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Electrical and Photovoltaic Properties of Ag:ZnO/Si Heterojunction Device Prepared by Spray Pyrolysis Methode

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Abstract

In this work, ZnO/p-Si and Ag:ZnO/p-Si heterostracture has been constructed on (111) oriented p-type silicon substrate using spray pyrolysis method. ZnO films were prepared with different doping ratios. The electrical and photovoltaic properties of these films have been investigated in order to get the optimum preparation conditions. The built- in potential (V_{bi}) is calculated under different Ag doping ratios, while from I-V measurements, the ideality factor (n) is calculated.

Keyword:ZnO polycrystalline film; Ag:ZnO/p-Si heterojunctions; electrical properties; spray pyrolysis ; photovoltaic properties.

Introduction

Polycrystalline films have received a rapidly growing interest due to their increasing area of applications in advanced technologies for microelectronic, photonic, and micromachined devices. The heterostructures for photodetection and photovoltaic device applications were obtained by using one of the following techniques, such as LPE, MOCVD, etc., which are very expensive for such applications. A good alternative low cost technology is based on heterojunctions with transparent conducting oxide (TCO) thin film, such as In_2O_3, SnO_2 have been widely used for photovoltaic devices and recently ZnO having a direct optical band gap of 3.37 eV, a large melting point of 1975 °C, a large exciton binding energy (60 meV), and a high transparency (>80%) for visible light, which can be obtained with low resistivity (10^{-3} Ω cm), is playing an important role for optoelectronic applications [1-6]. Transparent conductive ZnO films can be prepared by different methods, such as activated reactive or electron beam evaporation, magnetron- or electron beam-sputtering, spray pyrolysis, chemical vapor deposition with many variants, and recently by sol–gel technique [3, 4].

In addition, the ZnO films could be deposited at relatively low deposition temperature. The structural, physical, and electrical properties of ZnO films were governed by deposition parameters , post treatment , and doped material, such as Al, Ga, Sc, Y, Mn, Cu, Ag, etc. Among them, the Ag-doped ZnO (SZO) was taken in varied concentrations on the conductivity, photosensitivity, luminescent properties, nonlinearity, and electrical stability [7-9]. In addition, it has been found that the resistivity of ZnO films was changed by extrinsic impurities, therefore, ZnO films have been doped to enhance their properties with elements of Li, Al, Ga, In, and Ag, etc., [10]. However, there are not many reports on the study of Ag dopant effect on electrical and photovoltaic effect of Ag: ZnO/Si Heterojunction device. So that, in this paper, we have investigated the effect of Ag doping concentration on Ag: ZnO/p-Si properties.

Experimental Work

Square-shaped p-type silicon samples, each of 1×1 cm^2 area, of 1.5-4 (Ω.cm) resistivities were prepared using a wire-cut machine. Silicon wafers were washed ultrasonically in distilled water and were immersed in nitric acid HNO_3 for 3 min. in order to remove ionic contamination. The wafers were immersed in HCl: HNO_3 (3:1) for 3 min. to remove metallic films. They were etched in buffered hydrofluoric acid (34.6% NH_4F: 6.8% HF: 58.6% H_2O) for 2 min. to remove oxide films.

The silicon wafers were cleaned in distilled water and dried in furnace at 120 ^oC. The ZnO thin films were deposited on (111) p-type single crystal silicon substrate by spray Pyrolysis method at substrate temperature of (500) ^{o}C. The resistivity and type of conductivity of the Si substrates were measured by using four point probe (FPP) technique. Zinc oxide films are prepared from solution of 0.2 M of pure Zinc nitrate hexhydrate ($Zn(NO_3)_2.6H_2O$) dissolved in a deionizer water. The time of the deposition is (5 sec) each (1.5 min), carrier gas of 20 ℓ/min and the solution flow rate of 3 mℓ/min. A few drops of acetic acid are added to dissolve the reactant completely to avoid precipitation of Zinc hydroxide and maintain solubility of precursor. The management of substrate temperature and the solvent composition allow condensation of zinc oxide films in an almost one plane of growth with (002) preferred orientation. The silicon sample was used as substrate for TCO's/Si heterojunction. Ohmic contacts were fabricated by evaporating 99.999 purity aluminum wires for back and front contact using Edwards coating system.

The following chemical reactions explain that:

$$2Zn(NO_3)_2 \xrightarrow{\text{Heat}} 2ZnO\downarrow + 4NO_2\uparrow + O_2\uparrow \text{...(1)}$$

While for preparation of Ag: ZnO thin films the following reaction take place

$$2AgNO_3 \xrightarrow{\text{Heat}} 2Ag\downarrow + 2NO_2\uparrow + O_2\uparrow \text{ .... (2)}$$

The following figure explains the experimental set up:

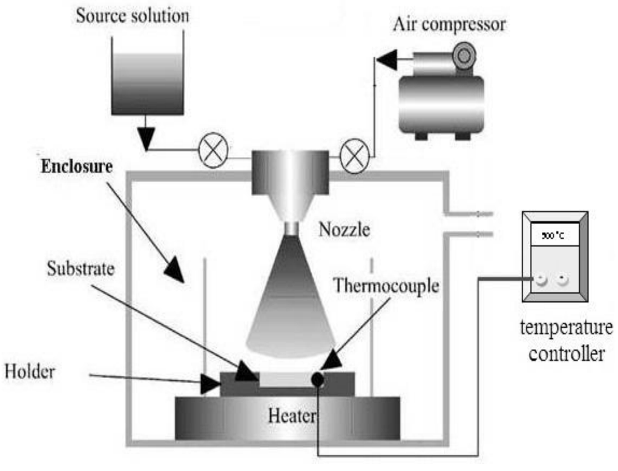

Fig.(1) Schematic set-up for spray Pyrolysis technique.

Characterization of Ag: ZnO/p-Si heterojunction:

1- Measurements of electrical properties

(A) Current-voltage (I-V) characteristics in the dark

A Kiethley-616 electrometer was used to measure the current flow in devices; manufactured from a structure produced in dark condition with voltage (0-4) V in forward biasing and (0-6) V in reverse biasing. This characterization was adopted to determine the ideality factor (n) as follows [11]:

$$n = \frac{q}{kT} \cdot \frac{\Delta V}{\ln \frac{J}{J_s}} \text{ ....(3)}$$

Where kT/q is the activation energy and J_S is the saturation current density

(B)Capacitance-voltage(C-V)Measurements

C-V characteristics of the heterojunction prepared were measured using a PM6306 programmable LRC meter supplied by Fluke. Under a reverse bias voltage (0.1-1.2) V. The cross point ($1/C^2=0$) of the ($1/C^2$-V) curve represents the built-in potential of the heterojunction.

2-Photovoltaic measurements

(A) Short-circuit current (I_{SC})

The short- circuit current (I_{SC}) represents amount of the current that can flow through the device as a function of the incident optical power. It was measured using the same Keithley-616 electrometer.

(B) Open-circuit voltage (V_{oc})

The open-circuit voltage (V_{oc}) represents the voltage drop across the device as a function of incident optical power. The incident optical power was varied by using a halogen lamp with variable applied voltage.

(C) Current-voltage characteristics under illumination

The manufactured solar cells were illuminated by varying light power from halogen lamp and the current was measured in reverse bias with a voltage range of (0.1-6) V.

The results explained that this device can be operated as a solar cell.

Results and Discussion

The X-ray diffraction spectra of Ag: ZnO films deposited at 500°C substrate temperature for various Ag dopant concentrations are found to show (002) preferential growth at low silver concentrations. The 2θ values found to be (34.385°) were compared with the standard ASTM data card (36-1451). With the increase in silver doping percentage, the intensity of the peak corresponding to the plane (002) is found to decrease for all films as confirmed by X-ray diffraction technique which leads to the introduction of defects in ZnO. Silver doping also significantly increased the electron concentrations, making the films heavily n-type. Typical optical transmittance values in the order of (85%) were obtained for all films. The lowest resistivity value of 0.074 Ω-cm was obtained for film with 4% silver doping.

The results of the current-voltage (I-V) measurements in the dark for Ag:ZnO/Si heterojunctions prepared at different doping concentrations of (0%,2%,4%) are shown in Fig.2 (a, b). These charecterstics are very important to describe the heterojunctin performance and all hetrojunction parameters depened on it.

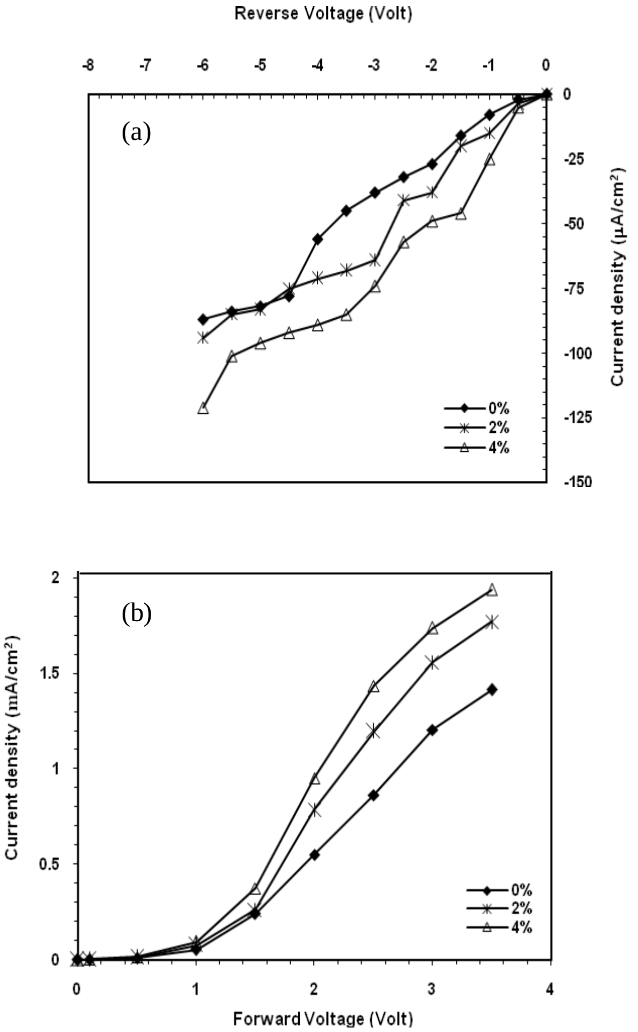

Fig.(2) (a, b) Dark I-V charecteristics under forward and reverse bias for Ag:ZnO\p-Si at different doping concentration of 0%, 2%, 4%.

In the former curves, the I-V characteristics were given for samples in forward and reverse bias. In the left hand part, it is clear that the curve contains two regions of reverse current ; the first is the generation region where the reverse current is slightly increased with the applied voltage and this leads to generate electron-hole pairs at low bias. In the second region, a significant increase can be recognized the reverse bias is increased. In this case, the current is resulted from the diffusion of minority carriers through the junction. We can also note from this figure the rapid increment in the reverse current at high reverse voltage, which is probably due to the leakage current arising from the surface layer.

The right hand part results in Fig.2 (b) give the I-V charecterisic behavior of the ZnO/p-Si and Ag:ZnO/Si heterojunctions in the forward bias. Two regions are recognized; the first one represents recombination current while the second represents the tunneling current. It is clear that a significant increase in the forward current with the present in the Ag dopants concentration, it seemed that doping is strongly influenced on the electrical properties of prepared films because metal dopants acted as donors. On the whole electrical resistivities were related to oxygen vacancies, Ag dopants and Zn concentrations at the interstitial sites, grain boundary [8]. The ideality factor of both junctions (ZnO/Si and Ag:ZnO/Si) was estimated at different doping concentrations and found to be (1.1),(1.2) and (1.4), respectively. These values refer to good rectification properties for all prepared junctions. Also we could recognize a significant enhancement in the junction quality with the increase in doping concentration . The large value of *n* (>1) suggests that in this voltage region, the recombination in these devices occurs primarily in the junction depletion region and/or at the junction interface.

One of the most important measurements is the capacitance-voltage since it determines different parameters such as built-in potential, junction capacitance and junction type deplation region width ,etc. Fig.(3) gives the $1/C^2$-V measurements at different doping concentrations. Results show that the junction capacitance is inversely proportional to the bias voltage for all prepared samples. The reduction in the junction capacitance with increasing bias voltage is resulted from the expansion of depletion layer with the built-in potential. The depletion layer capacitance refers to the increment in charge per unit area to the incremental change of the applied voltage. This property gives an indication about the behavior of the charge transition from the donor to acceptor region, which was found to be “abrupt” and this is confirmed when the relation between $1/C^2$ and reverse bias is a straight line.

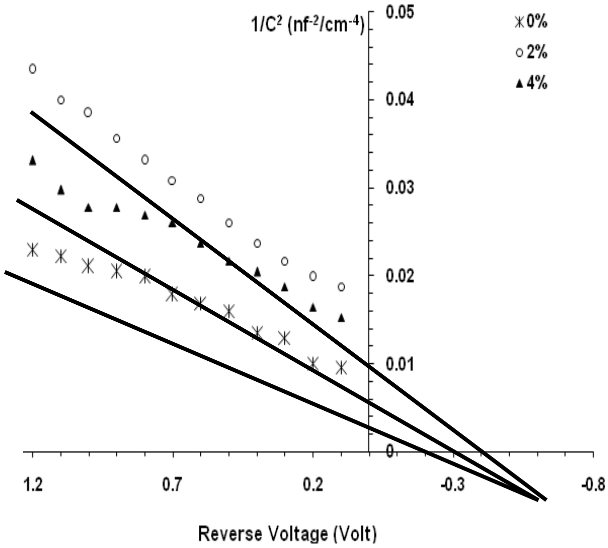

Fig.(3) Dark C-V charecteristics under reverse bias for Ag:ZnO\p-Si at different doping concentration of 0%, 2%, 4%.

The potential barrier at the junction can be measured by small-single capacitance-volt characteristic, since band bending is primarily on the Si side, the intercept of the curve on the x-axis is essienlly equal the diffusion potential within the silicon and it value is expected to depend on the Fermi level position in the conduction band at high carrier concentrations. The slope of the straight line gives the donor concentration, which its value correspond well with the known resistivity of silicon substrate. The cross point ($1/C^2=0$) of the ($1/C^2$-V) curve represents the built-in potential of the heterojunction, the charge-carrier density (N_d) at different Ag doping concentrations are calculated by the following equations [12]:

$$N_d = \frac{2}{q\varepsilon_s}[1/d(1/C^2)/dV] \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

The value of barrier height has been estimated depended on the estimated value of Fermi energy level. The built in potential (V_{bi}), the bulk Fermi level and the barrier height at different Ag doping concentrations are calculated and tabulated in the following Table (1).

Table (1)
The obtained results from the C-V measurements at different Ag doping concentrations.

Ag %	V_{bi} *(V)*	N_d *(cm^{-3})*	E_f *(eV)*	φ_B *(eV)*
0%	0.61	$6.3*10^{14}$	0.267	0.87
2%	0.63	$9.3*10^{14}$	0.257	0.88
4%	0.6	$11.6*10^{14}$	0.252	0.85

Fig.4 (a, b, c) exhibits the photoelectric behaiver of the junctions under the illumination condition. It is understood that the photoelectric effect is resulted from light-induced electron-hole generation at the junction and particularly at the depletion region of the p-type silicon. Under external reverse bias, depletion region of the detector extends and as a result, more incident photons will contribute in the electron-hole pairs generation that takes place in the depletion region and in the *n* and *p* regions, where the minority carriers are able to diffuse to the edge of the depletion region before recombine. The internal electric field in the depletion region causes the electron-hole pairs to separate from each other and this bias become larger with the applied external bias. From this Fig.4 (a, b, c) we can see the increasing in the photo-current with increasing the incident beam intensity, where the larg intensity refers to a great number of incident photons and hence large number of the separated electron-hole pairs. The results also show that the current saturates at higher bias voltage since the electric field is strong enough to separate any generated pair for a given incident power.

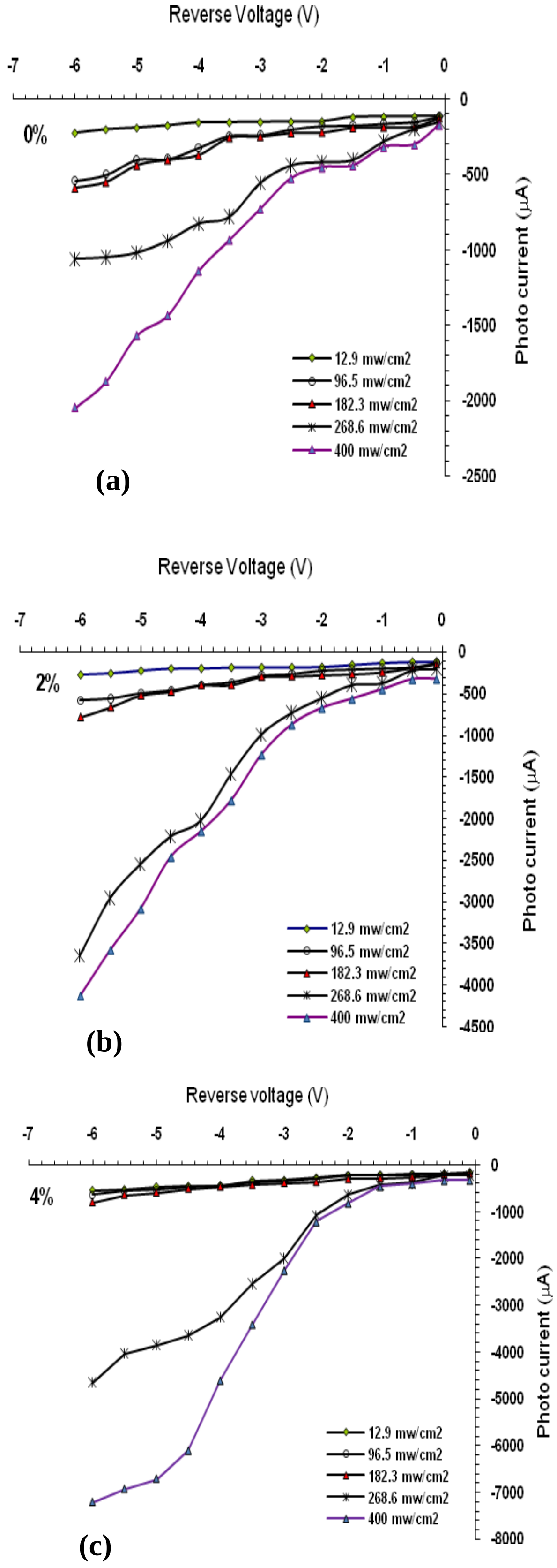

Fig.(4) (a, b, c): Photo-current as a function of reverse voltage at different values of incident light power density for Ag:ZnO\p-Si junctions at different doping concentrations of 0%, 2%, 4% respectively.

Effect of doping concentrations on the generated photo current is abvoiusly clear where the photo current a significant increase with the doping consentration due to the increase in the photo–generated elecron–hall pair because of the totally ionization of the impurities which take a subsititusional place and become an effective impurities.

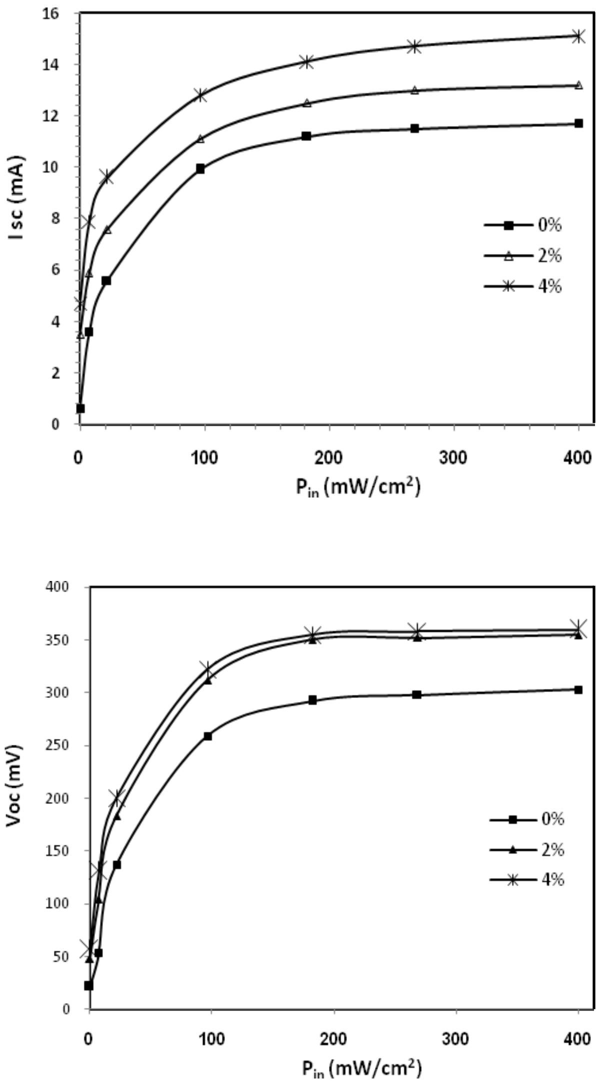

Fig.(5) (a, b) I_{sc} , V_{oc} charecteristics for Ag:ZnO\p-Si junctions at different doping concentration of 0%, 2%, 4%.

Fig.5 (a) and (b) show the dependence of the short-circuit current (I_{SC}) and open-circuit voltage (V_{OC}) on the incident photon power for different doping concentrations. We can recognize the linear relation between I_{SC} , V_{OC} and P_{in} to a maximum value, beyond which both values tend to saturate and become constant. This occurs due to the total separation of the photo-generated electron-hole pairs. It was found that the open-circuit voltage (V_{OC}) of the metal-insulator-semiconductor (MIS) structure might approach that of comparable ideal p-n junction by suitable chioce of the insulation layer [13]. Enhancement in the photovoltaic properties appears at higher doping concentration because metal dopants acted as donors, and thus play an important rule on the number of the generated electron– hole pair also it related to oxygen vacancies, Ag dopant and Zn concentrations at the interstitial sites, grain boundary.

In addition to that, maximum value of the open-circuit voltage obtained for Shottky barrier is related to the diffusion potential, i.e., difference between work function of TCO film and Si. However, an interfacial insulating layer can affect the diffusion potential, the magnitude of the open-circuit voltage, and other parameters of the device. Another purpose of the thin insulating layer is to increase the open-circuit voltage (V_{OC}) by varying the barrier height in Si, and by reducing the (extrapolated) dark saturation current.

The linear behavior of the V_{OC} versus the incident power refers to good linearity of the prepared junction to work as a solar cell or detector.

Conclusion

In summary, Ag:ZnO/p-Si junction has been prepared by using spray pyrolesis method of ZnO thin films on p-type silicon substrate at different Ag doping concentration. The electrical and photovoltaic characteristics of Ag:ZnO/p-Si heterojunction are strongly depended on the Ag dopant concentration. The measured values of 240 mV for V_{oc}, 15.1 mA for I_{sc} at 4% Ag doping concentration, while the C-V measurement revealed those prepared devices are of abrupt type.

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الخلاصة

في هذا البحث تم تحضير مفرق هجين من اوكسيد الزنك (ZnO/p-Si) واكسيد الزنك المشوب بالفضة (Ag:ZnO/p-Si) على قواعد من السليكون نوع p-type وعند نسب تشويب مختلفه باستخدام طريقة الرش الكيميائي. تم دراسة كلا من الخواص الكهربائيه والفولتائيه الضوئيه لهذه الافلام للوصول الى افضل الشروط المؤديه الى افضل النتائج.