Effect of ZnO Sputtering Time as Photoanode ITO-PEN/TiO2/ZnO on Microstructure and Optical Properties for Flexible DSSC

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Abstract. The development of renewable energy sources is urgently needed to reduce the use of fossil fuels globally, so renewable energy devices are needed to produce electricity supplies. The Flexible DSSC System photoanode (ITO-PEN/TiO_2/ZnO-D205) was developed as a photovoltaic device to produce high enough electrical energy and is flexible it is easy to apply compared to other DSSC systems. TiO_2/ZnO layer is deposited using the sputtering method with varying sputtering times of 0, 30 and 60 minutes which will give rise to different characteristics. The structural characterization and optical properties were tested using XRD and UV-Vis. The analysis results show that increasing the sputtering time causes a high XRD peak which then reduces the crystal size, increases the crystallinity, and the energy band gap decreases. The highest sample absorbance maximum value was recorded at 60 minutes, in the wavelength range of 405 nm with a band gap energy of 3.08 eV, and a crystal size of 16.31 nm and crystallinity of 43.9%. Thus, the novelty of the Flexible DSSC device with photoanode (ITO-PEN/TiO_2/ZnO-D205) has the potential to sustain research on renewable energy sources in the field of integrated solar cells.

Keyword : TiO2, ZnO, Sputtering, Flexible DSSC

INTRODUCTION

As time goes by, human energy needs are increasing, so the availability of energy, especially from fossil fuels, will become increasingly scarce. Currently, many efforts have been made to convert energy and store renewable energy to overcome environmental pollution [1], [2]. In the last few decades, solar cells have received a lot of attention because the manufacturing process is easy, environmentally friendly, cheap, and abundantly available (1.4 $\times 10^5$ TW) and does not involve a combustion reaction during the generation process[3], [4], [5]. Dye Sensitized Solar Cell (DSSC) is one of the most popular types of solar cells introduced by Michael Grätzel and Brian O'Regan at UC Berkley as a thin film photovoltaic technology using materials that are not sensitive to contaminants in the environment and can be produced in flexible forms[6], [7], [8].

DSSC consists of several components, namely substrate, photoanode, dye, electrolyte and counter-electrode (CE). The type of DSSC substrate commonly used is the FTO glass substrate which has high efficiency. However, because the glass substrate is thick and inflexible, its application is limited so a substrate with a more flexible material is needed which can be used as an innovation to develop the potential of DSSC[9], [10], [11]. The flexible conductive substrate that can be used is PEN (polyethylene naphthalate) coated with ITO (Indium Tin Oxide) [12]. Photoanode is a DSSC component which consists of semiconductor material as a place to transfer electrons and dye molecules. Among all semiconductor materials, TiO_2/ZnO nanoparticle materials attract widespread attention because they provide a high specific surface area for dye adsorption, thereby efficiently enhancing light harvesting [13]. In previous research, the performance of TiO_2/ZnO based DSSC photovoltaics produced an efficiency of 0.74% and 2.73% using the chemical bath method and FTO substrate which was less efficient in use [14], [13], [15]. The energy conversion efficiency obtained is good, but further development is needed towards a flexible and lightweight device system.

Apart from that, DSSC research based on flexible substrates with TiO_2 material produced an efficiency of 0.12%, this is because TiO_2 deposition still uses the doctor blade method, where this method requires quite high temperatures [16]. Because the ITO-PEN flexible substrate has a low melting point, it requires high-level technology such as sputtering to obtain maximum results. The sputtering method can be considered a good alternative due to its potential for upscaling large areas at much higher deposition rates, simplicity of use and providing a repeatable process[17],[11]. Research using the sputtering method with variations in the optimum sputtering time of 30 minutes and 60 minutes produces an efficiency of 5% and 7%[18],[19]. Therefore, the design of TiO_2/ZnO deposited on ITO-PEN as a photoanode for the F-DSSC system using a time-varying sputtering method was carried out to determine optimal parameters in order to obtain characterization such as structure, optical properties and maximum energy conversion performance. Studies on F-DSSC using the sputtering method are still very limited. Thus, research on optimizing the sputtering time of TiO2/ZnO photoanodes for flexible DSSCs using the sputtering method needs to be carried out.

METHODOLOGY

The TiO_2/ZnO photoanode was deposited using the sputtering method with varying sputtering times. Before the substrate was deposited with TiO_2/ZnO, it was cleaned with soap and demineralized water, soaked using an ultrasonic bath for 15 minutes each and then dried. Then the first layer was deposited with a Blocking Layer (BL) using a spin coating technique at a speed of 3000 rpm for 1 minute and then heated at temperatures of 100, 150, and 200℃, 30 minutes each. The second layer of TiO_2 uses the DC sputtering method with power parameters of 80 w, flow control 45 sccm, air pressure control 25% rotation 5 rpm, temperature 120 and time 1 hour. The third layer of ZnO was deposited using the DC magnetron sputtering coating method with varying times of 0, 30, 60 minutes and the same parameters as TiO_2. Then tested using XRD and UV-Vis to determine the structure and optical properties. After that, the TiO_2/ZnO film was soaked in a solution of 20 mL 2-propanol and 150 μL Titanium (IV) (triethanolaminato) isoproxide solution at a temperature of 80°C for 30 minutes, dried and then soaked in D205 dye for 24 hours in a dark room. Samples are indexed as TiO2, TiO_2/ZnO-30, TiO_2/ZnO-60.

RESULT AND DISCUSSION

In this research, ZnO deposition was successful on the ITO-PEN substrate using the sputtering method with a variety of different sputtering times. The ITO-PEN/TiO_2/ZnO thin film was characterized using XRD to determine the crystal structure. The results of the XRD data are in the form of a graph of the relationship between intensity and diffraction angle (2θ) as seen in Figure 1, where as the ZnO deposition time increases, the XRD peak becomes higher. The diffraction peaks show the crystal phase in the TiO_2 and ZnO phases. Several TiO_2 peaks were identified in the hkl (101), (004), and (200) planes with diffraction angles (2theta) 25.26°, 37.78°, and 48.02°. The ZnO peak was identified in the hkl (100) and (110) planes with diffraction angles (2theta) 34.51° and 51.63°. The results of the TiO_2 and TiO_2/ZnO peaks are in accordance with research carried out by Bakr et.al and. Siti et.al[20], [21].

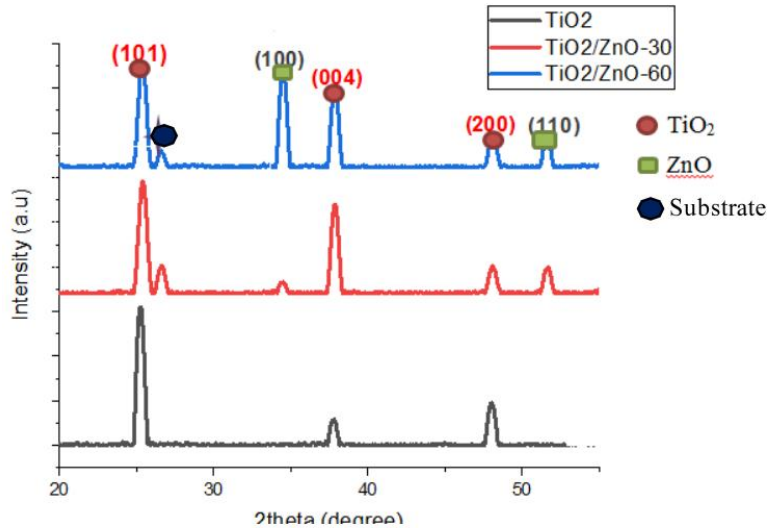

Figure 1. XRD Structure For TiO_2, TiO_2/ZnO

To analyze the crystal structure of the XRD results using the Rietica application and then refinement. Data processing using the Debye Scherrer equation in equation(1)

$$D = \frac{k\lambda}{\beta\cos\theta_\beta} = \frac{k\lambda}{FWHM(rad)\times\cos\theta_\beta} \quad (1)$$

There D is the crystal size, k is the Scherrer constant (0.9), λ is the wavelength of the light (0.15406 nm), β is FWHM and θ_β is the angle percentage. The crystal sizes obtained in each hkl plane are presented in Table 1.

Table 1. Crystal Size TiO_2/ZnO

Crystal Planes	**Sample**		
	TiO_2 (nm)	**TiO_2/ZnO-30 (nm)**	**TiO_2/ZnO-60(nm)**
(101)	15.96	14.00	14.34
(004)	18.16	16.40	16.38
(200)	17.31	16.37	16.04
(100)	-	17.26	16.57
(110)	-	17.98	18.20
Crystal Size Average	**17.14**	**16.41**	**16.31**

Based on table 1. The sputtering time does not have a significant effect, the difference between each sample is not too big, where the longer the duration of the sputtering time, the smaller the crystal size will be. Next, a crystallinity analysis was carried out using equation (2) where the longer the sputtering time, the greater the crystallinity and the results are shown in Table 2.

$$\text{Crystalline} = \frac{Area\ Crystal\ Fraction}{Area\ Crystal\ Fraction + Area\ Amorf\ Fraction} x100\% \quad (2)$$

Table 2. Crystalline TiO_2/ZnO

	Sample (%)		
	TiO_2 (%)	**TiO_2/ZnO-30 (%)**	**TiO_2/ZnO-60 (%)**
Crystalline	42.4	43.6	43.9

The optical properties and band gap energy of the TiO2/ZnO layer on the ITO-PEN conductive substrate were characterized by UV-Vis Spectroscopy in the wavelength range 200-1100 nm. Absorbance and band gap energy are presented in Figure 2 where the absorbance in a semiconductor material is related to the energy of excited electrons from the valence band to the conduction band.

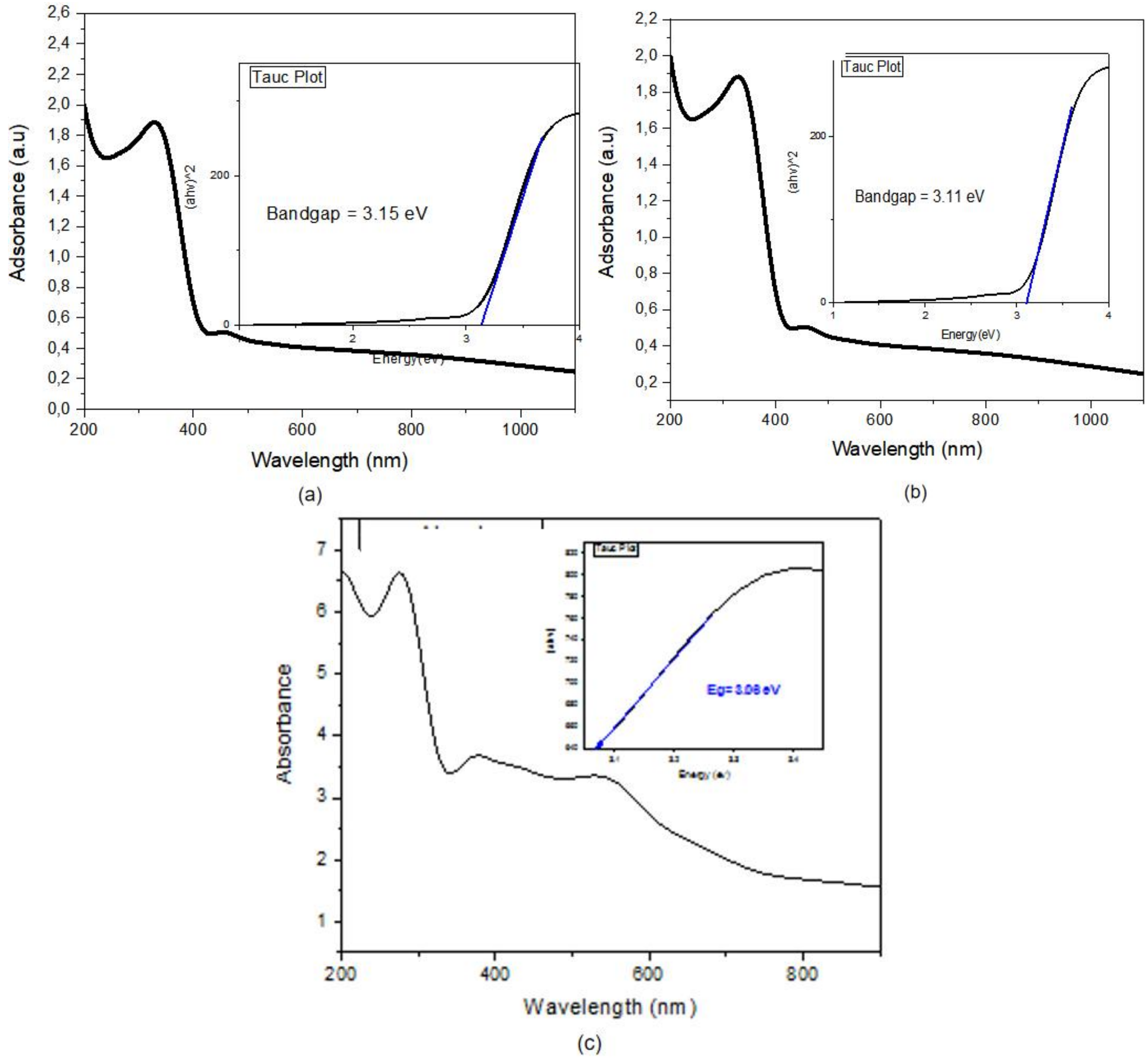

Figure 2. Absorbance and Bandgap Energy of (a) TiO2, (b) TiO_2/ZnO-30 and (c) TiO_2/ZnO-60

The analysis was carried out using the Tauc Plot method for direct band-gap with equation (3), where the longer the duration of the ZnO sputtering time, the smaller the bandgap until it reaches 3.08 eV and a wavelength of 405 nm which can be presented in table 3. This shows an increase in optical absorption. The increase in optical absorption in question is the increased light harvesting ability of a sample so that it will increase photogeneration from the redox couple process. The bandgap values of pure TiO2 and ZnO are 3.22 eV and 3.37 eV[22], respectively. The results obtained are not too far away or in accordance with research conducted by Upadhyay et.al and BethelAnucha et.al.[23],[24].

$$(\alpha hv) = A(hv - Eg)^2 \tag{3}$$

Table 3. Wavelength and Bandgap Energy of TiO_2/ZnO

Indicator	Sample		
	TiO_2	**TiO_2/ZnO-30**	**TiO_2/ZnO-60**
Bandgap (eV)	3.15	3.11	3.08
Wavelength(nm)	395	400	405

CONCLUSION

TiO2/ZnO thin films have been successfully deposited using the sputtering method on the ITO-PEN substrate with varying sputtering times of 0, 30, 60 minutes. The XRD results show that the average crystal grain sizes obtained are 17.14 nm, 16.41 nm and 16.31 nm respectively and crystallinity is 42.4%, 43.6% and 43.9%. The optical properties of the TiO2/ZnO photoanode thin film are demonstrated from the energy gap obtained from UV-Vis data calculations using the tauc plot method. The energy gap of the TiO2/ZnO photoanode thin film is in the range of 3.08 eV - 3.15 eV. The maximum absorbance is in the nm value ultraviolet wavelength range, where the absorbance value tends to increase as the sputtering time increases.

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