Fabrication and Characterization of ZnO/p-Si Heterojunction Solar Cell

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ABSTRACT

Zinc oxide thin films was deposited by chemical spray pyrolysis (CSP) at 400 °C substrate temperature and different thickness (60, 80, and 100) nm on the texturized p-Si wafer to fabricate ZnO/p-Si heterojunction solar cell. Structural, optical, electrical and photovoltaic properties are investigated for the samples. XRD analysis reveals that all the as deposited ZnO films show polycrystalline structure, without any change due to increase of thickness. Average diameter calculated from AFM images shows an increase in its value with increasing thickness, ranging from 59.82-95.7 nm. The optical reflections for samples are measured using UV-Vis spectrophotometer. Photoluminescence (PL) spectra of (CSP) grown ZnO/p-Si with different thickness were used to study the energy gap. The electrical properties of heterojunction were obtained by I-V (dark and illuminated) and C-V measurement. I-V characteristic of the ZnO/p-Si heterojunction shows good rectifying behavior under dark condition. The ideality factor and the saturation current density was calculated. Under illuminated the photovoltaic measurements (open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor ($FF$), and quantum efficiencies are calculated for all samples. The built-in potential ($V_{bi}$), carrier concentration and depletion width are determined under different thickness from C-V measurement.

Keywords: n-ZnO/p-Si, chemical spray pyrolysis, heterojunction solar cell
1. INTRODUCTION

Transparent conducting oxides (TCOs) based on ZnO are promising for application in thin film solar photovoltaic cells (PVCs) and various optoelectronic devices [1, 2]. ZnO has 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 and laser diodes [3]. It also can be used as a window layer and in heterojunction solar cells [4]. It is well known that undoped ZnO thin films generally indicate n-type conduction. ZnO thin films have been grown on Si substrates by several physical and chemical methods such as chemical vapor deposition, sputtering, atomic layer deposition, [5-8] pulsed laser deposition (PLD) [9] and chemical spray pyrolysis [10]. ZnO thin films with p-Si have been used in many applications such as photodetectors owing to its Good optical and electrical properties, ease of fabrication, low cost [11-13]. The aim of this study was focused on the fabrication and characterization of ZnO/p-Si heterojunction for solar cells with different thin film thickness utilizing spray pyrolysis technique.

2. EXPERIMENTAL

In this study, Mirror-like single-crystal p-Si (111) with a thickness of (500 µm) and a resistivity of 1-9 Ω cm was used as a substrate. These substrates were put in diluted 1% HF solution to remove the native oxide, washed with deionized water and dried with nitrogen gas. Square-shaped p-type silicon substrate, 1×1 cm² area, were prepared.

The condition of deposition was summarized in the following: (0.1M) solutions were prepared by dissolving zinc acetate (Zn(CH₃COO)₂·2H₂O) in deionized water. The adding of few drops of glacial acetic acid were done in order to obtain a stabilized solution. The substrate temperature was kept at 400 °C during the process of deposition. The carrier gas (compressed nitrogen (4 bar pressure) and solution are fed into a spray nozzle to obtain ZnO/silicon heterojunction with different thickness. Ohmic contacts of these devices were made by evaporating a thin AL sheet mask strips on the ZnO thin film and a thick Al on back surface of Si.

The thin film thickness was determined by using (LIMF-10 Optical Thin Film Measurement). X-ray diffraction (XRD) with CuKα radiation (λ = 1.5418 Å) was used in order to identify the structural of the deposited ZnO films. The surface morphology was studied by atomic force microscope (AFM). The optical reflection of the sprayed ZnO thin film could be calculated by using UV–VIS spectrophotometer at room temperature. The energy gap was determined by photoluminescence (PL) spectra using the spectrofluorometer (Lambda 45, Perkin Elmer, Waltham, MA, USA). The I-V characteristics of the Al-ZnO/p-Si heterostructure were measured using a Keithley source meter (model 2430). The measurements were performed in dark and under light. The most important PV parameters are short circuit current Iₛcdc and open circuit voltage Vₒc were also measured.

The capacitance–voltage (C–V) characteristic of a ZnO/p-Si heterojunction was obtained using an LCZ meter at a fixed frequency of (1 MHz). The spectral responsivity of the solar cell was measured in the spectral region of (300-900 nm).
3. RESULTS AND DISCUSSION

3.1. Structural Properties

Figure (1) shows the XRD spectrum of different thickness 60, 80, and 100 nm of ZnO thin films grown on silicon. All the samples show reflection peaks from ZnO thin film and Si substrate. The peak of Si substrate from (111) plane was clearly distinct than ZnO thin films peaks.

Three noticeable peaks belong to (100), (002), and (101) for the wurtzite structured ZnO phase was ascertained. It can be deduced that all the as deposited film show strong c-axis (002) direction growth. In sample (a) deposited at (60 nm) interval, (002) and (101) diffraction peak was detected. Good crystallinity obviously, at higher thickness were noticed. The average crystallite size (Gs) of ZnO thin films/Si heterojunction was calculated from the following Scherrer’s formula:

\[ G_s = \frac{0.94 \lambda}{\beta \cos \theta} \]  

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the full-width at half-maximum of the main peak, and \( \theta \) is the reflection angle [14], and found to be (15.01, 30.50, and 26.19) nm of different thickness (60, 80, and 100) nm respectively.

![Figure 1. XRD patterns of ZnO thin films on Si substrate at different thickness: (a) 60 nm, (b) 80 nm, and (c) 100 nm.](image-url)
Figure 2. 2Dx3D Atomic force microscopy (AFM) of ZnO/Si heterojunction with different thickness 60 nm, 80 nm, and 100 nm
Figure (2) shows two-dimensional (2D) surface morphology on the left and the three-dimensional (3D) on the right of ZnO thin films with different thickness. From this, it can be deduced that these films have spherical grains granting 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 (1.16, 14.2, and 2.18) for the different thickness (60, 80, and 100 nm) respectively. The grain size has been observed (59.82, 90.95, and 95.7) for (60, 80, and 100 nm) respectively. Therefore, the average diameter of ZnO thin film with high thickness (see Fig. 2, c) is larger than ZnO thin film (Fig. 2, a, b).

3.2. Optical Properties

In order to probe the energy transitions within ZnO and determine the defect structure the photoluminescence measurements were studied. The PL spectrum of the prepared ZnO thin films on Si is shown in Figure (3) with different thickness. Two luminescence peaks can be observed, the first peak is the UV emission corresponding to the nearest band edge emission (NBE) at about (361 nm (3.43 eV), 366 nm (3.38 eV), and 378 nm (3.28 eV)) for thickness 60, 80, and 100 nm respectively. The highly crystalline ZnO as shown by XRD would be expected to generate strong near band emission [15] observed the increasing thickness lead to increase in intensity peaks. The another peak is in the visible region, which may be due to the defect, related to deep level emission. Second luminescence peak, shows a broadband peak at (746 nm (1.66 eV), 762 nm (1.62 eV), and 735 nm (1.68 eV)) for thickness 60, 80, and 100 nm respectively. This energy emitted at 1.66 eV is almost equal to half the value of energy emitted in near band-edge emission (3.30 eV) calculated above. This was clearly indicates that these mid gap defect states giving rise to emission at 747.8 nm are exactly at the center of the band gap of ZnO. These mid gap states may arise due to deep level defects in ZnO [16].
Figure 3. PL spectra of ZnO thin films grown on p-Si semiconductor with different thickness.
The reflection spectrum of ZnO thin film was calculated. Figure (4) showed the reflection spectrum for pure Si and ZnO/Si with different thickness. The pure Si surface shows a monotonic decrease from visible to infrared range and the reflection spectrum for ZnO thin film ought to decrease with the increase of thickness. The reflectance values were between 10% and 80%. The reflectance of deposited films shows the same behavior, that their values decreased with the increasing in wavelength. These results agree with other researchers [17, 18].

Figure 4. The reflection spectrum for pure Si and ZnO/Si with different thickness.

3.3. Electrical and Photovoltaic Properties

Figure (5) represents the current–voltage (I–V) curve of ZnO/Si heterojunction solar cell under dark and illumination conditions in the forward and reverse directions with different thickness (60, 80, and 100) nm. Good rectifying and photoelectric properties were noticed for this device. It is observed that the ZnO/Si heterojunction solar cell device display a great photovoltaic effect and rectifying behavior.

The photocurrent caused by the (160 mW) white lamp is clearly much larger than dark current. For the (I–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.

The rectification ratio IF/IR (IF and IR stands for forward and reverse current, respectively) of the structure of (1V) is found to be as high as (3.43, 1.35, and 2.81) for 60, 80, and 100 nm respectively. It was reasonably exhibited good rectifying behavior, denoting the formation of heterojunction solar cell ZnO/Si.
Figure 5. I-V Characteristics curves for ZnO/Si solar cell in (a) dark and (b) under illumination for at different thickness.

Figure 6. In (J) versus V for fowared bais of dark for ZnO/Si heterojuction at different thickness.
The plot of $(\ln(J))$ versus $V$ (forward bias) of heterojunction is shown in Figure (6), we can see that the current at low voltage ($V < 0.2$ V) varies exponentially with voltage. The characteristics can be depicted by the standard equation: $J = J_0 (e^{qV/K_B T} - 1)$ where $(q)$ is the electron charge, $(V)$ is the applied voltage, $(K_B)$ is the Boltzmann constant, $(n)$ is the ideality factor and $(J_0)$ is the saturation current density [19]. The value of the ideality factor of the ZnO/Si heterojunction solar cell is gained from the slope of the straight line region of the forward bias log $I$-$V$ characteristics for dark curve. Calculation of the ideality factor, barrier height $(\Phi_b)$, tunneling factor $(\gamma)$, current photo $(I_{ill}-I_{dark})$ in reverse $(I_{ph})$, and the reverse saturation current density measurement is shown in Table (1). From Table (1) one can see that the ideality factor and saturation current density increase with the increasing of thickness, while the barrier height $(\Phi_b)$ could be seen to decrease. This result agrees with [20].

**Table 1.** Ideality factor, Barrier height, and Saturation current density values for ZnO/Si heterojunction at different thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Ideality Factor (n)</th>
<th>Barrier Height $(\Phi_b)$ (eV)</th>
<th>Saturation Current Density $(J_s)$ ($\mu$Amp/cm$^2$)</th>
<th>Tunneling factor $(\gamma)$ ($v^{-1}$)</th>
<th>Current photo $(I_{ph})$ ($\mu$Amp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.32</td>
<td>0.747</td>
<td>0.83</td>
<td>4.26</td>
<td>6.8</td>
</tr>
<tr>
<td>80</td>
<td>1.706</td>
<td>0.69</td>
<td>6.14</td>
<td>3.57</td>
<td>8.64</td>
</tr>
<tr>
<td>100</td>
<td>1.774</td>
<td>0.66</td>
<td>20.4</td>
<td>3.35</td>
<td>16.9</td>
</tr>
</tbody>
</table>

I-V characteristics of ZnO/Si heterojunction solar cell under illumination shown in Figures (7). And the open-circuit voltage $(V_{oc})$, short-circuit current density $(J_{sc})$, fill factor $(FF)$ and conversion efficiency $(\eta \%)$ are calculated in Table (2) for different thickness. The ZnO/Si heterojunction solar cell exhibits an obvious photovoltaic effect. Now by comparison between samples, we can find that the photovoltaic effect of (100) nm ZnO/Si heterojunction is much higher than (60) nm ZnO/Si heterojunction.

**Table 2.** Photovoltaic measurement for ZnO/Si heterojunction solar cell at different thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$V_{oc}$ (Volt)</th>
<th>$I_{sc}$ ($\mu$Amp)</th>
<th>$V_{max}$ (Volt)</th>
<th>$I_{max}$ ($\mu$Amp)</th>
<th>FF</th>
<th>$\eta %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.18</td>
<td>11.3</td>
<td>0.11</td>
<td>5</td>
<td>0.27</td>
<td>1.15</td>
</tr>
<tr>
<td>80</td>
<td>0.1</td>
<td>21</td>
<td>0.07</td>
<td>12.5</td>
<td>0.417</td>
<td>1.82</td>
</tr>
<tr>
<td>100</td>
<td>0.11</td>
<td>29</td>
<td>0.08</td>
<td>16.3</td>
<td>0.409</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Figure 7. I-V Characteristics under illumination for ZnO/Si Solar Cell at different thickness.

We can observe that $I_{sc}$ is increasing with thickness increase, the variation of the fill factor was also listed in Table (2). This result agrees with [21]. As can be seen the efficiency initially increases with the increasing of thickness because of the increase in photo generated current ($I_{ph}$).

The capacitance-voltage measurements led to calculate different parameters such as built-in potential, junction capacitance, carrier concentration and depletion width. Figure (8) gives the $(1/C^2-V)$ measurements at different thickness. From these results, it can be seen that junction capacitance is inversely proportional to the bias voltage for all samples, which can be explained by the expansion of depletion layer with the built-in potential.

The capacitance-voltage (C-V) characteristics of ZnO/Si heterojunction solar cell was shown in Figure (9) with different thickness 60, 80, and 100 nm. From Table (3) we will note that the increase with thickness decreases the capacitance at zero bias voltage ($C_o$) of ZnO thin film.

This behavior was attributed to the increase in depletion region width ($W$) which leading to the enhancement of built-in potential ($V_{bi}$). The width of depletion layer increases with increasing thickness that is due to the decreasing in the carrier concentration ($N_D$) which leads to a decrease of the capacitance as shown in Table (3). Such behavior is nearly in agreement with [22].
Figure 8. The variation of $1/C^2$ as a function of reverse bias voltage for ZnO/Si heterojunction solar cell with different thickness.

Figure 9. The variation of capacitance as a function of voltage for ZnO/Si heterojunction solar cell with different thickness.
Table 3. Values of $C_0$, $W$, $N_D$ and $V_{bi}$, for ZnO/Si heterojunction with different thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$C_0$ (nf)</th>
<th>$W$ (nm)</th>
<th>$V_{bi}$ (volt)</th>
<th>$N_D$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>12.8</td>
<td>105</td>
<td>0.5</td>
<td>2.79E+13</td>
</tr>
<tr>
<td>80</td>
<td>10.2</td>
<td>132</td>
<td>0.6</td>
<td>1.72E+13</td>
</tr>
<tr>
<td>100</td>
<td>9.1</td>
<td>148</td>
<td>0.8</td>
<td>1.07E+13</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

High quality ZnO thin films were successfully deposited on silicon substrates by chemical spray pyrolysis. The XRD analysis shows that all the deposited films were polycrystalline and the crystallite size was highly oriented in (002) direction. Photoluminescence show a strong UV photoluminescence matching ZnO band edge with trivially small photoluminescence in the visible region. Good rectifying and great photovoltaic behaviors are examined and analyzed by $I$-$V$ measurements minutely. The ideality factor and the saturation current density of ZnO/Si heterojunction solar cell are obtained with different thickness. The ideality factor is less than 2, indicating that the diode exhibits an ideal behavior. The heterojunction shows a great photovoltaic effect under power (160 mW) White lamp illuminate. The quantum efficiency initially increases with the increasing of thickness, while the C-V measurement revealed that those prepared devices are of abrupt type.

References


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