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# Effect of annealing times on electrical properties of ZnO films

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***Abstract*— This work shows how the variation of deposition time allows the control of structural, electrical and optical properties of the Zinc Oxide (ZnO) films. The studied compact films have been fabricated on the flexible plastic substrates (Indium Tin Oxide coated polyethylene naphthalate (ITO/PEN), 15 $sq^{-1}$, Peccel, Japan) by doctor blade technique and are sintered at low temperature 150°C. It is shown that annealed ZnO thin films grow with the hexagonal preferred c-axis perpendicular to the substrate surface with the lattice parameters: a= b = 3.2498Å and c = 5.2066Å. They show more crystallinity order as the time annealing was increased. We have used Pd Phthalocyanine dye as sensitizer of ZnO electrodes. The absorption spectra of the ZnO thin films immersed in Pd Phthalocyanine dye were measured and studied using UV–Vis spectrophotometer in the wavelength range 300–1000 nm. We have studied the electrical properties, using different thermal excitation, of realized films versus annealing temperature times. The activation energies for deposited ZnO thin films annealed at 150°C are found in the range 0.72 meV to 8.68 meV when the times change and correlated to energy gap values showing an n type semiconductor material.**

***Keywords*— *ZnO, flexible plastic substrates, Pd Phthalocyanine, Flexible Dye sensitized solar cell, semiconductor.***

## I. INTRODUCTION

The excessive global use of fossil energy sources with the environmental problems initiated many research approaches geared towards the use of renewable energy. Solar energy presents the ability to meet thus considerations and it is produced by-based semiconductor materials devices that convert light energy into electric current. Flexible dye Sensitized Solar Cells (semiconductor electrode/ electrolyte/ metal counter electrode) present a low cost devices alternative to solid state photovoltaic solar cells. However, to make such cells practically viable for long term practical application, the semiconductor electrode must be optimized. Zinc oxide is a transparent material that has a bandgap of about 3.3 eV [1], which enables to classify among wide bandgap semiconductor. It attracts a lot of research attention due to its high thermal conductivity, high heat capacity, medium dielectric constant, high resistivity and low water absorption, ZnO is a material that can be easily synthesized in a variety of nanostructures [2, 3]. Zinc oxide is transparent in the visible and absorbs ultraviolet radiation below 380 nm. For the production of ZnO films, many efforts have been made, such as doctor blade, chemical spray pyrolysis and pulse laser deposition (PLD), molecular beam epitaxy and sputtering [4-6].

In this study, Structural, optical and electrical properties of ZnO films deposited on ITO/PEN plastic substrates were studied. We have varied annealing time from 2.5 h to 4h at 150°C to investigate the material properties. The determined parameters of ZnO films synthetized with Pd Phtalocyanine were introduced in a developed software program using Matlab to predict the I-V characteristics in DSSC.

## II. STRUCTURE AND PRINCIPLE OF FLEXIBLE DYE SENSITIZED SOLAR CELL

Fig. 1 shows the structure of studied flexible dye sensitized solar cell.

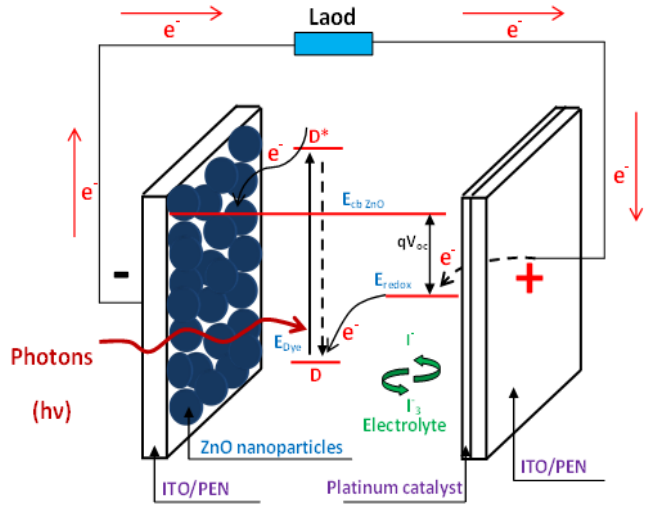


Fig.1: Schematic structure of flexible dye-sensitized solar cell.

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The dye sensitized solar cell is composed of an electrode and a counter electrode (fig.1). The electrode comprises a nano-porous film that is dye-sensitized; it is attached to a conductive plastic substrate (ITO/PEN). The counter electrode is also made of a conductive plastic substrate covered with a layer of platinum catalyst to reduce the charge transfer resistance. The gap between the two electrodes is filled with an electrolyte based on the iodide/tri-iodide redox ions couple ($I^-/I_3$) used to transport electrons from the counter electrode to reduce the oxidized dye molecules.

The dye captures the photons from the sun; it passes in its excited state then transfers an electron to the conduction band of the semiconductor which has the role of transporting electrons to the external circuit. Due to the presence of the redox couple in the electrolyte the excited dye is returned to its ground state. Finally, the iodide is in turn regenerated by the reduction of triiodide to the counter electrode, the electrical circuit being completed by the migration of electrons through an external load. The main processes, of a DSCC are listed below [7]:

$$D + h\nu \rightarrow D^* \quad (1)$$

$$D^* + ZnO \rightarrow D^+ + e_{cb}^-(ZnO) \quad (2a)$$

$$D^* \rightarrow D \quad (2b)$$

$$2D^+ + 3I^- \rightarrow 2D + I_3^- \quad (3a)$$

$$D^+ + e_{cb}^-(ZnO) \rightarrow ZnO \quad (3b)$$

$$I_3^- + 2e^-(catalyst) \rightarrow 3I^- \quad (4a)$$

$$I_3^- + 2e^-(ZnO) \rightarrow 3I^- + ZnO \quad (4b)$$

Where D, D*, and $D^+$ are the energy levels of dye molecules corresponding to ground, excited, and oxidized states, respectively, $h\upsilon$ is the energy of incident photons, and $e_{cb}$ denotes the electrons in the conduction band of semiconductor.

## III. Theoretical Model

When the cell is illuminated from the side of ITO/PEN substrate, the injected electrons from excited dye molecules go to the porous semiconductor (ZnO), and recombine with electrolyte at the ZnO/electrolyte interface. It can be described by the following equations [8]:

$$D.\frac{\partial^2 n(x)}{\partial x} - \frac{n(x)-n_0}{\tau} + \phi.\alpha.\exp(\alpha.x) = 0 \quad (5)$$

Where $n(x)$ is the excess electrons at a position $x$, $n_0$ is the dark electron concentration, $\tau$ is the electrons lifetime in the conduction band, $\phi$ is the incident irradiance, $\alpha$ is the dye absorption coefficient and $D$ is the ZnO layer electron diffusion coefficient.

Recombination rate (R) is given by:

$$R = \frac{n(x) - n_0}{\tau} \quad (6)$$

If both electrodes cell is short-circuited, the current density ($J$) corresponds to the short circuit current density ($Jsc$), then the density of electrons diffused towards the counter electrode is constant. The two boundary conditions are follows:

$$n(x=0) = n_0 \qquad and \qquad \left(dn/dx\right)_{x=d} = 0 \quad (7)$$

Solving equation (5) with the boundary conditions given by equations (7), we can deduce the short-circuit current:

$$J_{sc} = \frac{\Phi.l.\alpha.q}{1-(l.\alpha)^2}.\left[-l.\alpha + \tanh\left(\frac{d}{l}\right) + \frac{l.\alpha.\exp(-d.\alpha)}{\cosh\left(\frac{d}{l}\right)}\right] \quad (8)$$

Where $q$ is the electron charge, $d$ is the photo-active layer thickness (ZnO + dye + electrolyte), and $l$ is the electrons diffusion length, given by:

$$l = \sqrt{D.\tau} \quad (9)$$

The relationship linking the excess photogenerated electron concentration in contact with the back photoelectric voltage is the following:

$$\left|V_{ph}\right| = \frac{k.T}{q}.m.\ln\left(\frac{n_{contact}}{n_0}\right) \quad (10)$$

$m$ is the ideality factor, $k$ is the Boltzmann's constant equal $1.38\times10^{-23}m^2Kgs^{-2}K^{-1}$, $T$ the absolute temperature and $n_{contact}$ is the concentration of photo generated electrons in contact back.

Using equation (10) and the solution of equation (5), we obtain an expression that connects the current density $J$ and the voltage $V$:

$$V = \frac{m.k.T}{q}.\ln\left[1 + \frac{(J_{sc}-J).l}{q.D.n_0.\tanh\left(\frac{d}{l}\right)}\right] \quad (11)$$

From equation (11) the current density J is as follows:

$$J = J_{sc} - \frac{q.D.n_0}{l}.\tanh\left(\frac{d}{l}\right).\left(\exp\left(\frac{q.V}{k.T.m}\right) - 1\right) \quad (12)$$

## IV. Experimental Details

### A. Materials

Indium Tin Oxide coated polyethylene naphthalate (ITO/PEN), 15 sq-1, was obtained from Peccel, Japan; zinc oxide, ZnO (<50 nm particle size (BET), >97%), ethanol, acetone and isopropanol were obtained from Sigma-Aldrich; distilled water. We have used pipets, mortar, pestle, and

tweezers, scotch Magic, hot plate (Stuart). Pd-Phthalocyanine dye.

### *B. Preparation of ZnO thin films*

ZnO electrode has been prepared using a paste containing 3gram of ZnO nanoparticles dispersed in 5ml of mixture solvents of ethanol, isopropanol and distilled water. We grind the zinc oxide paste for 30 min to make a homogeneous paste. We cleaned ITO/PEN plastic substrates with acetone and paper towel, the conductive side of ITO/PEN was identified by using Ohmmeter. The deposition area and the thickness of the ZnO were defined by using scotch Magic tape for four sides. After that, the as prepared paste was deposited on the ITO/PEN substrates by using doctor blading technique. These electrodes were then placed on a hot plate and the temperature was gradually increased to 150 °C, with a time interval of 15 min to remove the binders in the films and solidify ZnO on the plastic substrates. The realized samples were annealed for different times 2.5, 3, 3.5 and 4 h.

### *C. Thin film characterizations*

The crystal structure of ZnO films after annealing process was analyzed using X-ray diffractometer (XRD) method and were performed using X'pert Pro X-ray diffractometer with Cu Kα1 radiation (λ= 0.15406 nm).

The absorption spectra of Pd Phthalocyanine dye diluted in dimethyl formamide (DMF) and the ZnO thin film immersed in dye were measured and studied using UV–Vis spectrophotometer (Beckman DU640) in the wavelength range 300–1000 nm.

The electrical measurements have been carried out as a function of temperature. The electric properties were recorded a Keithley 6517A electrometer, in the temperature range of 300-460 K by introducing the samples in a He closed cycle cryostat and contacting the probes with soft Ag wire in the four point geometry.

## V. RESULTS AND DISCUSSIONS

Fig. 2 shows the crystalline structure and orientation of the deposited ZnO thin films annealed at 150°C for different times 2.5, 3, 3.5 and 4h. In this figure we show a good crystalline quality as indicated by the diffraction line, with a high intensity peaks at 2θ = 32.3°, 2θ = 34.4° and 2θ = 36.5° which are identified are (1 0 0), (0 0 2) and (1 0 1) planes indicate a preferred orientation. These results are in good agreement with JCPDS card no.01-080-0074 and 01-075-1526.

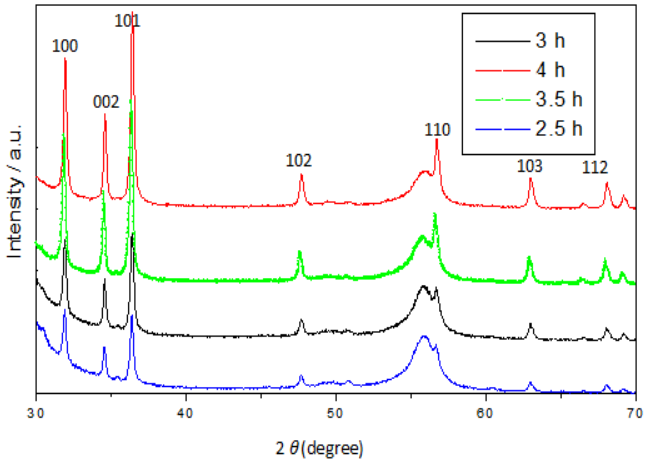


Fig 2: Diffraction pattern for ZnO films obtained on ITO/PEN substrates at150 °C.

It is shown that annealed ZnO thin films grow with the hexagonal preferred c-axis perpendicular to the substrate surface with the lattice parameters: a=b=3.2498Å and c=5.2066Å. We show that the peaks intensity become more significant with increasing annealing times giving the improvement of the crystalline structure.

TABLE I
EVOLUTION OF STRUCTURE PARAMETERS OF ZNO THIN FILMS CALCULATED FROM XRD PATTERNS VERSUS TIME OF ANNEALING.

| Ann. Time | 2θ (°) | D (n ) |
|---|---|---|
| 2.5 h | 34.42 | 42 |
| 3 h | 34.43 | 44 |
| 3.5 h | 34.45 | 44.7 |
| 4 h | 34.45 | 48.6 |

According to Sherrer equation in DRX and crystallography [14], the average crystallite sizes D, are indicated in Table 1 and deduced from eq. 13.

$$D = \frac{K.\lambda}{\beta.\cos\theta} \qquad (13)$$

Where k = 0.9, λ= 0.15406 nm is the wavelength of Cu(Ka) radiation, θ is the Bragg angle of the X-ray diffraction peak and β represents the corrected experimental full-width at half-maximum of the diffraction peak in units of radians. The calculated nano crystallite sizes were found to be in the range of 42 nm – 48.6 nm. The profile of the diffraction line for the ZnO thin films is well approximated by a Gaussian distribution.

Fig. 3 shows the absorption spectrum of pure ZnO and dyed ZnO measured using UV–Vis spectrophotometer.

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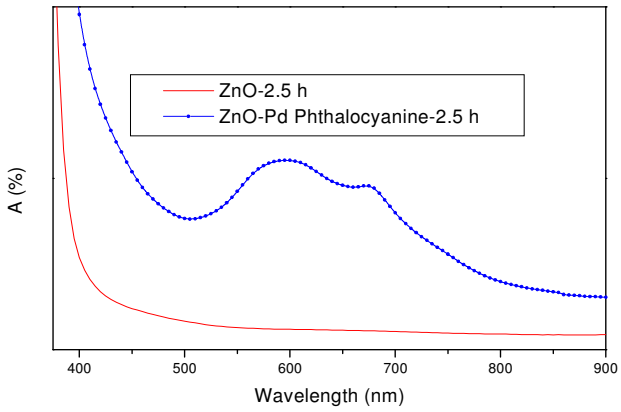


Fig.3: Absorption spectra UV -Vis of pure and dyed ZnO annealed at 150°C.

We note that the pure ZnO does not absorb above 380 nm. There for making a good solar cell photo anode material, the zing oxide need a photosensitizer which should be able to harvest the sunlight and transfer it into electrical energy by absorbing the visible light spectrum from red to blue so that it can sensitize the wide band gap of the semiconductor. From these curves we observed two peaks, one in the green close to 580 nm and the second in the red close to 675 nm. The absorption spectrum of the dyed ZnO revealed the improvement of the light photon absorption and the extension of the absorption edge which is shifted to the higher energy compared to the pure ZnO. This late can be interpreted by that these dye molecules are strongly adsorbed to the zinc oxide surface which leads to the improvement of the absorption.

The value of the energy gap of the studied pure ZnO is determined from the absorption curve as a function of energy; it was be found as 3.26 eV.

Fig.4 shows a semiconducting temperature dependence of the electrical conductivity σ, for deposited ZnO thin films annealed at 150°C for different times 2.5, 3, 3.5 and 4 h. The electrical conductivity of the ZnO thin films can be analyzed by the Arrhenius relation [9].

$$\sigma = \sigma_0 \exp\left(\frac{-Ea}{K.T}\right) \qquad (14)$$

Where $\sigma_0$ is a pre-exponential factor, *Ea* is the activation energy for electrical conductivity.

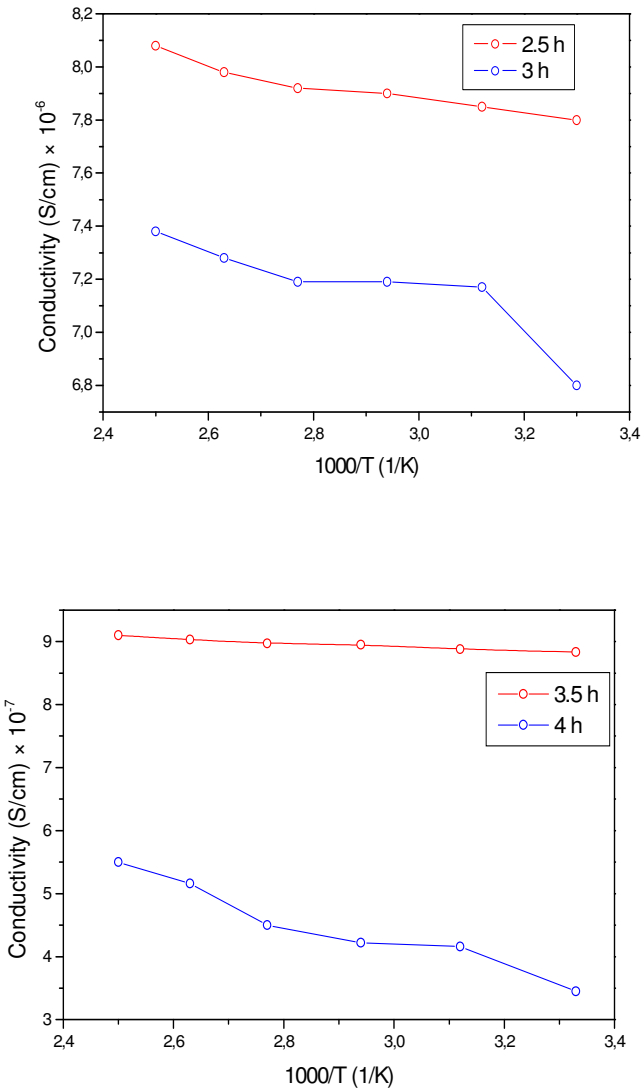


Fig.4: Plot of conductivity vs 1000/T of ZnO thin films at different annealing times

From these figure we can observe that the electrical conductivity decreases with increasing annealing times, this can be attributed to the improved crystallinity leading to reduction in the traps or reduction in the size of the crystallites in the films. The electrical conductivity is affected by grain boundary scattering [10]. This grain boundaries act as traps which capture electrons and lead to the formation of a potential barrier. Also we show that the electrical conductivity decreases with increase of temperature. The calculated activation energies for deposited ZnO thin films annealed at 150°C are found in the range 0.72 meV to 8.68 meV when the times change and correlated to energy gap values showing an n type semiconductor material. The same observation was mentioned by M. Assiri et al. [11].

TABLE II

DETERMINED PARAMETERS OF ZNO FILM USED IN THE SIMULATION.

| Material parameters | Value |
|---|---|
| $l$ ($cm^{-1}$ $s^{-1}$) | $4.12*10^{-3}$ |
| α ($cm^{-1}$) | 5000 |
| m | 2.68 [12] |
| D ($cm^{-2}$ $s^{-1}$) | $1.7*10^{-4}$ [13] |
| $n_0$ | $10^{17}$ [14] |
| τ (ps) | 1 [15] |
| T(K) | 300 [16] |
| d (µm) | 15 |

In order to tune the effect of ZnO immersed in the dye, we have used a simulation taking into account the parameters given in table 2. We have optimized the deposit conditions to have good properties of the film immersed in the dye. From the obtained results we observed that the film sintered at 150°C for 2.5 h gives the best conductivity. Using equation (11) and equation (12), we obtain a short circuit current value in order of 16 mA $cm^{-2}$. Fig. 5 shows the J-V characteristics simulated using experimental parameters.

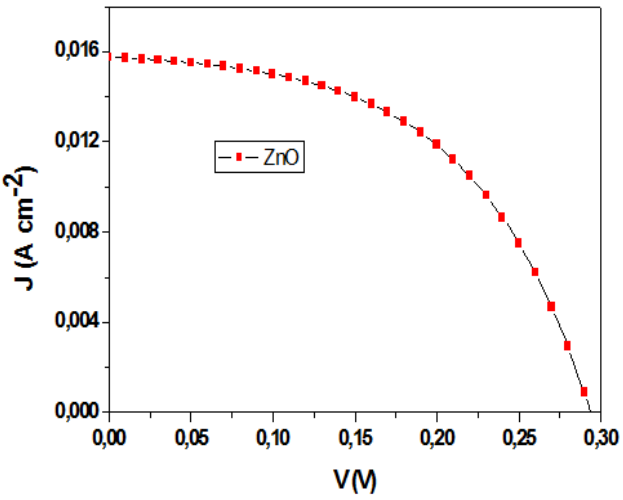


Fig. 5: Simulated J-V characteristics.

## VI. CONCLUSIONS

Structural, optical and electrical properties of ZnO films deposited on ITO/PEN plastic substrates were studied. To investigate the material properties, we have varied deposition time by using annealing temperature of 150°C. We notice that annealed ZnO thin films grow with the hexagonal preferred c-axis perpendicular to the substrate surface with the lattice parameters: a=b = 3.2498Å and c = 5.2066Å. We show that the peaks intensity become more significant with increasing annealing times giving the improvement of the crystalline structure. We observed that the electrical conductivity decreases with increasing annealing times. The activation energies for deposited ZnO thin films annealed at 150°C are found in the range 0.72 meV to 8.68 meV when the times change. The obtained results show that the film sintered at 150°C for 2.5 h gives the best conductivity. From simulation using developed equations in the case of DSSC, we obtain a short circuit current value of 16 mA $cm^{-2}$.

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