Effect of surface modification of Si wafers on solar cell efficiency ZnO/P-Si thin films prepared by plasma sputtering

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Abstract

Zinc oxide thin films were deposited by DC sputtering at thickness (100) nm on the glass and p-Si wafer to fabricate ZnO/p-Si solar cell. All films annealed at 400°C and 500°C temperatures. Structural, optical, electrical and photovoltaic properties were investigated before and after treatment by plasma. XRD analysis revealed that all the ZnO films showed polycrystalline hexagonal structure. Average grain size calculated from AFM images showed a decrease in its value after plasma treatment, ranging from (47) nm- (25) nm. The optical transmission for samples were measured using UV-vis spectrophotometer, were used to study the energy gap. The optical characterization showed that the film has band gap that ranged in the between 3.7 eV, the average transmittance of films was found to be range of 70% to 85% in the VIS-IR regions. The electrical properties were obtained by J-V measurement. The saturation current density was calculated. The photovoltaic measurements, short-circuit current density Jsc, fill factor, were calculated for all samples.

Keywords: solar cell, ZnO/p-Si, thin films, plasma sputtering

1. Introduction

ZnO is a semiconducting material having direct band gap about 3.37eV at room temperature [1]. Transparent conducting oxides (TCOs) based on ZnO are promising for application in thin film solar photovoltaic cells. ZnO had been studied in recent years due to its unique properties such as wide band gap, high transparency and low resistivity and its applications in optoelectronic devices [2]. Some properties of Zinc Oxide and Si are shown in table (1) [3].

Table (1): Some properties of ZnO and Si at Room Temperature
Various techniques have been used for deposition of Zinc oxide films such as: vapor deposition [4], pulsed laser deposition [5]. Sol-gel process [6] chemical spray Pyrolysis [7]. Electrochemical Deposition [5], and sputtering which is used in this work and its advantage in compassion to other methods. Especially we have been challenging the deposition using a direct current (DC) sputtering technique [9] that is not used so often for oxide material. It was reported that the post-deposition annealing can well enhance the crystalline quality of ZnO both on the Si and glass substrates. The aim of this study was focused on the fabrication and characterization of ZnO/P-Si for solar cell at 100nm thickness using DC sputtering and annealed at 400°C and 500°C.

2. Experimental

In our study, we used two kinds of Si wafer one of them: (100) p-type silicon wafer with a resistivity between (1 and 10) Ω∙cm, equipped from Al-Mansour general company, another Si wafer was standard cell. Prior to the deposition of ZnO thin film, the Si wafer was cleaned ultrasonically using ethanol, and distilled water, respectively. The cleaning Si wafer was then subjected to 1%HF acid treatment to remove native SiO₂. The HF treated wafer was then thoroughly rinsed in distilled water to remove HF acid and dried in air. After cleaned Si wafers were etching by plasma (Ar, O₂ and CF₃Br) gas mixture under work condition [1.3Kv, 4x10⁻² mbar]. The obtained silicon samples were used as a substrate, and ZnO was deposited onto it. The substrate was not intentionally heated during the deposition. After the deposition, annealing was performed by an electric furnace at (400 and 500) °C for a 1 hour in the air. Sputtering on glass and P-Si, the experiments process, negative bias was added to increase the energy of particles.

All the SHJ solar cells were formed of thin ZnO layer deposited using n-type ZnO target with diameter (5cm) and thickness of (0.5cm) was used to deposit thin films on glass slices and p-type silicon wafer. The solar cell (2.5x2.5cm) is based on a p-type Si wafer absorber material. The front Al grids were evaporated with the thickness of 100 nm and the width of the bus bar1 mm. The back surface of wafer covered with Al for the back contact. The energy conversion efficiency (η) and the fill factor (FF) are calculated from (I-V) characteristics diagrams.

$$\eta = \frac{I_{MPP} \cdot V_{MPP} \cdot P_{incident}}{P_{incident}}$$
$$FF = \frac{J_{sc} \cdot V_{oc} \cdot FF}{J_{sc} \cdot V_{oc}}$$

Where used to calculate the energy conversion efficiency (η) and FF, where 120 W/cm² is the power per area for the halogen lamp, measured by power meter. Also equation (FF=\( J_{MPP} \cdot V_{MPP} / J_{sc} \cdot V_{oc} \)) is used to calculate FF therefore, the probability of (100) and (101) surface growth which may be related to the pyramid-like textured ZnO film, was increased. The sputtering parameters were listed in table (2).

| Table (2): Sputtering conditions of ZnO films used in this work. |
|-----------------------------------------------|
| Parameter     | Condition                  |
| Target        | ZnO                        |
| Substrate     | P-Si                       |
| etching       | 80%CF₃Br+20%O₂             |
| Etching time  | 15 minute                  |
| Sputtering    | 95%Ar+5%O₂                 |
| Deposition time| 1-2 hour                   |
| Sputtering pressure | 8x10⁻² mbar   |
| thickness     | 100 nm                     |
| Substrate temperature | 70°C            |
The obtained samples were examined by means of an X-ray diffraction (XRD) measurement. In this study X-ray diffractometer type SHIMADZU, power diffraction system with Cu-Kα X-ray tube (λ = 1.54056 Å) is used. The X-ray scans are performed between two angles 30° and 70°. In order to study the surface morphology and, especially, the effect of the particulate formation on the quality of the thin-film surface, AFM (Digital Instruments, Nano scope III USA) Scanning Probe Microscope (AA3000) was used. The light transmission of thin film was identified by UV-VIS spectrophotometer A double-beam UV-IR (JASCO V-670 /Japan), with wavelength in the range of (300-900) nm. The electrical measurements are achieved on the prepared thin films including, DC measurement conductivity, Hall Effect. The resistivity of ZnO films is measured by DC measurements after depositing metal electrodes (Al) on the samples using appropriate masks. The method comprises a temperature controlled oven. Electrical resistance is then measured directly for all steps with a digital multimeter. The resistivity is conventionally calculated from measured electrical resistance. The D.C electrical Conductivity of thin films is a very important parameter for all applications the bias voltage was supplied by (FARNELLE 350) power supply. The current readout was made by (Hantek 365 multimeter) multimeter. Combined conductivity and Hall voltage measurements are widely used methods for quantitative evaluation of electrical properties of semiconductors. Hall-effect analysis is performed using the Van der Pauw method. The measurement is carried out by connecting two of the electrodes with insulated copper wires, to the two ends of a D.C. power supply type Tandem. They are connected in series with an Ammeter type Kithley-616 Digital Electrometer; the other two electrodes are connected with the same type of copper wires, to a voltmeter type Kithley. The solar cell illumination I-V characteristics were measured using a solar simulator of type (photo physics) with two atmospheric masses which is normalized to 60 mW/cm² and associated with a Keithley power supply. The source meter provides voltage in the range from ±5µV sourcing and ±1µV was measuring to ±200V DC and current from ±1pA to 1A. From the data obtained, I-V curves can be plotted to calculate the fundamental cell parameters (Jsc, Jm, Vm, FF and η).

3. Results and Discussion

3.1. The Structure and Surface Morphology Characteristics of ZnO Films and P-Si.

Figure (1) shows the XRD spectrum of 100 nm thickness of ZnO thin films grown on glass before and after annealing. Three noticeable peaks belong to (100), (002), and (101) for the wurtzite structured ZnO phase was made sure of. The sharp diffraction peaks indicated the good crystallinity of the prepared sample. The sample exhibited preferential orientation along the (101) plane. At 500°C annealing temperature the single peaks near 34°, which corresponds to diffraction from the (002) ZnO planes. Post deposition annealing also led to narrower diffraction peaks with greater intensity, corresponding to increases in crystallite sizes. That annealing leads to a recovery or “precrystallization” process where strained crystallites reduce the number of defects. The major peak identified is comparable with JCPDS file 89-0510 (International Centre for Diffraction Data). The average crystallite size (D) was calculated from the diffraction line, as it is present in all samples using Scherer formula [3]:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]
Fig. (1) XRD patterns of ZnO films sputter deposited on glass.

Normally XRD was used to calculate different parameters which could be used to clarify the studies of the prepared films which are shows in table (3) and were in good agreement with those reported earlier by others [6]. The lattice constant (a) can be calculated by using equation [3].

\[
\frac{1}{d^2_{hkl}} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}.
\]

Table (3): Characteristics XRD patterns of ZnO thin films before and after annealing.

| Deposition condition | (2θ) (deg) | FWHM (deg) | d(002) (Å) | d(A) (Å) | a (Å) | c (Å) |
|----------------------|------------|------------|------------|----------|-------|-------|
| Without Ta | 34.49 | 0.4895 | 2.5088 | 2.547 | 3.249 | 5.206 |
| 400°C | 34.30 | 0.4651 | 2.51387 | 2.547 | 3.201 | 5.174 |
| 500°C | 34.51 | 0.3650 | 2.3470 | 2.547 | 3.163 | 5.067 |

Optical microscope images for p-Si before and after treatment by plasma as shown in Figure (3) shows the image of optical microscope for P-Si wafer before and after treatment by plasma.
fig(2) Optical microscope images for p-Si before and after treatment by plasma

Table (4): AFM parameters for P-Si before and after treatment. Figure (3) shows two-dimensional (2D) surface morphology and surface roughness of the P-Si over a cross-sectional area. Root mean square (RMS) surface roughness values for these wafers were 11.8, 21.6 and 23 nanometer, indicating that the films are indeed quite smooth. It was also observed that annealing had little to no effect on the surface roughness. From this, it can be deduced that these wafers have spherical grains allow the smooth surface morphology. The values of surface roughness and the grain sizes are calculated. It has been observed that a surface roughness were equal to (19.9 nm) for the thickness (100 nm). The grain size has been observed (47nm, 25nm) before and after treatment by plasma respectively.

Fig(3): 2D (AFM) of (P-Si) before and after treatment by plasma.

Fig.(4):. 2D (AFM) of (ZnO/P-Si) thin film prepare by plasma spurting
Table (4): AFM parameters for P-Si before and after treatment

| Sample                        | RMS(μm) | Grain Size(μm) | Roughness average(μm) |
|-------------------------------|---------|----------------|-----------------------|
| p-Si before treatment with plasma | 21.8    | 47             | 9.36                  |
| p-Si after treatment with plasma | 21.6    | 37             | 16.8                  |
| ZnO:P-Si                      | 23      | 25             | 19.9                  |

3.2 Optical properties

The transmittance spectra of samples are shown in figure (5). We can calculate the band gap energy using Tauc’s relation.

$$\alpha h\nu = A \left( h\nu - E_g \right)^n$$

Where $\alpha h\nu$ is the photon energy, $E_g$ is the band gap, $n = 1/2$ for direct band gap transition and $A$ is constant which is different for different transitions [Vishal Mathur].

UV-VIS transmittance spectrum has less effect in scattering than absorption. The sudden decrease of transmittance at a particular wavelength, corresponding to the optical band gap means that the particles are almost uniformly distributed in the sample.

![Fig.(5): Transmittance spectra of ZnO before and after annealing](image)

The band gap of the ZnO nanoparticles was calculated by extrapolating the curve drawn between $(h\nu)$ and $(\alpha h\nu)^2$ (shown in Fig 6). Where $\nu$ is the frequency and $\alpha$ is the optical absorption coefficient. The band gap energy obtained by extrapolating curve is found to be approximately 3.7 eV. This value is higher than that of 3.3 eV reported in the literature [12]. Band gap energy increases with decreasing particle size due to quantum size effects.
3.3 Electrical and Photovoltaic Properties

The electrical properties of ZnO/P-Si Films at 100nm thickness before and after annealing will be presented. These properties include the Hall Effect which gives information about the type of conduction, density and mobility of carriers. Moreover, the dark conductivity of ZnO/P-Si film has been studied as a function of temperature. Measurements were made for the temperature dependence of the sample conductivity [ lnσ vs (1/T)] to determine activation energies for samples thicknesses of ZnO/p-Si films deposited at 100nm thickness as illustrate in figure (7). Several values of activation energies obtained are listed in table (5). It has been noticed that in general, the d.c conductivity (σ) of all films increases with increasing the temperature this is the natural state which reflect the normal property of semiconductors that have a resistance of negative thermal coefficient, the concentration of carriers increase with increasing the temperature [9]. It is clear that the plots consist of linear regions either side of transition regions and vary exponentially according to the well-known relation:

$$\sigma = \sigma_0 \exp \left(-\frac{\Delta E_a}{kT}\right)$$

The XRD investigations of ZnO/p-Si films show that it is polycrystalline. Therefore, there is a need to calculate two activation energies for low and high temperatures within thermal range (20-150) °C. The conductivity values of all samples increase with operating temperature.

| Annealing temperature°C | Ea (eV) at L.T | Ea (eV) at H.T |
|-------------------------|---------------|---------------|
| RT                      | 0.4           | 0.025         |
| 400                     | 0.45          | 0.03          |
| 500                     | 0.5           | 0.035         |

In this sense, we believed that such difference in the resistivity values of the films with different thickness could be associated mainly with the changes in the mobility of charge carriers. These results are in good agreement with those obtained by [5].
For the ZnO/p-Si at 100 nm thickness, where we observe an increase in the conductivity and activation energy values after annealing at 500°C. This is due to the fact that reduces the crystalline defects and thus reduces the local levels which lead to increasing the energy gap i.e increases the activation energy and table (5).

The results of measurements of ZnO thin films show that these films have good conductivities and results obtained from Hall Effect indicate that the ZnO films were (n-type), which is in accordance with the findings of other workers like [8].

The values of electrical resistivity found here are smaller than for pure ZnO. We observed that all carrier concentration values are positive (RH) in the ZnO films, which indicates that the films exhibit n-type conduction. The Hall mobility of the films increased from (1.822x10$^3$ to 1.9x10$^3$ (cm$^2$V$^{-1}$s$^{-1}$) with the increase of annealing temperature, as shown in table (6).

Table (6): The result of electrical measurement at different annealing temperature of ZnO films.

| Annealing temperature(ºC) | RH(m$^2$/C ) | pH(Cm$^{-1}$/o.S) | n (cm$^{-3}$) | $\sigma$ (Ω.Cm$^{-1}$) |
|---------------------------|-----------|-------------|-----------|----------------|
| RT           | 1.78x10$^5$ | 2.23x10$^4$ | 3.5x10$^{15}$ | 1.25     |
| 400          | 1.006x10$^6$ | 1.86x10$^5$ | 6.21x10$^{15}$ | 1.65     |
| 500          | 6.798x10$^7$ | 1.922x10$^6$ | 9.182x10$^{15}$ | 2.48     |

3.4 Solar cell J-V characteristics

Figure (8) represents the current density-voltage (J-V) curve of ZnO/p-Si solar cell under dark and illumination conditions in the forward and reverse bias for solar cell without treatment by plasma. Figure (9) represents the current density-voltage (J-V) curve of ZnO/p-Si solar cell under dark and illumination conditions in the forward and reverse bias for solar cell with treatment by plasma.

Solar cell good rectifying and photoelectric properties were noticed for this device. It is observed that the ZnO/p-Si solar cell device display a great photovoltaic effect and rectifying behavior. For the (J-V) curve in dark, the current values increase exponentially with increasing in
the forward bias voltage. Moreover, it is seen from the figure that the device has high forward current that reverse current.

Fig. (8): J-V Characteristics curves for ZnO/p-Si solar cell in dark and under illumination for 100nm thickness before plasma treatment.

Fig. (9): J-V Characteristics curves for ZnO/p-Si solar cell in dark and under illumination for 100nm thickness after plasma treatment.

From figure (10), the open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor ($FF$) and conversion efficiency ($\eta$ %) are calculated in Table (7) before and after treatment by plasma. The ZnO/p-Si solar cell exhibits an obvious photovoltaic effect. Now by comparison between samples, we can find that the photovoltaic effect before treatment of ZnO/p-Si is much higher than after treatment ZnO/p-Si.

As can be seen the efficiency initially increases with the ZnO/p-Si treatment by plasma because of the increase in photo generated current ($I_{ph}$). I-V characteristic indicates good rectification property of the prepared ZnO/P-Si in the measured treatment by plasma. The current-voltage relation of the ZnO/P-Si was studied using standard diode equation [13.]:

$$I = I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]$$

Where $I_0$ is the saturation current, $q$ is the electronic charge, $V$ is the applied voltage, $k$ is the Boltzmann’s constant, and $T$ is the temperature in Kelvin and ‘$\eta$’ is the ideality factor. The output parameters of ZnO/n-Si cell; open circuit voltage $V_{oc}$, short circuit current density $J_{sc}$ and fill factor FF are 0.45 mV, 0.14 mA/cm$^2$ and 0.32 respectively. This poor performance was expected since the as-deposited ZnO films have relatively high sheet resistance. This behavior was attributed to the fact that, the relatively poor conducting ZnO films have the porous structure.
which allows oxygen to pass through it. The penetrated oxygen through ZnO layer increase thickness of the interfacial silicon dioxide layer for ZnO/p-Si cells [12].

![Graph](image1.png)

**Fig(10):a- (I-V )for ZnO/p- Si solar cell before treatment by plasma etching b- (I-V)for Si solar cell after treatment.**

**Table (8): Photovoltaic measurement for ZnO/P-Si solar cell before and after treatment with plasma**

| ZnO/P-Si solar cell | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm²) | P(mW) | FF | η% |
|--------------------|---------------|-------------------|-------|----|----|
| Without treatment with plasma | 0.50 | 0.072 | 6.07 | 0.33 | 0.78 |
| Treatment with plasma | 0.45 | 0.14 | 4.9 | 0.52 | 0.84 |

**Conclusion**

ZnO films were deposited onto porous silicon by a DC sputtering method and investigated mainly by means of X-ray diffraction measurements. As-deposited ZnO films are oriented along (002) on the surface. Annealing enhanced the crystalline quality; the FWHM were sharpened and the peak shift was eliminated. The effect of post-deposition annealing on crystallization and film stress had also been characterized, and annealing had been found to improve the quality of the films while having negligible effect on the surface roughness. The as grown ZnO thin film on P-Si was used to fabricate n-ZnO/p-Si heterojunction diode. I-V characteristic in the temperature range 25°C to 150°C shows that the heterojunction was found to stable and has good rectification property. The heterojunction shows great photoelectric effect under power (160W) lamp illuminate. The photocurrent responses were detected for the solar cell. The solar cell exhibited a short-circuit current density of 0.14 mA/cm², circuit voltage of 0.54 mV for films treatment by plasma.
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