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# Evaluation of Structural and Optical parameters of spray deposited ZnO thin films for Dye-Sensitized Solar Cell Application

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**ABSTRACT**

ZnO films are prepared on glass plates with concentrations of 0.025 M, 0.05 M and 0.1 M each consisting of 50 ml of solution using the spray pyrolysis technique. A dye sensitized solar cell (DSSC) is constructed by means of the obtained film for 0.1 M which is also coated above the ITO substrate. N-719, iodide and platinum coated ITO glass plates are used as the dye, electrolyte and counter electrode respectively. XRD confirms that the structure of the film is polycrystalline having wurtzite structure. The surface with pores is found from the SEM studies. The optical transmittance is about 75% in the visible region. Cyclic voltammetry analysis is measured for the evaluation of the mechanism of charge transfer.

**KEY WORDS:** Zinc Oxide, Spray pyrolysis, thin film, DSSC, Dye-Sensitized Solar Cell.

## 1. INTRODUCTION

Dye sensitization of metal-oxide wide-band-gap semiconductors (TiO2, ZnO, SnO2, etc.) has gained attraction for solar cell applications. Significant advancement has been made by the work of Regan (1991). Dye-sensitized solar cells (DSSCs) are an attractive solar cell option because of their relatively low manufacturing costs and simple process technology. Recently, ZnO semiconductors were also used as photo electrode in DSSCs. This is due to its band gap, electron affinity, and electron injection efficiency which are nearly the same as those of TiO2. It is cheap, abundant, chemically stable and non-toxic. ZnO is an n-type semiconductor that displays a hexagonal crystalline wurtzite-type structure, with lattice parameters a=b=0.3250 nm and c=0.5207 nm, a direct wide band gap of 3.3 eV giving high optical transparency at room temperature, a large free exciton binding energy (60 meV), a wide range of resistivity (10−4–1012 Ω.cm) and a high electron Hall mobility (200 cm2 V−1.S−1). Besides the attractive electrical properties, ZnO is a material that can be easily synthesized in a variety of nanostructures, thus allowing for optimization of the nanomaterials' properties for application in the DSSC. Numerous trials have been devoted to regulating the shape and size of ZnO nanomaterials in order to obtain high surface area that can strengthen the absorptive amount of dye molecules and improve the properties of DSSCs based on ZnO electrode. However, it should be noted that the highest conversion efficiency of ZnO-based DSSCs is achieved by ZnO nanoparticles. Much effort has been made to control the size and shape of ZnO nanomaterials. ZnO nanostructures with different morphologies have been prepared by different physical, chemical and electrochemical methods.

In this study, ZnO thin films of 0.025 M, 0.05 M and 0.1 M are prepared using the spray pyrolysis technique. The structural, morphological and optical properties are studied. Also the solution of 0.1 M is deposited above the Indium Tin Oxide (ITO) coated glass substrate as the photo anode. N-719 and platinum coated ITO substrates are chosen as the photo sensitizer and counter electrode respectively which can be utilized for the fabrication of a dye-sensitized solar cell. An electrochemical method namely cyclic voltammetry analysis is measured for the evaluation of the mechanism of charge transfer.

## 2. EXPERIMENTAL DETAILS

The dye-sensitized solar cell consists of an Indium Tin Oxide coated glass plate. The ZnO thin film is deposited above the ITO glass plate. The obtained film is immersed in the dye solution and then sandwiched with the platinum coated ITO glass plate. The intermediate space is filled with the electrolyte. The two ITO glass plates are connected by means of an external load.

The prepared photo anode film is studied by X-ray diffraction (XRD) using a D/max-2400 X-ray diffraction spectrometer (Rigaku) with the radiation of Cu Kα which is operated at 40 kV and 100 mA from 20 to70º, and the speed of scanning is 15º min−1 at a step of 0.02º in order to confirm the structure. The morphology of the surface and the size of the particles of the ZnO films are determined using scanning electron microscopy (SEM, JOEL 6320 F). A UV-Vis spectrophotometer (Jasco-V-570) is used for measuring the absorbance and transmittance of the cell. Voltammetric experiments are performed with the electrochemical workstation CV-50W Voltammetric Analyzer (BASi or Bioanalytical Systems, Inc.), which is connected to an external desktop computer.

## 3. RESULTS AND DISCUSSION

**3.1. Structural Analysis:** The X-ray diffraction analysis observed is shown in Fig.1.and is used to determine the phase of the crystal and size of the nanocrystalline material. The peak obtained is (101); this confirms that the film is polycrystalline in nature with hexagonal wurtzite structure. No other characteristic peaks of other impurities are observed in the XRD pattern and confirm the formation of single phase of ZnO with JCPDS Card no.36-1451. The

grains are perpendicular to the glass substrate situated in the c-axis. The size of the crystallite is calculated using the Scherrer equation,

$$D=0.9\,\lambda/\beta\cos\theta \quad (1)$$

Where D, the crystallite size, β, the broadening of the diffraction line measured at half of its maximum intensity (rad.) FWHM and λ, the X-ray wavelength (1.5406 Å) which is consistent with the SEM image.

Dislocation density and number of crystallites per unit area (N) are calculated using the crystallite size and thickness of the film.

$$\text{Dislocation density} = 1/D2 \quad (2)$$

$$\text{Number of crystallites per unit area (N)} = t/D3 \quad (3)$$

The c-axis strain (εzz) values are calculated by using the following formula

$$\varepsilon\_zz=(C-C\_o)/C\_o \times 100\% \quad (4)$$

For hexagonal crystals, the stress, σ film, in the plane of the film can be calculated by using the biaxial strain model observed in Eq. (4).

$$\sigma\_film = (\ 〖2C〗\ \_13\text{^}2 - C\_(33)\ 〖(C〗\ \_(11) + C\_(12)\ ))/\ 〖2C〗\ \_13\ .\varepsilon\_zz \quad (5)$$

Where εzz is construed as the average uniform lattice strain along the c-axis and Cij represents the elastic stiffness constants (C11=208.8 GPa, C33=213.8 GPa, C12=119.7 GPa and C13=104.2 GPa). This equation yields the following numerical relations for stress, XRD film= −233εzz (GPa).

The total stress in the film commonly consists of two components. One is the intrinsic stress may be arise due to impurities, defects and lattice distortions in the crystal, and the other is the extrinsic stress arise due to the lattice mismatch and thermal expansion coefficient mismatch between the substrate and film. The extrinsic stress in thin films normally relaxes if the thickness of the film is larger. In the present case, thickness of all the films is above 100 nm.

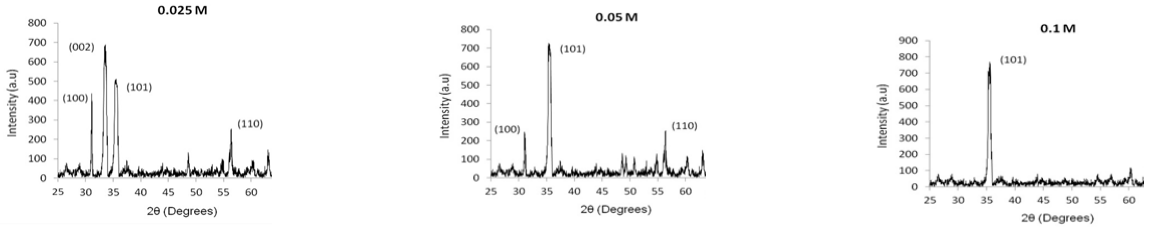


**Fig.1.X-ray diffraction spectra of ZnO thin films for different precursor salt concentrations**

**Table.1.Structural parameters of ZnO thin films deposited for different concentrations**

| Concentrations Mol/Litre | D (nm) | Dislocation intensity $1/D^2$ | Number of grains/ unit area | Strain $\varepsilon_{zz}$ | Stress (GPa) |
|---|---|---|---|---|---|
| 0.025 | 36.7 | 0.742 | 0.142 | -0.0903 | 0.2101 |
| 0.05 | 45.6 | 0.479 | 0.738 | -0.0903 | 0.2101 |
| 0.1 | 34.1 | 0.857 | 0.177 | -0.0903 | 0.2102 |

**3.2. SEM Analysis:** The ZnO thin film is studied for morphology of the surface as shown in Fig.2. The surface is smooth consists of discrete and closely packed particles that cover uniformly all over the surface exactly with good adherence with more pores.

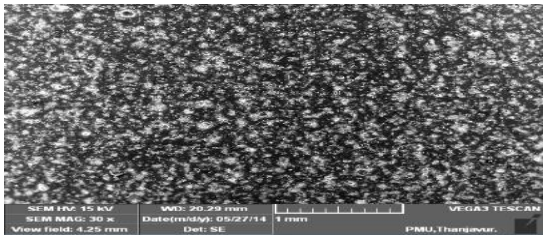

**Fig.2.SEM image of ZnO thin film obtained for 0.1 M of precursor salt concentration**

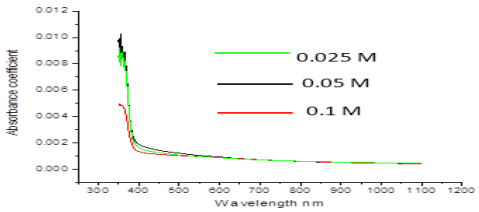


**Fig.3a.Variation of absorbance coefficient Vs wavelength for various concentrations**

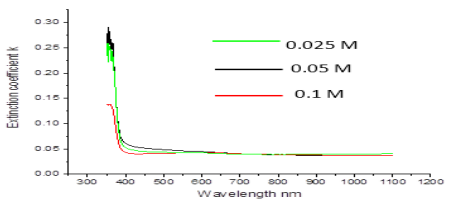


**Fig.3b. Extinction coefficient Vs wavelength for various concentrations**

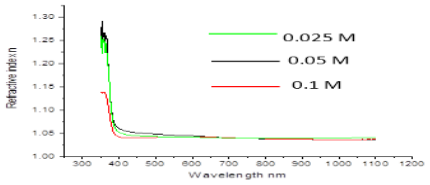


**Fig.3c.The variation of n Vs wavelength for various concentrations**

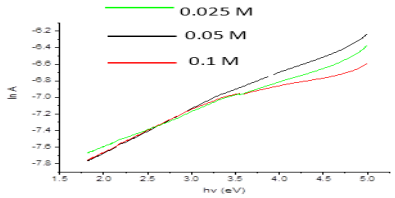


**Fig.3d.Plot of ln A Vs photon energy for various concentrations**

**Table.2.Optical parameters of ZnO thin films deposited for different concentrations**

| Concentration Mol/Litre | Band gap eV | Urbach energy eV | Extinction coefficient k | Refractive index n |
|---|---|---|---|---|
| 0.025 M | 3.28 | 0.84 | 0.041 | 1.0415 |
| 0.05 M | 3.25 | 0.62 | 0.043 | 1.0434 |
| 0.1 M | 3.2 | 0.60 | 0.048 | 1.0486 |

**3.3. Cyclic Voltammetry analysis:** Cyclic voltammetry is a method for investigating the electrochemical behaviour of a system. In this technique current flowing between the electrode of interest (whose potential is monitored with respect to a reference electrode) and a counter electrode is measured under the control of a potentiostat. The voltammogram determines the potentials at which different electrochemical processes occur. The working electrode is subjected to a triangular potential sweep, whereby the potential rises from a start value $E_i$ to a final value $E_f$ then returns back to the start potential at a constant potential sweep rate. The sweep rate applied can vary from a few millivolts per second to a hundred volts per second. The current measured during this process is often normalised to the electrode surface area and referred to as the current density. The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material. Cyclic voltammetry makes possible the elucidation of the kinetics of electrochemical reactions taking place at electrode surfaces. In a typical voltammogram, there can be several peaks. From the sweep-rate dependence of the peak amplitudes, widths and potentials of the peaks observed in the voltammogram, it is possible to investigate the role of adsorption, diffusion, and coupled homogeneous chemical reaction mechanisms.

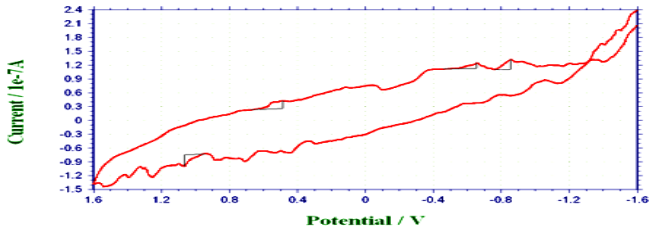


**Figure.4. Voltammogram**

## 4. CONCLUSION

ZnO thin films of various concentrations are prepared using the spray pyrolysis technique. The solution of 0.1 M is also deposited above the ITO substrate. It is sandwiched with the platinum coated ITO substrate. The intermediate space is filled with the iodide electrolyte. The terminals are taken from the two ITO coated glass substrates through the external load. The surface consists of discrete and closely packed particles for good absorption of dye. The absorption spectrum confirms that, for efficient injection of electron, the dye is exactly anchored to the surface of ZnO. Various parameters are calculated from structural and optical studies for each concentration. The mechanism of charge transfer is studied using cyclic voltammetry analysis.

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