Realization and Characterization of ZnO/n-Si Solar Cells by Spray Pyrolysis

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Indium doped zinc oxide (ZnO: In) thin films have been prepared using spray pyrolysis technique. The used spray solution has a molarity of 0.2 M of chemical pure hydrated zinc acetate (Zn $(CH_3CO_2)2H_2O$) and 2% by weight of indium chloride ($InCl_3$). Zinc acetate was dissolved in a mixture of bidistilled water and methyl alcohol (80%H_2O:20% CH_3OH). The ZnO/n-Si solar cells have been realized by depositing the ZnO: In on Si wafers separated by a thin interfacial SiO_2 layer ameliorating the barrier height. The realized ZnO /n-Si solar cells shows rapid degradation of the cell performance with storage time in dark. This could be attributed to the porosity of ZnO films which allows the oxygen to diffuse through it increasing the thickness of the interfacial SiO_2 layer due to the reaction with Si. The degraded characteristics of ZnO/n-Si junction solar cells can be minimized by depositing a conducting layer of indium tin oxide (ITO) as a barrier layer on ZnO/n-Si. A thin layer of ITO is deposited on ZnO films to suppress the oxygen diffusion to Si wafer. The best output parameters obtained for ITO/ZnO-nSi cells are; open circuit voltage $V_{OC} = 0.44$ V, short circuit current density $J_{SC} = 20$ mA/ cm^2, fill factor FF =0.6 and efficiency $\eta = 5.28\%$.

1. Introduction:

Transparent Conducting Oxides (TCO) has been widely studied and received considerable attention in recent years. The band gaps of these materials are large enough to be transparent to most of the useful solar spectrum and the resistivity is small enough to avoid series resistance effect. Indium doped zinc oxide (ZnO:In) has emerged as one of the most promising window materials due to its large band gap (3.2 eV), high transparency and low resistivity managed by doping and heat treatment. ZnO thin films have been prepared by wide variety of techniques such as sputtering [1], evaporation

[2], chemical vapour deposition (CVD) [3], sole-gel [4] and spray pyrolysis [5]. Spray pyrolysis deposition is particularly attractive since it is relatively fast, vacuumless, simple and more economics. The electro–optical properties are generally dependent on the deposition and post deposition conditions, because these properties changed significantly with the absorption and desorption of oxygen that occurs during these process.

2. Experiment:

Phosphorus doped two-inch diameter monocrystalline n-Si wafers with thickness of 280-300 μm and resistivity of 10-20 Ωcm, oriented in (100) plane were used. They were cut into relatively small segments (1cm × 1cm) to be used as base semiconductor for semiconductor-insulator–semiconductor (SIS) solar cells. The process steps of the ZnO/n-Si solar cells are shown in Fig. (1).
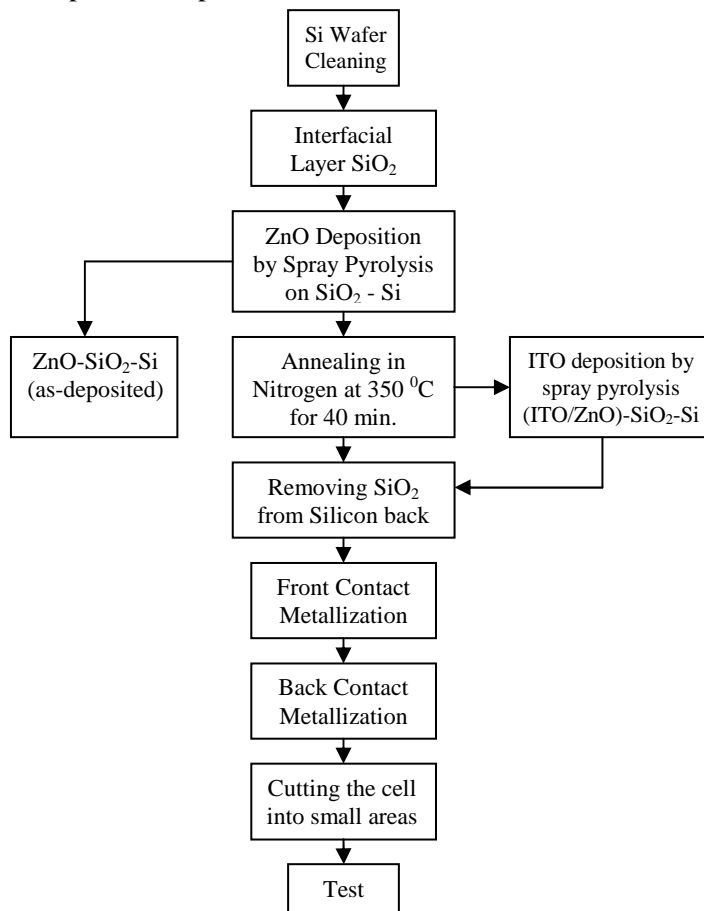
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┌──────────────┐
│  Si Wafer    │
│  Cleaning    │
└──────┬───────┘
       ▼
┌──────────────┐
│  Interfacial │
│ Layer SiO₂   │
└──────┬───────┘
       ▼
┌──────────────────┐
│  ZnO Deposition  │
│ by Spray Pyrolysis│
│  on SiO₂ - Si    │
└──────┬───────────┘
       ▼
┌──────────────┐   ┌──────────────────┐        ┌──────────────────┐
│ ZnO-SiO₂-Si  │   │  Annealing in    │───────▶│ ITO deposition by│
│(as-deposited)│   │ Nitrogen at 350 ⁰C│        │  spray pyrolysis │
└──────────────┘   │  for 40 min.     │        │ (ITO/ZnO)-SiO₂-Si│
                   └──────┬───────────┘        └──────────────────┘
                          ▼
                   ┌──────────────┐
                   │ Removing SiO₂ │◀───────────
                   │from Silicon back│
                   └──────┬───────┘
                          ▼
                   ┌──────────────┐
                   │ Front Contact│
                   │ Metallization│
                   └──────┬───────┘
                          ▼
                   ┌──────────────┐
                   │ Back Contact │
                   │ Metallization│
                   └──────┬───────┘
                          ▼
                   ┌──────────────┐
                   │Cutting the cell│
                   │into small areas│
                   └──────┬───────┘
                          ▼
                   ┌──────────────┐
                   │    Test      │
                   └──────────────┘
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Fig. (1): The general Processing for the three solar cell configurations (as -deposited ZnO/n-Si, annealing ZnO/n-Si and (ITO/ZnO)/n-Si solar cells)

The Cleaning Sequences are:

- The silicon wafers were washed ultrasonically in distilled water.
- They were washed in boiling acetone, then in boiled propanol for 5 minutes to remove greasy films.
- They 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 drier furnace at 120 ^{o}C.

The Interfacial Layer Formation

The insulator SiO_2 layer on the front surface of silicon wafers was prepared by heating the silicon wafer at 450 °C in dry oxygen for different times (2-10 min.). .Since there is no ellipsometer to measure the formed SiO_2 film thickness accurately, the time of oxidation could be considered as a monitor of the film thickness.

The Top Window Layer Deposition

The ZnO thin films were deposited on microscope glass (Menzel-Gläser, Germany) slices by spray pyrolysis. The structural, optical and electrical characteristics were correlated with preparation parameters to optimize the best conditions fitting the solar cell performance. Some studies were carried out on the realized ZnO films published in previous papers [6]. Zinc oxide films are prepared from solution of 0.2 M of pure hydrated zinc acetate Zn $(CH_3CO_2)_2.2H_2O$ dissolved in a mixed solution of 80% bi-distilled water and 20% methyl alcohol (80%H_2O:20%CH_3OH) at substrate temperature of 425 ^{0}C for 30 minute spray time, 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 as shown in Fig.(2). The high electrical resistivity of pure ZnO can be reduced by adding indium chloride $InCl_3$ as a dopant to the precursor zinc acetate solution. The ZnO thin film incorporated with 2% In gives high conductivity 0.384×10^2 $(\Omega.cm)^{-1}$. All the

obtained films exhibit a high transmission ~90% in the visible region with sharp absorption edge at 380 nm as shown in Fig. (3). The energy band gap of obtained ZnO films has a high value 3.26 eV and hasn't change by indium addition and the refractive index is 1.9. These values enable the prepared ZnO acting as window and antireflection coating materials.
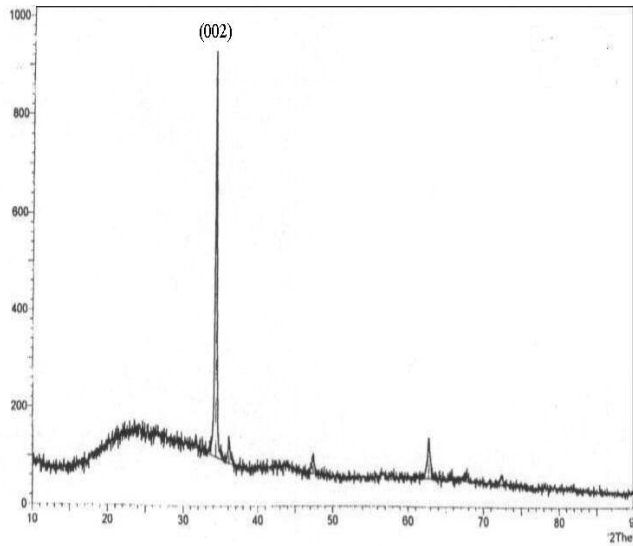

Fig. (2): XRD pattern for ZnO film prepared at 425^0C for 30 min spray time and the solvent is 80% H_2O:20% CH_3OH.

The Front and Back Contact

Before the contact process, the backside of the devices was exposed to 10% HF acid to remove the silicon dioxide SiO_2 layer to decrease the series resistance. Indium has been found to form a good ohmic contact to the ZnO, therefore 0.8 μm In is evaporated on the ZnO film through a metal shadow mask. The back contact was formed by evaporating about 1μm Ag over the entire back side of the silicon. After the metallization process, the device is ready for evaluation and carrying out the required physical measurements. The edge portion of the silicon specimen was cut off to have electrical isolation between the rear and front surfaces.
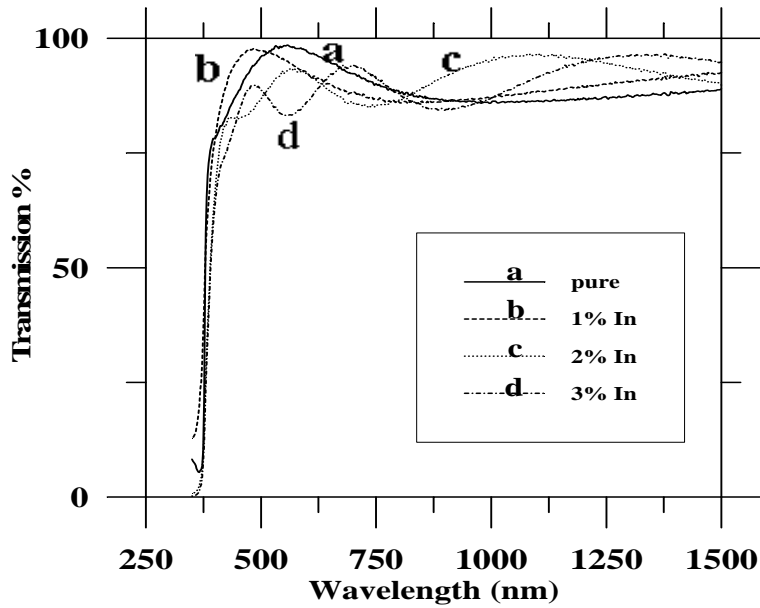
Fig. (3): The transmittance spectra of pure and doped ZnO thin films.

3. Results and Discussions:

3.1. As-deposited ZnO/n-Si solar cells

The illuminated I-V characteristics of as-deposited ZnO/n-Si solar cell prepared at 5 min. oxidation time exhibits a poor photo response. The output parameters of ZnO/n-Si cell; open circuit voltage Voc, short circuit current density Jsc and fill factor FF are 232 mV, 2.15 mA/cm^2 and 0.3 respectively. This poor performance was expected since the as-deposited ZnO films have relatively high sheet resistance. Such type of cell shows tendency to rapid degradation in performance after a short time (~3days) although it is stored in dark. 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/n-Si cells. Therefore, the SiO$_2$ interfacial layer with an optimum thickness is needed to control the barrier height between ZnO and n-Si. Table (1) indicates the cell output parameters measured immediately after fabrication and 3 days latter.

Table (1): Photovoltaic parameters for as-deposited ZnO/n-Si solar cell measured immediately after fabrication and after 3 days.

	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
Immediately	232	2.15	0.33	0.18
After 3 days	150	1	0.1	-

3.2. Annealed ZnO/SiO$_2$/n-Si solar cells

Generally, the electrical characteristics of ZnO could be enhanced by a proper doping with   trivalent element and/or a suitable heat treatment in a reducing atmosphere (hydrogen) to change the stoichiometry of ZnO layer or inert atmosphere at certain temperature for a certain time to minimize the imperfections and increase the crystal size which allows an increase in the J_{SC}. As well the adsorbed oxygen on the zinc oxide surface and that diffused into the bulk are evolved leaving behind a donor state which increase the free carriers. Baik *et al*. [7] perform annealing at about 450 ^{o}C for 1 hour in hydrogen on ZnO/SiO$_2$/n-Si, also H. Kobayashi *et al*. [8] annealed at 300 ^{o}C for 1 hour in vacuum and. Tomar *et al*. [9] perform annealing in nitrogen at 350 ^{o}C to improve the cell performance. In the present work, the heat treatment is carried out by annealing the cell at 350 ^{o}C in N$_2$ for 40 minuets. It is observed that, heat treatment in nitrogen (N$_2$) results in large reduction of ZnO film sheet resistance because of oxygen desorption from the surface pores and grain boundaries, resulting in creation of vacant sites which will act as donor states The sheet resistance reduced from 2.11 K Ω /□ (Ω/ Square cm) for the a-deposited film to a low value in the range 257 Ω / □ (Ω/ Square cm) as shown in Fig. (4). It is clear that the cell output parameters are improved and the stability was extended for long time as indicated in Table (2).

Table (2): Photovoltaic parameters for annealed ZnO/n-Si solar cell measured immediately after fabrication and after 30 days.

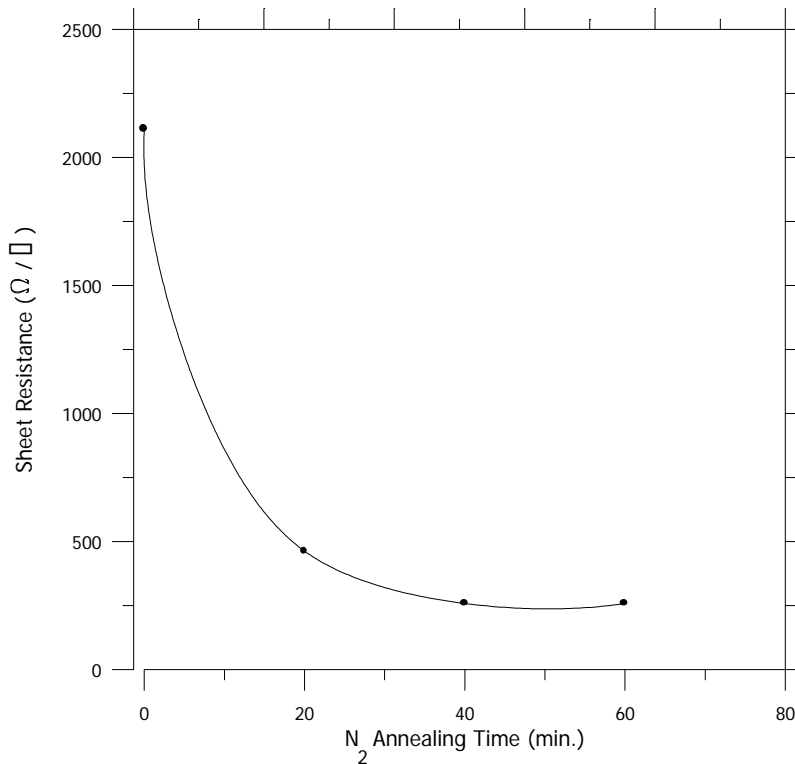|	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
Immediately	350	19	0.5	3.32
After 30 days	300	16	0.4	1.92

Fig. (4): The sheet resistance of ZnO: In annealed in N_2 at $350\,^{o}C$ for different time**.**

3.3. ITO/ZnO/n-Si solar cells

The degraded characteristic of ZnO/n-Si junction solar cells is minimized by depositing barrier layer for oxygen diffusion on the ZnO/n-Si. A thin layer of ITO is deposited on ZnO/n-Si to suppress oxygen diffusion from the environment. ITO is highly transparent in the visible region (~90%) and has high electrical conductivity (σ~ $10^4\,\Omega^{-1}cm^{-1}$). Solar cells covered with ITO are tested immediately and after 3 months from fabrication. Figure (5 : a, b) shows the dark and illuminated I-V curves for ITO/ZnO-nSi solar cell under light intensity 100 mW/cm^2 .It is observed that, the cell output parameters and the stability is further improved as indicated in Table (3). The observed stability of ITO/ZnO-nSi solar cell could be attributed to almost constant thickness (which could not be measured) of intentionally formed SiO_2 layer. In contrast to ZnO/Si solar cell, the oxygen diffuse through porous ZnO layer to Si substrate allowing more degradation of the cell performance due to the uncontrollable induced SiO_2 layer.

Table (3): Photovoltaic parameters for ITO/ZnO/n-Si solar cell measured immediately after fabrication and after three months.

	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η %
Immediately	440	20	0.6	5.28
After 3 months	435	19.8	0.57	5.1

0.5 mA/ div

0.2 V/div
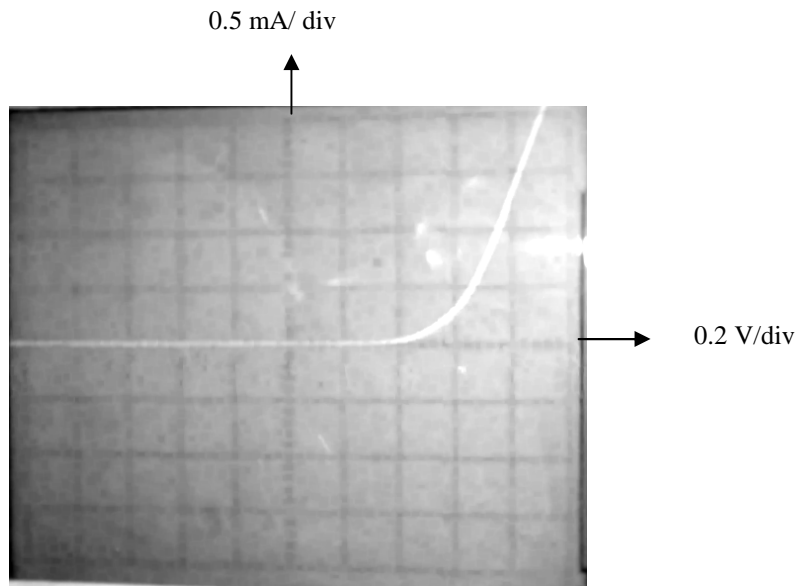
Fig. (5-a): Dark I-V characteristic of ITO/ZnO/n-Si solar cell prepared at 5 min oxidation time

3.4. The effect of oxidation time

The capacitance-voltage (C-V) characteristics are useful in obtaining information about the potential barrier at the junction, the semiconductor doping concentration and the presence of traps in materials. The plot of $1/C^2$ versus reverse bias for ITO/ ZnO/Si solar cells at different oxidation time (2-10 min.) is shown in Fig. (6). The donor concentration N_D and the built in potential V_{bi} are estimated from the slope and the intercept of $1/C^2$ versus V_a respectively. The barrier height φ_b is related to built in potential V_{bi} by the following formula [10]:
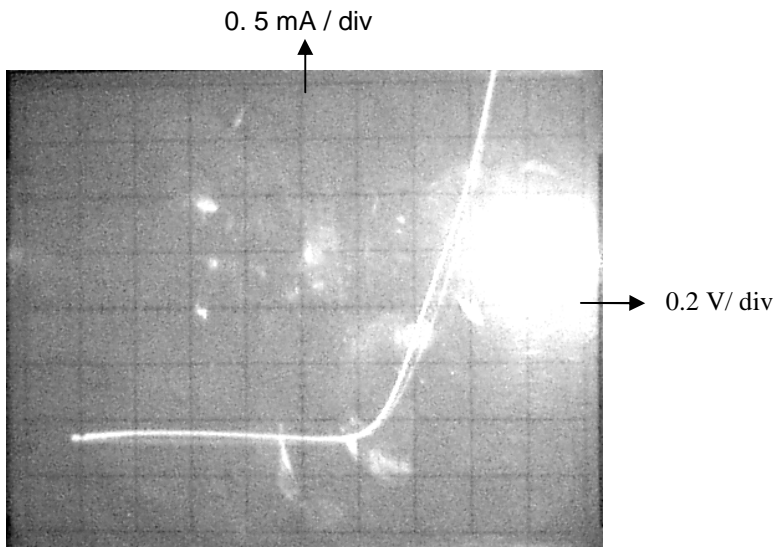
0. 5 mA / div

0.2 V/ div

Fig. (5-b): Illuminated I-V characteristic of ITO/ZnO/n-Si solar cell prepared at 5 min oxidation time tested after 3 months of fabrications.
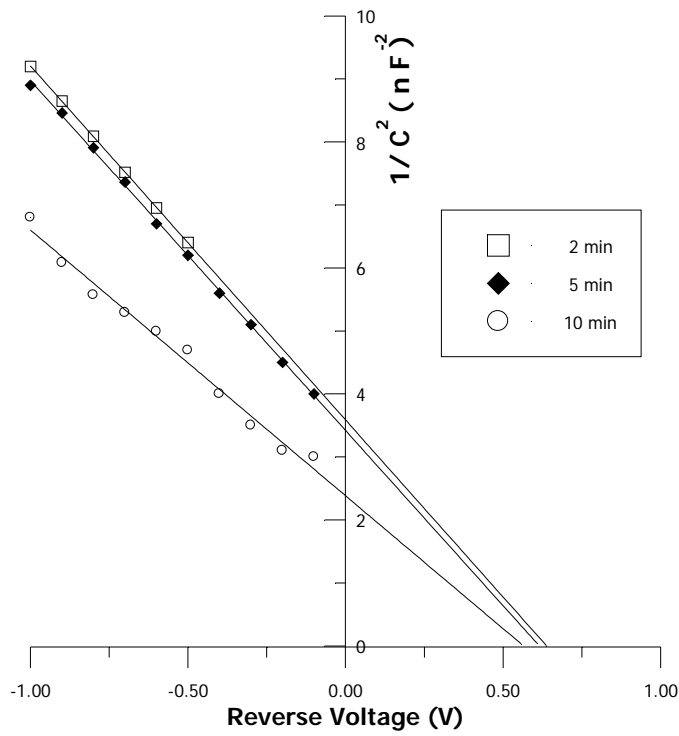

Fig. (6): The plot of $1/C^2$ versus reverse voltage for ITO/ZnO/n-Si at different oxidation time.

$$\Phi_b = qV_{bi} + (E_C - E_F) \tag{1}$$

where $E_C - E_F$ is the difference between the conduction band energy and Fermi energy and depends upon the doping density and it is given by [11],

$$E_C - E_F = \frac{KT}{q} \ln(\frac{N_C}{N_D}) \tag{2}$$

where N_C is the effective density of states in conduction band equal to 2.8×10^{19} cm^{-3} for silicon [10], K is the Boltzmann constant equal to 1.381×10^{-23} J/K[10] , T is the temperature in Kelvin and q is the electronic charge equal to 1.6×10^{-19} C [10]. The Si side doping concentration N_D can be determined from the slop of straight line according to the following equation [10].

$$N_D = \left(\frac{2}{q\varepsilon_s\varepsilon_o A^2}\right)\left(\frac{\Delta V_a}{\Delta \frac{1}{C^2}}\right) \tag{3}$$

where ε_s is the relative permittivity of silicon equal 11.9 [10], ε_o is the permittivity of free space equal 8.85×10^{-12} F/m [10] and A is the cell area equal 20 mm^2.

The bulk Fermi level E_F in the silicon is calculated to be 0.289 eV from equation (1) after calculation the doping concentration using equation (3) below the conduction band edge E_C. The extrapolated built in potential V_{bi} and the calculated donor concentration for ZnO / SiO$_2$ /Si structure at 10 min oxidation time is 0.57V and 4.16×10^{14}cm^{-3} respectively. The calculated values of N_D are consistent with the known resistivity of the used silicon as depicted from the following equation [11]

$$\rho = \frac{1}{q\mu_n N_D} \tag{4}$$

where μ_n is the mobility of electron in silicon and equal 1350 cm^2/V.S [10]. The above equation gives a resistivity 11 Ω.cm while the used resistivity is in the range 10-20 Ω.cm. It is observed that the decrease of photovoltage is caused by lowering the energy barrier height. The variation of open circuit voltage V_{oc}

and barrier height φ_b as a function of oxidation time are shown in Fig. (7). The obtained results was supported by Ashok *et al.* [12], who reported the changes in built-in voltage in the range 0.80 to 0.65 V with increasing the oxidation time (0 - 15 min.), while the obtained results changes in the range 0.0.67 to 0.57 V. with increasing the oxidation time (2-10 min.).
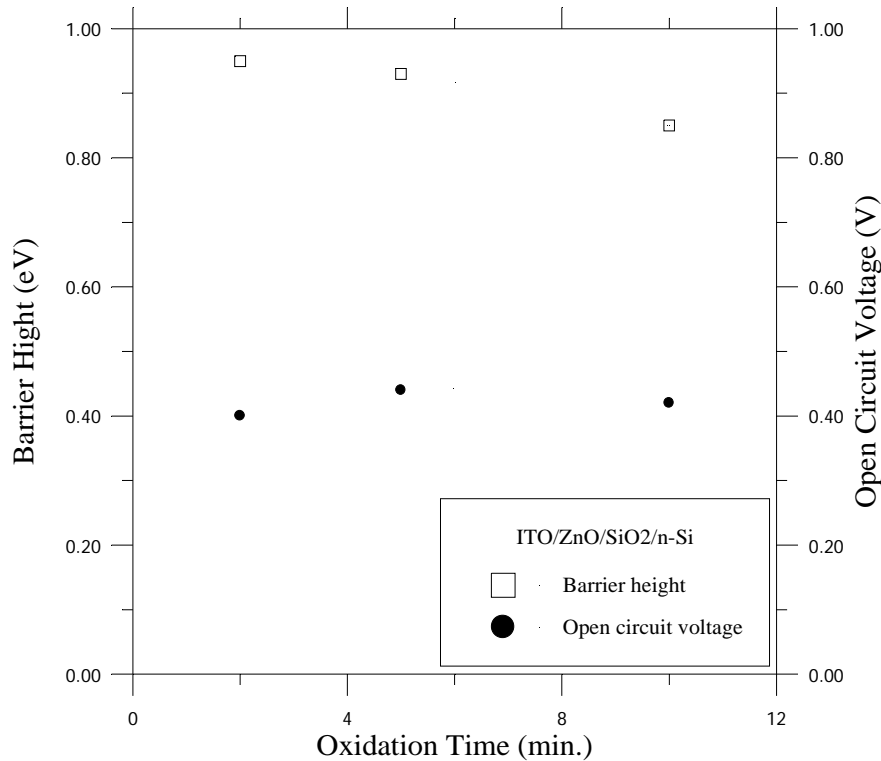

Fig. (7): The variation of the barrier height (φ_b) and open circuit voltage (V_{oc}) as a function of oxidation time.

4. Conclusions:

Zinc oxide/ monocrystalline silicon solar cell is realized by spraying 0.2 M zinc acetate dissolved in a solvent composed of 80% H_2O:20% CH_3OH. The ZnO/Si solar cell with an interfacial SiO_2 layer formed by oxidation shows a considerable degradation of its performance. To minimize cell degradation a layer of ITO is deposited on the ZnO surface. The ITO layer almost prevent diffusion of atmospheric oxygen to Si wafer which allowing the increase of the intentionally formed SiO_2 interfacial layer.

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