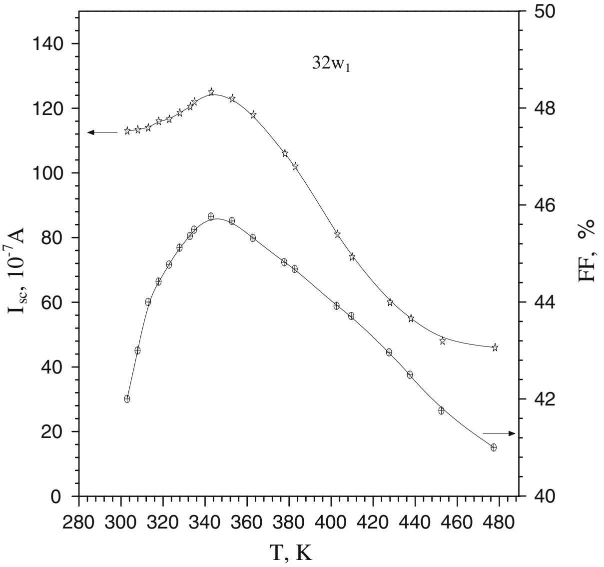

Fig. 4 Variation of short-circuit current and fill factor with temperature

A decrease of the voltage temperature coefficient reduces the rise of the series resistance as [13]

$$\Delta R_s \leq [(\partial V_{oc}/\partial T)/(\Delta I) + R_s(\partial I \partial T)/(\Delta I)]\,\Delta T \tag{4}$$

So it is clear from Eqs. 3 and 4 that the increase of the fill factor ($\text{FF} = I_m V_m / I_{sc} V_{oc}$) is due to the decrease of the open-circuit voltage (V_{oc}) and the fall-off of the series resistance at higher temperatures. The increase of the short-circuit current density up to $125 \times 10^{-5}\,\text{A}\cdot\text{cm}^{-2}$ at 343 K is a result of the carrier diffusion length increase at higher temperatures and also a result of the absorption edge shift to the lower energies caused by the ΔE_g decrease [12]. As a whole we can conclude that *the increase of the fill factor and the short-circuit current density is the contributory effect for the decrease of the open-circuit voltage* (V_{oc}) *due to the decrease of the voltage temperature coefficient* $K_T(V_{oc})$ *and the fall-off of the series resistance at higher temperatures.* Above 343 K, both the fill factor and the short-circuit current density are found to decrease. The temperature of 343 K is an optimal value that delivers the maximum power of the junction and therefore the existence of peaks in the fill factor and short-circuit current density. At higher temperature, $T > 343$ K, although the open-circuit voltage (V_{oc}) increases (fill factor decreases) due to an increase of the voltage temperature coefficient, we cannot explain this behavior as it contradicts the well known open-circuit voltage (V_{oc}) expression $[V_{oc} = kT/q \ln(I_{sc}/I_o + 1)]$ as with an increase in temperature, the saturation current (I_o) also increases. Our assumption is based on the increase of the volume polarization of the ionic oxide at higher temperatures ($T > 343$ K), which is associated with the neutral region between the semiconductor layer and the counter electrode.

Since ZnO is an oxide semiconductor, some ionic oxides are formed due to decomposition of ZnO at the time of film deposition. At the time of film formation, a large number of oxygen ions (O_2^-) are chemisorbed and incorporated at the grain boundaries and also on the surface of the film producing potential barriers, which hinder the electrical transport causing a reduction in the conductivity [2]. The result is an increase of the volume polarization of the ionic oxide, which is associated with the neutral regions of the semiconductor layer of (n)ZnO and of Sn (counter electrode) after making the junction. This will further increase at higher temperatures and help to increase the series resistance. The ultimate result is the decrease of the short-circuit current density as well as the fill factor. We tried to prepare a number of Sn/(n)ZnO junctions by varying the doping concentration, N_d, and composing the experimental arrangement such that the temperature dependences of the parameters (J_o, n, J_{sc}, V_{oc}, etc.) vary in such a way that the junction delivers maximum power at 343 K.

A major issue is the close relationship between the limitations in *PV* efficiency and the performance limitations in doping to improve junction devices. The efficiency of the *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 the input power. Figure 5 shows the variation of the efficiency with respect to the doping concentration N_d (donor) under constant illumination of 7508 lux at room temperature. Since the power loss increases due to the series resistance increase when the doping concentration is decreased, and since the photocurrent decreases due to the dependence of the mobility, diffusion length, and lifetime on the doping concentration, the efficiency decreases on both sides of the optimal value of the doping concentration. The nature of the curves agrees well with the reported nature of the Au–SiO_2–nSi solar cell [14]. However, a theoretical explanation to optimize the efficiency within the limitations of the doping concentration is still undergoing a wide spectrum of opinion.

The junctions were studied for their *PV* performance at room temperature (Fig. 6). The structures showed that the *PV* effect is characterized by a high series resistance in their *I*–*V* characteristics. The open-circuit voltage and short-circuit current of a typical junction (for a doping concentration $N_d = 3.88 \times 10^{15}\,\text{cm}^{-3}$) were found to be 124 mV and 113×10^{-7} A, respectively, with a fill factor of 0.42. Similarly for a doping

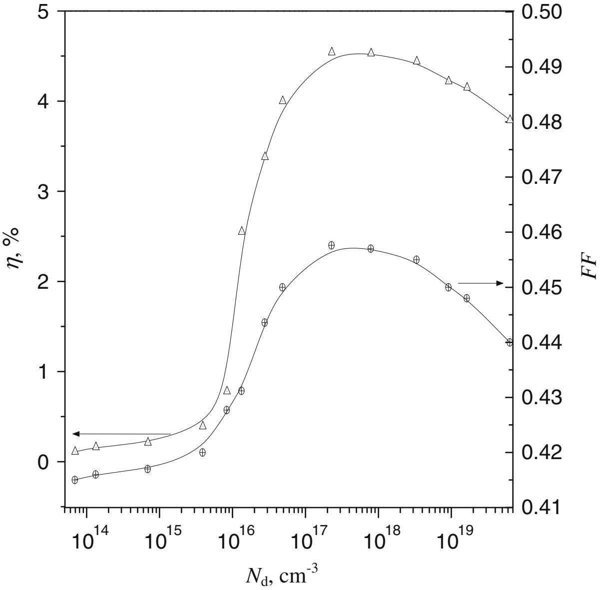

Fig. 5 Effect of doping concentration on efficiency of Sn/(n)ZnO junction

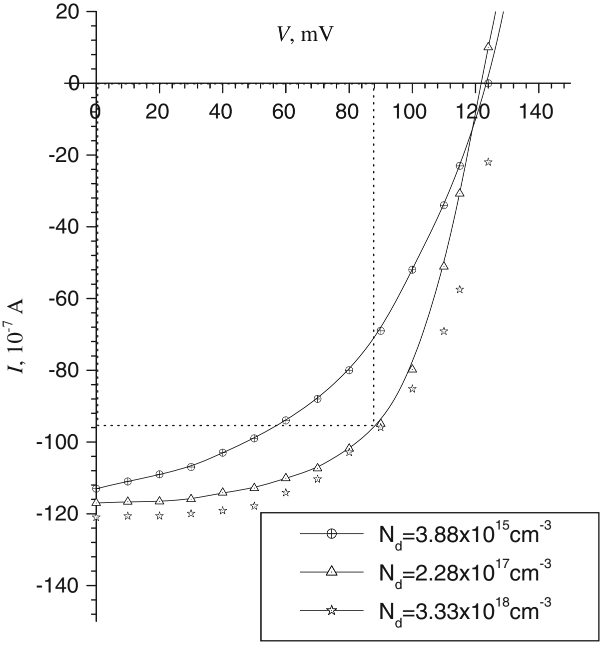

Fig. 6 Photovoltaic effect of a typical Sn/(n)ZnO junction with different doping concentrations (illumination, 7508 lux)

Table 3 Variations of *PV* parameters with doping concentration of a typical Sn/(n)ZnO junction of electrode area of 1×10^{-2} cm^{-2}

Doping concentration N_d (cm^{-3})	Short-circuit current (10^{-7}A)	Open circuit voltage (10^{-3} V)	Fill factor (%)	Efficiency (%)
3.88×10^{15}	113	124	42.00	0.39
8.33×10^{15}	114	124	42.77	0.78
1.33×10^{16}	114	125	43.12	2.55
2.77×10^{16}	115	125	44.36	3.38
4.83×10^{16}	116	123	45.00	4.00
2.28×10^{17}	117	122	45.76	4.54
7.87×10^{17}	119	122	45.70	4.53
3.33×10^{18}	121	126	45.50	4.44

concentration $N_d = 2.28 \times 10^{17}$ cm^{-3}, these values were 122 mV, 117×10^{-7} A, and 0.46 (Table 3). Results show that the device possesses a high series resistance that has been found to decrease with increasing doping concentration. More improvement of the *PV* performance of this junction has been achieved with a hydrogenated (n)ZnO thin film before making the junction (not shown here).

4 Conclusions

The *PV* parameters were found to change significantly with variations of doping concentration and temperature. The conversion efficiencies varied with temperature and were observed to have an overall improvement up to 343 K. A high series resistance results in a considerable reduction in the solar-cell efficiency. The forward current has shown an exponential dependence on the forward voltage with an ideality factor greater than unity. Proper doping, annealing, and hydrogenation are necessary to reduce the series resistance so as to achieve an ideal and high efficiency *PV* converter.

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