INVESTIGATION OF ZnO/ITO THIN FILMS ON STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES

Saw Shine Ko[1], Thida Win[2], Than Than Win[3] and Yin Maung Maung[4]

Abstract

The investigations of structural, optical and electrical properties of ZnO/ITO thin films have been presented. The ZnO nanocrystalline thin films were prepared by Chemical Bath Deposition method. Zinc chloride and sodium hydroxide (NaOH) were used as precursor materials. Thin films of ZnO were deposited onto ITO (indium tin oxide) substrate post annealed temperature at 300°C, 400°C in the muffle furnance. X-ray diffraction (XRD) of the ZnO films showed hexagonal structure. Debye Scherrer equation was used to calculate crystallite size. Scanning electron microscopy (SEM) study provides better topographic feature of the sample surface. The optical band gap was analyzed by absorption spectra of ZnO.$1/C^2$ – V properties of ZnO thin films were determined from C-V measurement. The photovoltaic properties of these films were investigated by current density-voltage characteristic. The photoconversion efficiency was influenced by the open-circuit voltage.

Keywords: *X-ray diffraction, Scanning electron microscopy, Optical band gap, photo conversion efficiency*

Introduction

A solar cell (also called a photovoltaic cell) is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect. It is a form of photoelectric cell (in that its electrical characteristics e.g. curent, voltage, or resistance vary when light is incident upon it) which, when exposed to light, can generate and support an electric current without being attached to any external voltage source. By the basic nature of photovoltaic phenomena ,it follows that a photovoltaic devices should essentially be comprised of the absorbed layer and the window (buffer layer).In selecting suitable absorber materials, there are three important materials parameters need to be considered, band gap, absorption coefficient and minority carrier

1. PhD Candidate, Physics Department, University of Yangon
2. Physics Department, Mandalay University of Distance Education
3. Physics Department, Mandalay University

diffusion length. Solar cell devices can be divided into three major categories: silicon solar cells, inorganic compound semiconductor solar cells and organic solar cells.

At present, crystalline silicon solar cells have high photovoltaic conversion efficiency, but production cost is high. For amorphous silicon solar cells, the production cost can be significantly reduced, but the main problem is that the photovoltaic conversion efficiency is low. Organic solar cells in general have a severe problem of poor stability. As an alternative, a compound semiconductor solar cells are considered to increase the conversion efficiency and effectively reduce production cost. Chemical Bath Deposition technology is based on slow controlled precipitation of the desired compound from its ions in a reaction bath solution. A ligand or complexion agent acting as a catalysts is usually employed to control the reaction in a suitable medium as indicated by the pH to obtain crystal growth. Otherwise, spontaneous reaction and sedimentation of materials will be obtained. The key point of CBD technique are low cost, large area and relatively low deposition temperature. Accordingly, CBD technique is becoming an important deposition technique for thin film of compound materials like chalcogenides, oxides and halides. However, CBD has some drawbacks in the classical beaker configuration, the material yield for film formation is very low, about a few percent, leading to an un-necessary waste production and increased treatment costs. The reason is that the volume to surface ratio is very high and that only a small part of the solution is contributing to the film formation, the remaining one leading to the formation of colloids in the bulk of the solutions. Also, it suffers from the formation of particles that leads not only to the generation of a lot of waste but also the creation of defects in the deposition film. [Danaher W.J and Lyons L.E ,1978] and [Basol B.M,1984] . Metal oxide semiconductor thin film have been widely researched and have received considerable attention in recent years due to their optical and electrical properties. Because they are good for transparent conducting oxide (TCO) films [Hongxia,2005]. Zinc oxide is a wide band gap (~3.37eV at T=300K) semiconductor (II-VI) which has been widely investigated in the past years for more literature. ZnO also has a high exciton binding energy of 60meV which is higher than the value of other used band gap materials [Zahedi and Darini ,2012]. ZnO increasingly attracted attention due to its excellent chemical stability, non-toxity, good electrical, optical and piezoelectric property. Since, the propeties of ZnO strongly depend on its morphology and microstructure, ZnO thin film have been studied as the active channel materials in thin film transistors development because of its exhibiting n-type semiconductor characteristic and excellent thermal stability and can be well oriented crystalline on various substrates. [Masuda,2003] and [Ramamoorthy K , 2004].Zinc oxide has one of the most promising materials and has a lot of research in terest due to the irunique structure and crystallite size dependent electrical, optical and mechanical properties. ZnO nanostructure were studied extensively owing to their potential applications in nano-devices and optical materials. Different technique to synthesized nano and micro range phosphor such as Spray pyrolysis, plasma enhanced chemical vapour deposition, sol-gel, sputtering, pyrolysis, solid state reaction, co-precipitation and combustion which have been. used. In recent time, much interest has been generated around the chemical route technique. This technique is cost, effective , reproducible and the material are ready available material. As compared to other oxide material ZnO is much cheap and easily available materials. Another advantages of the CBD method over other method is that the film can be deposited at different shapes and size of substrates [Vijayan .T.A, 2008] and [Widoyastuti W,2014]. ITO films have been widely used as Transparent conductive oxide (TCO) in electronic and optoelectronic devices. (such as flat panel solar cells). A series of ITO films are mostly deposited on P-type silicon or glass substrates at room temperature. The carrier concentration in the indium tin oxide film increases, the conductivity of the ITO film will be improved distinctly. In ITO films, the doped tin oxide SnO_2 ions in the ITO films diffuse from grain boundaries and intestinal position into the substitutional position of indium site and the four valence Sn ion is activated and contributes free carriers. ITO film deposited onto the silicon or glass substrate can be used as the antireflection layer. [GAO Mei-Zhen et al.,2008].

Experimental

Film deposition

5.5g of Zinc chloride is dissolved in 100 ml of distilled water. It is stirred continuously with magnetic stirrer and its temperature is raised to 63.8ºC. Once the temperature of zinc chloride solution is reached 63.8ºC, add 5g of NaOH dissolved in 25ml deionized water solution poured drop by drop touching the walls of the container by using burrete. The aqueous solution turned into a milky white colloid without any precipitation. The reaction was allowed to proceed for two hours after complete addition of sodium hydroxide. After the complete reaction, the Indium Tin Oxide (ITO) glass substrate was immersed vertically at the center of reaction bath solution in such a way that it should not touch the walls of the container. Triethanolamine (TEA) 8ml was used drop by drop either directly or as aqueous solution with varying concentration of TEA to prepare various samples. The deposited layer were post annealed or heated inserted into evaporate solvent and organic residuals. The annealing temperature used in this research were 300ºC and 400ºC respectively.

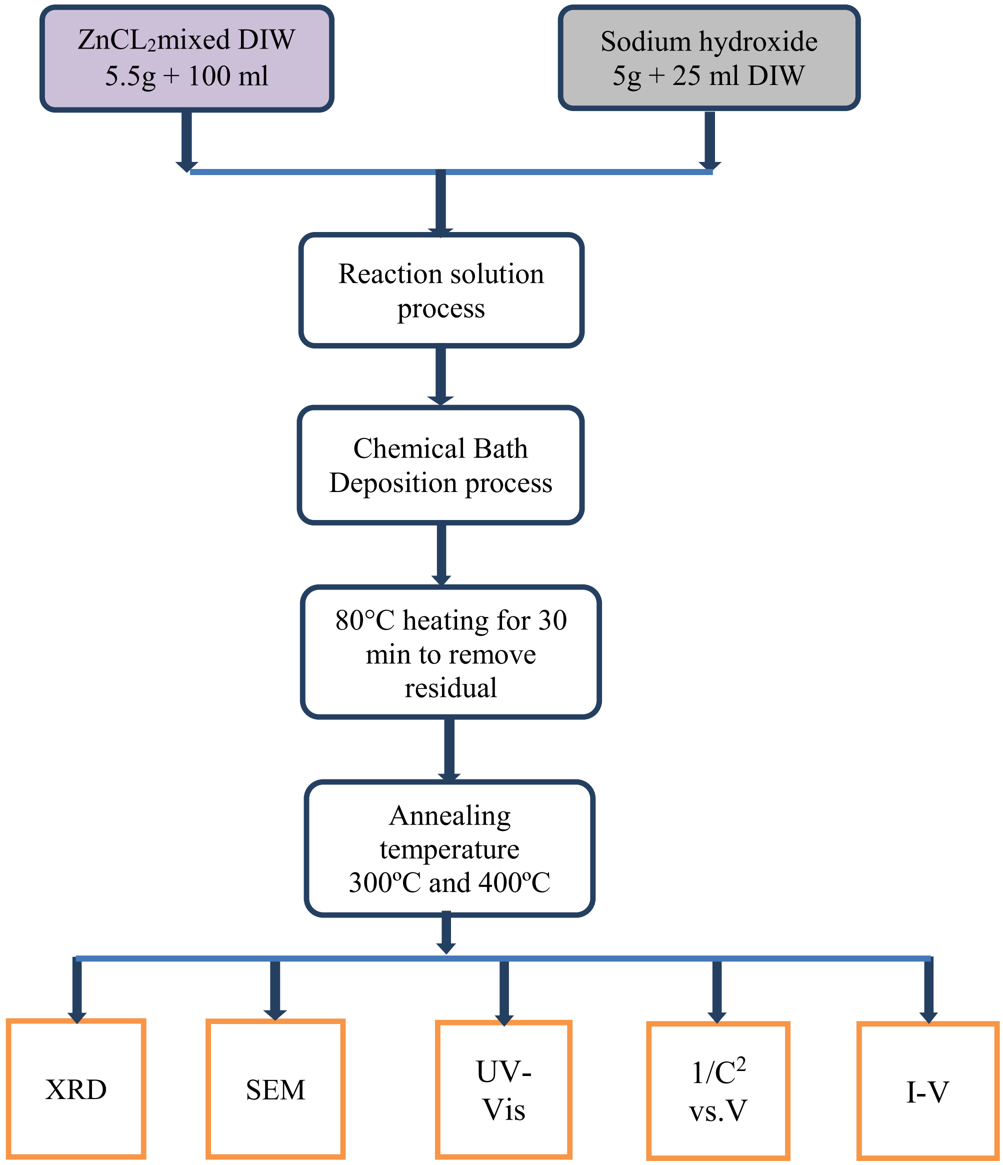


Figure 1. Flow chart of preparation for ZnO/ ITO thin film on ITO glass substrate by using Chemical Bath deposition at various annealing temperature.

Result and Discussion

Structural properties of ZnO/ITO thin film by XRD

To examine the crystal structure and phase formation of ZnO/ITO thin films, they were performed using monochromatic CuKα radiation (λ= 1.54056 Å) operated at tube voltage 40kV and 40 mA (tube current). The X-ray diffraction patterns for zinc oxide thin films were shown in Fig 2(a). The upper side of XRD profile was represented the observed profile while the lower side showed the standard JCPDS (Joint Committee on Powder Diffraction Standards). From the Fig 2(a), three of nine diffracted peaks between 30° and 40° angle were perfectly matched with those of ZnO standard. On the XRD parttern from Fig 2(b), three distinct were formed on observed spectrum. Three of eight diffracted peaks were perfectly matched with those of Zinc oxide standard. According to the XRD pattern from Fig 2(a), the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) peaks and from Fig 2(b), (1 0 0), (0 0 2)and (1 0 1) peaks were clearly observed. They were compared the data with library or standard file. The most dominant peak was also occur at (1 0 1) for both 300°C and 400°C thin films. On the other hand, Table (1) and (2) were also indicated the value of lattice distortion for ZnO/ITO films. Bragg's angle (2θ), interplaner spacing (d-values) and crystallite size of ZnO/ITO thin films. The crystallinity of the ZnO/ITO films determined from the full width half maximumvalues.

$$D = \frac{k\lambda}{\beta cos\theta} \quad \text{----------------------(1)}$$

Where D is the size of the crystallites, β is the full width at half maximum (FWHM) of a diffraction line located at angle θ, λ is the X-ray wavelength and k is a Scherrer's constant (0.9), which depends on the peak breadth, crystallite shape, and crystallite size distribution. The crystallite sizes were found to be increasing with increasing temperature because of the crystallite size for 300°C and 400°C ZnO/ITO thin films were found to be 28nm and 36.904nm. Improved in crystallinity quality with raising annealing temperature. As a result, oxygen defects are favorable to the merging process to form larger grains size while increasing the annealing temperature.

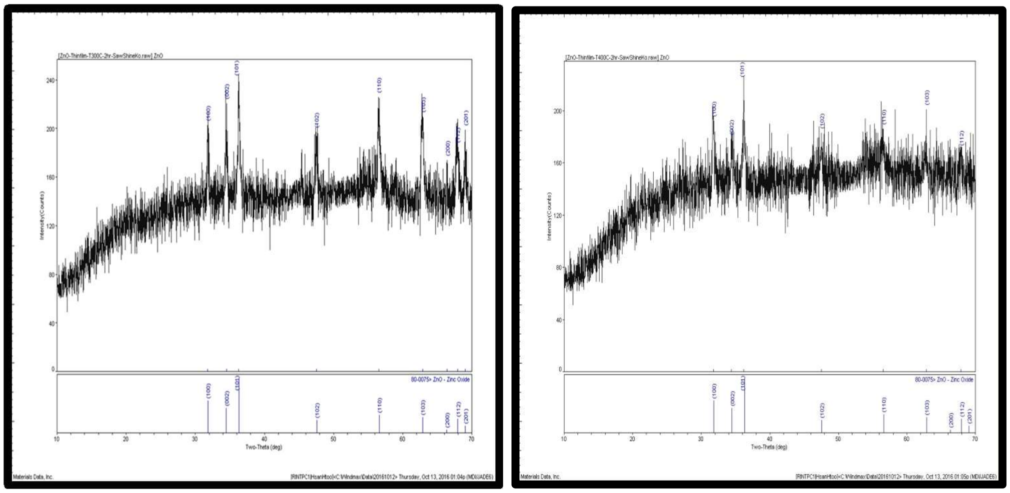


Figure 2(a) and 2(b) XRD patterns of annealed and reference JCPDS file of ZnO/ITO film annealed at 300ºC and 400ºC

Table 1. The values of lattice distortion for ZnO/ITO thin films

ZnO/ITO	**Annealing temperature** (℃)	**Lattice constant**		**Hexagonality (c/a)**
		a (A)	**c (A)**	
(1 0 1) peak	300	3.2483	5.2108	1.6042
(1 0 1) peak	400	3.2560	5.1963	1.5959

Table 2. Diffraction angle, interplaner spacing and crystallite size for (1 0 1) plane of ZnO/ITO films

ZnO/ITO	**Crystallite size (nm) along diffraction planes**		
	2θ(rad)	**d(A)**	**Crystallite size (nm)**
(1 0 1)peak	36.260	2.4754	28
(1 0 1)peak	36.215	2.4784	36.904

Morphology and phaseanalysis

The microstructural properties of Zinc oxide thin films deposited onto ITO glass substrate were observed by SEM analysis. The width of the nanorods were measured by using well known bar code system. Bar code size was formed to be 2μm with magnification of 13000. SEM images of Zinc oxide thin films on the ITO glass substrate revealed rod shape distribution some portion of the surface of the substrate .Fig 3(a) showed the SEM image of ZnO film at temperature 300°C and Fig 3(b) provided the rod shape structure on their film. The average width of nanorods would be measured by the bar code system and its width were 105.44 nm for 300°C and 107.11nm for400°C.

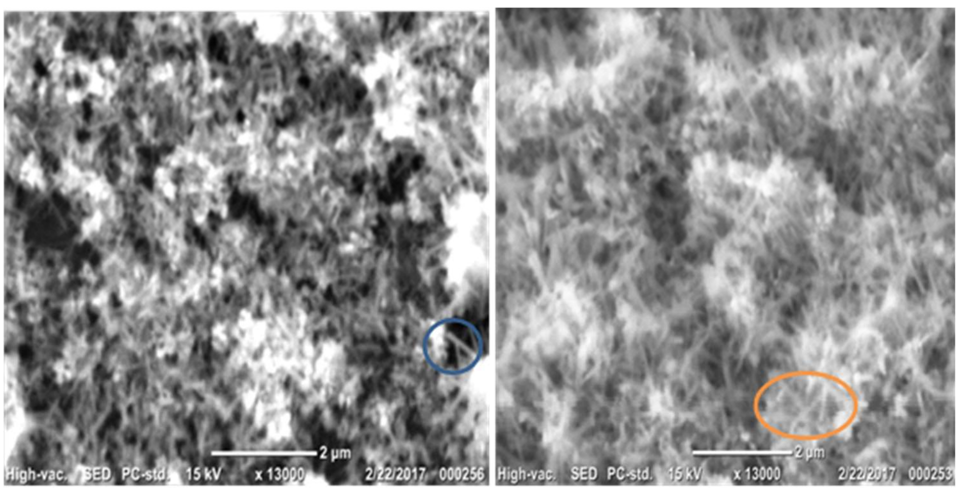


Figure 3(a) and 3(b) showed the SEM photograph of the ZnO/ITO thin film annealed at 300ºC and 400ºC

Optical Properties

UV-VIS analysis

The preparation of ZnO/ITO film, ZnO/ITO films were characterized by UV absorbance spectra. The optical properties of ZnO/ITO film are determined from absorbance measurement in the range of 300nm to 800nm for annealing temperature 300C and range 280nm to 800nm for annealing temperature 400C respectively. The maximum absorbance edge was found at 364.5nm for ZnO/ITO films for 300C and 369nm for 400C annealing temperature. The absorption spectra of ZnO/ITO was shown in figure 4(a). From the dependence of the absorption band edge on wavelength, the energy gap of the material can be determined. When the energy of the incident photon is greater than that of the band gap ($h\upsilon > E_g$) the absorption coefficient 'α ' is given by

$$\alpha h\mu = A(h\mu - Eg)^{1/2} \text{----------} (1)$$

From the curve $\alpha h\upsilon^2$ versus hυ, the band gap was identified by extrapolating the linear region of the curve to the energy axis. The energy band gap value of ZnO/ITO film were measured in figure 4(b). In these results, the band gap value of ZnO/ITO film were examined to be 3.66eV and 3.3408 eV for annealing temperature 300ºC and400ºC.

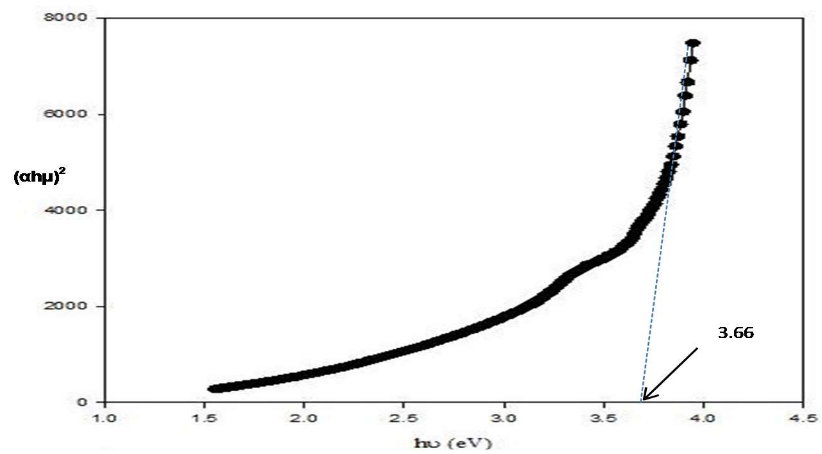


Figure 4(b) Plot of $(\alpha h\mu)^2$versus photon energy of ZnO/ITO thin film annealed at 300°C

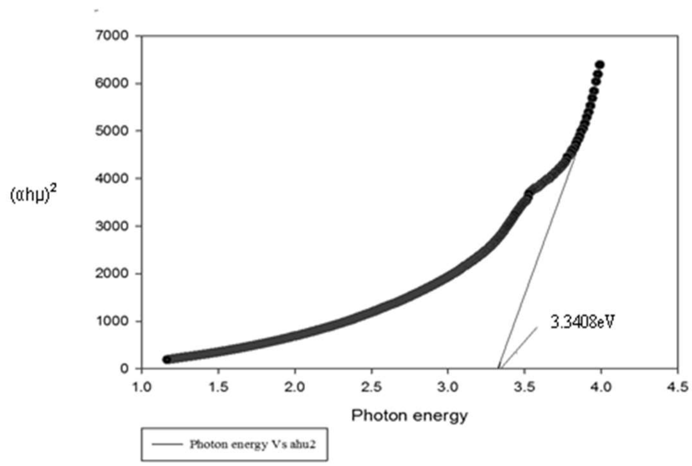


Figure 4(b) Plot of $(\alpha h\mu)^2$versus photon energy of ZnO/ITO thin film annealed at 400°C

Table 3. Optical band gap (Eg) values for ZnO/ITO thin film

ZnO/ITO thin films	**Energy band gap (Eg)**	
Annealed at 300°C	3.66 eV	
Annealed at 400°C	3.3408eV	
Reference (Sandeepsanjeev and Dhananjaya ., 2015	300ºC	3.22eV
	400ºC	3.16eV

lower band gap of the oxide film annealed at 400 °C may indicate better oxidation since the band gap of bulk ZnO was reported to be ~ 3.37 eV. Moreover, the ZnO/ITO films showed another lower The energy band gap of 3.3408 eV. This lower energy band gap may be due to absorption involving defect states.

Electrical Properties

C-V analysis

In order to examine for more details in electrical behaviors' of ZnO/ ITO films, C^{-2}-V analysis was also studied in this work. The capacitance-voltage (C-V) measurement of ZnO/ITO glass substrate thin film was accomplished at 50KHz, in the "dc" bias voltage from-5V to +5V.The rate was set 0.5V for all cases. Measurements were performed at room temperature and the quantities of Schottky's contact were estimated from the analysis of the experimental results. Reverse C-V characteristics exhibited a linear $1/C^2$ versus V plot. The slope calculation of C^{-2}-V representations provided to determine the dopant concentrations. The values of build in potential (V_{bi}), acceptor concentration (N_a), donor concentration (N_d)and depletion layer width (W) of Zinc oxide deposited ITO glass substrate films were calculated and summarized. Table 5,$1/C^{-2}$ vs V showed increasing annealing temperature decreasing built in potential. In some references, the induced built in potential reduces the recombination. The $1/C^2$ vs. V intercept is shown to decrease with increase in annealing temperature.

Table 3. $1/C^2$-V analysis data of ZnO/ITO thin film deposited by Chemical Bath deposition technique

Annealing temperature(°C)	Build in Potential V_{bi}(eV)	acceptor concentration N_a(cm^{-3})	Depletion width W(cm)
300°C	0.3950	1.63E+30	8.131E-11
400°C	0.3250	1.47E+30	8.148E-11

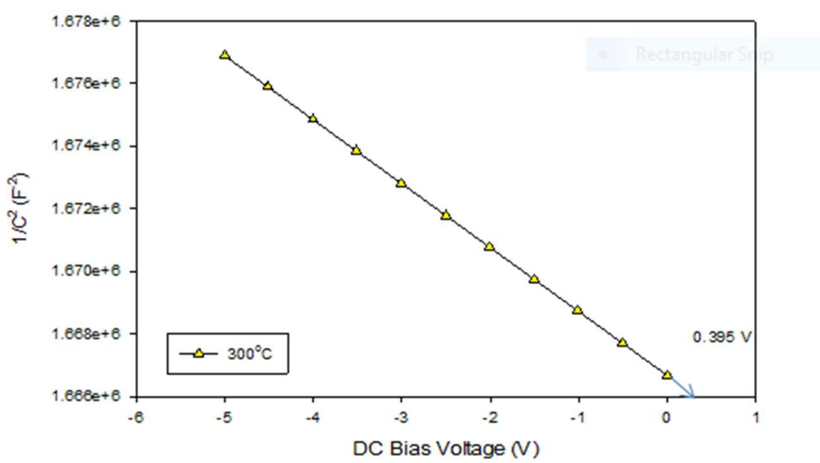


Figure.5(a).$1/C^2$vs V characteristic of ZnO/ITO thin film annealed at 300°C

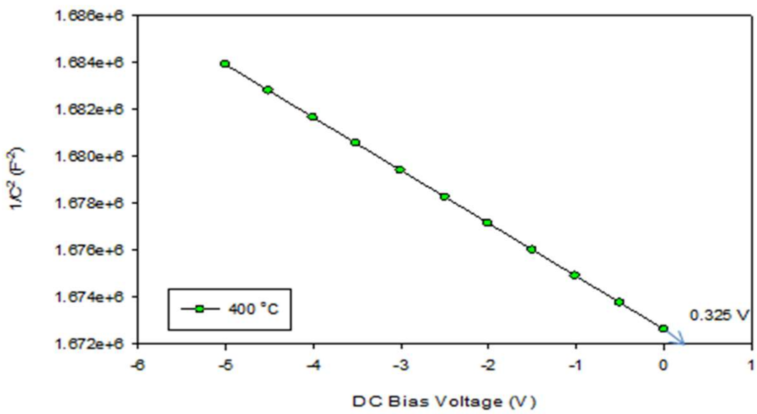
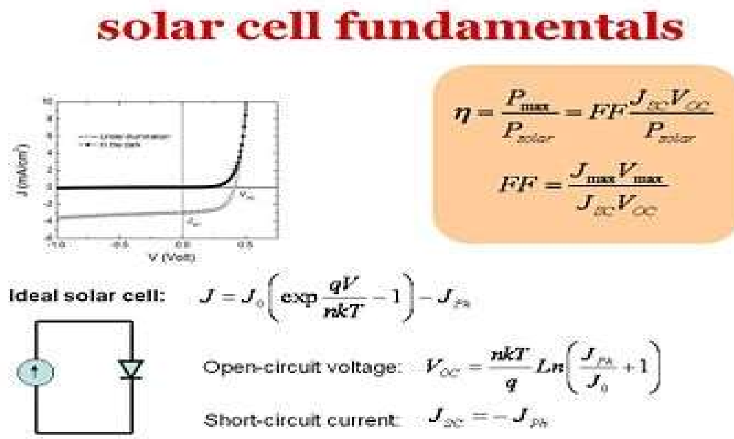


Figure 5(b). $1/C^2$ vs V characteristic of ZnO/ITO thin film annealed at 400°C

Electrical and Phovoltaic properties

Figure 6(a-d) represents the current –voltage (I-V) curve of ZnO/ ITO film solar cell under dark and illumination conditions in the forward and reverse directions with different annealing temperature (300ºC and 400ºC) respectively. Good rectifying and photovoltaic properties were noticed for this device. It is observed that the ZnO/ITO thin film solar cell device display a great photovoltaic effect and rectifying behavior. The photocurrent caused by 200mW/cm^2 halogen lamp is clearly much greater than dark current. For the (I-V) curve in dark, the current values increases 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 value of ideality factor of the ZnO/ITO thin film solar cell is gained from the slope of straight line region of the forward bias log I-V characteristics for dark curve. Calculation of the ideality factor, barrier height is shown in Table (4.a.). One can see that the ideality factor of different annealing temperature. I-V characterization of ZnO/ITO thin film solar cell under illumination shown in figure (6c-d). And the open circuit voltage (Voc), short circuit current (Isc), Fill Factor (FF) and conversion efficiency (η) are calculated in Table (4.b.) for different annealing temperature.

Formulae for PV cells, Under illumination condition;



Formula for PV cells, under dark condition,

$$\mathbf{I_s = AR^* T^2 \exp\left(-\frac{q\varphi}{KT}\right)\text{-----------------}(1)}$$

$$\mathbf{I = I_0 \left(\exp\frac{qv}{kT} - 1\right)\text{ -------------------}(2)}$$

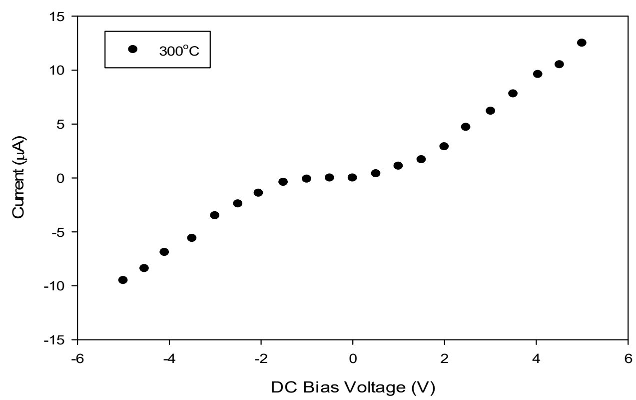


Figure 6(a). I-V characteristic of dark condition ZnO/ITO thin film annealed at 300ºC

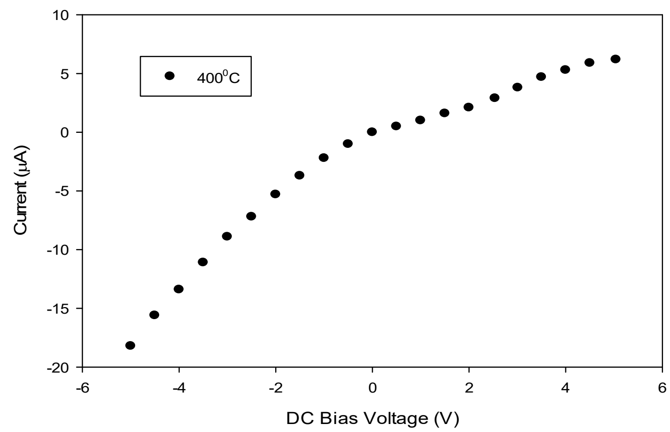


Figure 6(b). I-V characteristic of dark condition ZnO/ITO thin film annealed at 400ºC

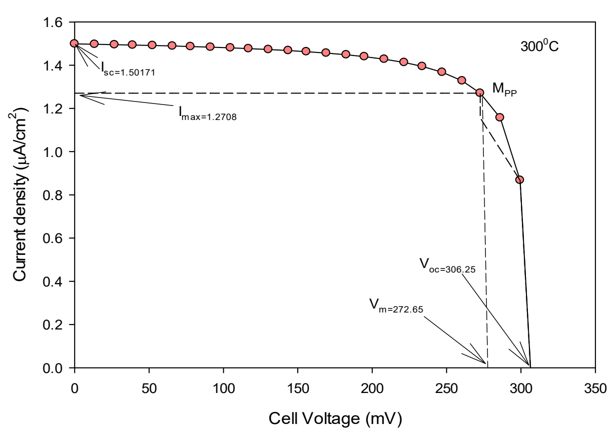


Figure 6(c). I-V characteristic under illuminated condition ZnO/ITO thin film annealed at 300ºC

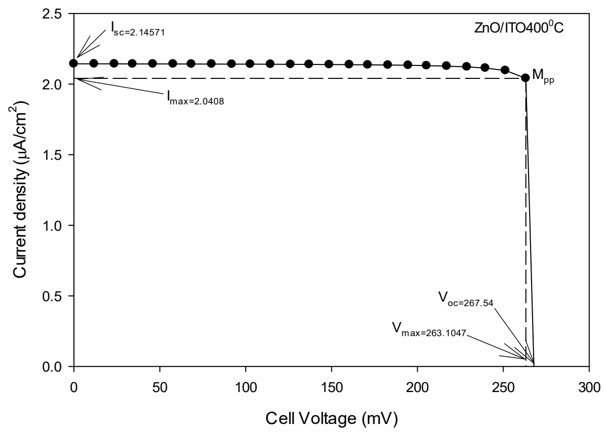


Figure 6(d). I-V characteristic under illuminated condition ZnO/ITO thin film annealed at 400ºC

Table .4.a Ideality factor, Barrier height, and Saturation current values for **ZnO**/ITO thin film solar cells at different annealing temperature

Annealing temperature	Ideality factor	Barrier height(eV)	Saturation current (μAm)
300ºC	1.51	0.3371	0.541
400ºC	1.55	0.3532	0.291

Table 4.b. Photovoltaic measurement for ZnO/ITO thin films solar cell at different annealing temperature.

Annealing temperature	Voc (mV)	Isc (μAm)	Vmax mV	Imax μAm	FF	Efficiency %
300ºC	306	1.50	272.65	1.27	0.75	0.23
400ºC	267.54	2.15	263.10	2.04	0.94	0.36

Conclusion

In Summary, deposition of ZnO/ITO thin films prepared by the successive immersion of ITO glass substrate in solutions of NaOH and Zinc chloride reaction solution at 63.5°C ~80°C have been studied. Hexagonal (wuritze structure) phase can be easily obtained by CBD method. The ZnO/ITO thin films have mainly (101) and (002) crystalline orientations. At temperature of 300°C, the crystallite size was found to be 29.63nm at prominent peak (101) and 400°C provided 38.87 nm respectively. Therefore, we may deduce the crystallite size were found to be increased with increasing annealing temperature. Improved in crystallinity quality with rising annealing temperature. As a result, oxygen defect are favorable to the merging process to form larger grains size while increasing the annealing temperature. The surface morphology of deposited ZnO/ITO thin films on ITO substrate show nanorods shape structure. Optical band gap of the ZnO/ITO films, measured by employing a UV-Vis spectrophotometer, lies at 3.66eV~ 3.3408eV at 300°C and 400°C annealing temperature respectively. This lower energy band gap may be due to absorption involving defect states. According to the C^{-2}Vs V measurement, we can deduce that build in voltage for different annealing temperature is slightly different. All I-V characteristics showed the photovoltaic behavior. The fill factor FF for all ZnO/ITO films were flexible for cell design. By the conclusion, the ZnO/ITO film at various annealing temperature were credible and promising use for thin film solar cell by non-expensive and unsophisticated method.

Acknowledgement

I am greatly indebted to Professor Dr Khin Khin Win, Head of Department of Physics, University of Yangon, for her kind permission to carry out this research.

I would like to thank Professor Dr Soe Soe Nwe, Department of Physics, University of Yangon, for her valuable advice in the preparation of this paper.

I wish to express my warmest thanks to Supervisor Dr Thida Win, Lecturer, Department of Physics, University of Yangon, for her valuable advice and supervising throughout in this research.

I am also deeply grateful to Co- supervisor Dr Marlar Wai, lecturer, Department of Physics, University of Yangon, for her valuable advice in my experiment work

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