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Effect of TBOT Concentration n-nanorod TiO_2 and p-Cu_2O for Heterojunction Thin Film Solar Cell Application

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ABSTRACT

This experiment is about fabrication of heterojunction n- TiO_2 and p- Cu_2O thin film were fabricated using hydrothermal and electrodeposi-tion method, respectively. The TiO_2 thin film exhibited optimum parameter at 16 hours duration of hydrothermal process with the concentra-tion of TBOT used was 0.05 M. After that, p-Cu_2O layer was deposited on nanorod TiO_2 thin film for heterojunction formation. Prior to the p- Cu_2O deposition on nanorod TiO2 /FTO substrate, cyclic voltammetry (CV) measurement was carried out. The p- Cu_2O thin film was deposited at -0.4 vs. Ag/AgCl based on the CV measurement result. The effect of deposition time was also investigated during electrodepo-sition to improve the properties of the p-n junction semiconductor material. P-type Cu_2O thin film were fabricated by using copper acetate based solution through potentiostatic with pH value of 12.5. The Cu_2O was successfully developed on the TiO_2 layer with high crystallinity and lower resistance. The TiO_2 /Cu_2O thin film exhibited optimum parameter at 150 minutes deposition time with 40 °C water bath during electrodeposition process. Morphological, structural, optical and electrical properties were characterized using X-Ray Diffractometer, Field Emission Scanning Electron Microscopy, Ultraviolet-visible Spectroscopy and Four Point Probe, respectively.

Key words : Hydrothermal, Electrodeposition, TBOT, deposition time, TiO_2/Cu_2O thin film

1. INTRODUCTION

A nanostructured titanium dioxide (TiO_2) thin film gives high transmittance and good refractive index in the visible region with chemical stability and good durability in environments. TiO_2 thin films have been widely used for many applications such as photocatalyst [1] [2], multilayer optical coating, thin and structural properties. Copper oxide thin films are being considered in thin film solar cells for its unique properties [3]. film devices for solar cell and also in sensor applications [2] due to its promising features in optical, electrical, chemical In order to fabricate highly efficient solar cells, the heterojunction process is introduced and this is proven by researches, that solar cells can be fabricated using the heterojunction process [4].

Heterojunction is choose instead of homojunction because it was recognized that heterojunction can improve the performance of the photovoltaic devices [5] . The nanostructures of TiO_2, such as nanorods, have attracted enormous attention because they could offer direct electrical pathways for photogenerated electrons [6]. It is also stated in [7] [8] [9] that, the electrical power conversion efficiencies of TiO_2 / Cu_2O heterojunction, are still below than 2 %. The improper electron mobility between the n and p layer is believed to be one of the reason.

Other than electrodeposition method, there has a various technique to deposit Cu_2O thin film such as thermal oxidation [10], solvothermal method [11], radio frequency magnetron sputtering [12], pulsed laser and deposition [6]. Between these methods, electrodeposition was mainly used to fabricate Cu_2O thin film due to its low cost and processing temperature which is also a simple process [7]. By using electrodeposition, the thickness of the production of Cu_2O thin film can be precisely control [8]. In addition, Cu_2O film can be easily deposit into the desired substrate which the thickness of the film can be control by adjusting the electrodeposition parameter [9]. Hence, this can answer the first objective of the research paper which was to fabricate the n-type of Cu_2O thin film by using electrodeposition method. The structural, morphological, optical and electrical characteristic of n-type cuprous oxide thin film was studied using X-ray Diffraction (XRD), Field emission-scanning electron microscope (FE-SEM), Atomic Force Microscopy (AFM) and four point probe respectively.

2. EXPERIMENTAL PROCEDURES

In this study, n-TiO_2 were fabricated using hydrothermal method to produce nanorod structures. Wide range of Titanim butoxide (TBOT) concentration were optimized on fabrication of n-type TiO_2 Nanorod thin film on FTO substrate. Next, Cu_2O thin films were electrodeposited on TiO_2/FTO substrate in an electrochemical cell that contained an aqueous solution of cupric sulphate, lactic acid and sodium hydroxide that act as a pH regulator. The working, counter and reference electrode were FTO substrate, platinum electrode and Ag/AgCl, respectively. Cu_2O thin film were prepared at mixture of pH solution 12.5 and bath temperature 40 °C and at -0.4 V vs. Ag/AgCl deposition potential

In order to enhance the properties of the fabricated nanorod structures, the TBOT concentration were varied from 0.04 to 0.07 mol. Table 1 shown the fixed parameter for hydrothermal process. Table 2 shown the various TBOT concentration parameter for each samples, respectively. The optimum deposition time were investigated at 120 and 150 minutes. Table 3 shown the fixed deposition parameter during electrodeposition conducted.

XRD was used to analyse the structural properties of both TiO_2 and Cu_2O thin film. Next, FE-SEM was used to characterize the sample in term of their morphology. Atomic Force microscopy used to obtain the surface roughness of sample. Four point probe was also used in order to determine the electrical properties of the sample.

Table 1: Hydrothermal parameter.

Hydrothermal parameter	
HCL (ml)	130
DI water (ml)	120
Baking Temperature (°C)	150
Time (Hours)	16

Table 2: TBOT concentration

Sample	TBOT concentration (mol)
1	0.04
2	0.05
3	0.06
4	0.07

Table 3: Deposition parameter

Deposition parameter	
pH	12.5
Deposition Time (minutes)	150
Bath Temperature (°C)	40
V vs. Ag/AgCl (V)	-0.4

3. EXPERIMENTAL RESULT

3.1Fabrication of n-TiO_2 Nanorod Thin Film

3.1.1 Structural properties

For structural properties, the TiO_2 thin film that was characterized by using X-ray Diffraction (XRD) method. The graph showed several peaks obtained from the XRD pattern. Various peaks detected at 27.43, 36.12, 39.19, 41.24, 56.02 and 62.75° with corresponding orientations of TiO_2 were found to be at (110), (011), (020), (111), (220) and (020). Sample deposited using 0.05 mol exhibit the highest intensity and crystallinity at 36.12 and 78.61° compared others. There were no other peaks corresponding to other impurities were observed.

By comparing the TBOT volume of solution during hydrothermal process, sample with 0.05 mol exhibit better crystallinity and highest intensity obviously compared sample which TBOT volume were 0.04, 0.05, 0.06 and 0.07 mol. These different results is related to the thickness of the thin films produced [13]. As the volume increases, the thickness of the thin film also increases leading to a decrease in the peak intensity of FTO. All the samples showed high crystallinity considering the strong and sharp diffractions produced with no broad peaks detected. From the XRD, growth of the TiO_2 nanorods are (011) preferentially oriented. XRD pattern for FTO substrate and n-type TiO_2 thin films deposited at 0.04, 0.05, 0.06 and 0.07 mol were showed in Fig. 1. Table 4 shows the Corresponding plane for TiO_2 reflection peaks.

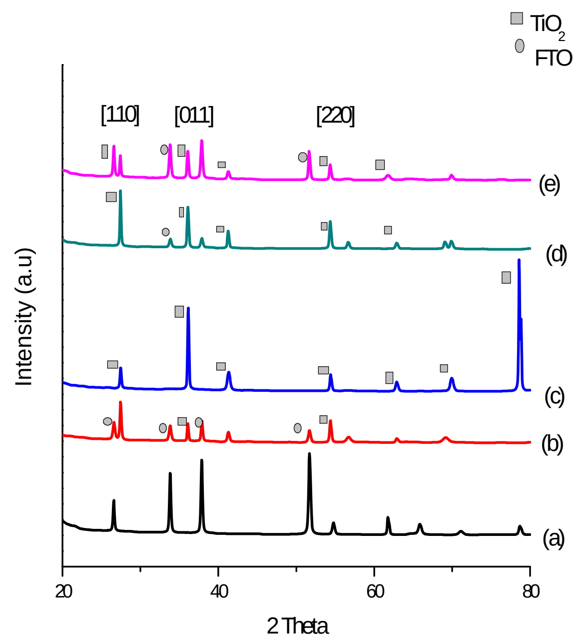

Figure 1: XRD pattern for (a) FTO substrate and Titanium Dioxide with different TBOT volume (b) 0.04, (c) 0.05, (d) 0.06 and (e) 0.07 mol, respectively.

Table 4: Corresponding plane for TiO_2 reflection peaks.

2 Theta (Degree)	Phase [h k l]
27.44	[110]
36.06	[011]
41.22	[111]
56.44	[220]

3.1.2 Morphological properties

Based on the findings, all sample exhibited tetragonal shape with flat-end facets which believed to be TiO_2 at preferential orientation of (110) in structural properties with corresponding parameters. All sample with 16 hours hydrothermal process seem growth fully covered the FTO glass substrate from 0.04 until 0.07 mol. It showed that the nanorod started to form at 0.04 mol TBOT as the nanorod shape was thinner compared others. The size of the nanorod increase with the increment of TBOT volume. Fig.2 showed the FE-SEM morphological images for sample deposited at 0.04, 0.05, 0.06 and 0.07 mol, respectively.

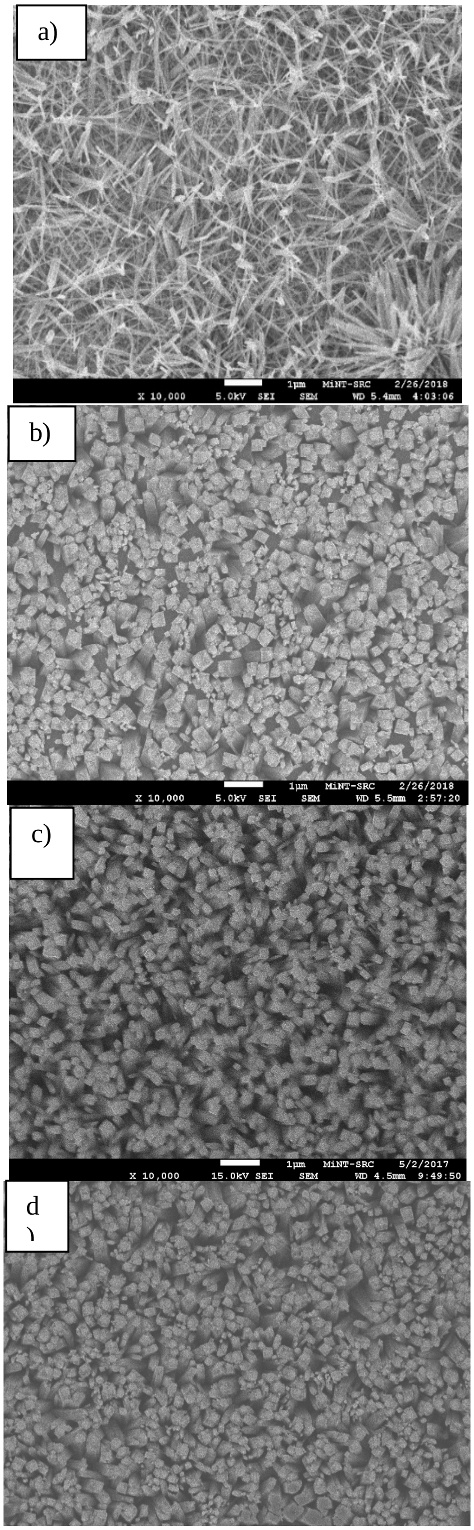

Figure 2: FE-SEM morphological images at a) 0.04, b) 0.05, c) 0.06 and d) 0.07 mol at 10K magnifications

3.1.3 Topological properties

The average surface roughness of each sample was obtained for 16 hours TiO_2 thin films which had been deposited using wide range volume of TBOT 0.04 until 0.07 mol. From the results, the average surface roughness of the sample decreased with the increment of the volume of TBOT. The average surface roughness of the sample with 0.07 mol of TBOT was the smallest compared to all other samples. Meanwhile, the highest average surface roughness was the sample with 0.04 mol of TBOT. This can be explained by the number of small grain which was recorded to be highest when the volume of TBOT decreasing. Thus, the topological properties of the TiO_2 would be influenced by the volume of HCL used in the hydrothermal method. The roughness for n-type TiO_2 thin film are presented in Table 5

Table 5: The roughness of n-type TiO_2 thin films corresponding TBOT volume of sample

Volume of TBOT (mol)	Average Roughness (nm)
0.04	515
0.05	409
0.06	334
0.07	295

3.1.4 Electrical properties

Table 6 shows the sheet resistivity of the n-TiO_2 thin films with different volume of TBOT. From the results obtained, the sheet resistivity increase when the volume of TBOT increase. However, the sheet resistivity decline after 0.06 onwards. Decrease in sheet resistivity is due to increase of the grain size and decrease of the surface roughness [14]. The lowest resistivity was recorded with the sample that using 0.04 mol TBOT volume. However, the highest resistivity was the sample with 0.06 mol TBOT.

Table 6: Sheet resistivity during different with different volume of TBOT

Sample	Tbot concentration (mol)	Sheet resistivity (Ω/sq) x 10^4
Sample 1	0.04	2.70
Sample 2	0.05	7.17
Sample 3	0.06	15.40
Sample 4	0.07	12.60

3.2 Deposition of Cu_2O on n-TiO_2/FTO substrate

3.2.1 Structural Properties

The graph showed several peaks obtained from the XRD pattern. Various peaks detected at 36.45, 42.35, 61.44 and 73.59° with corresponding orientations of Cu_2O were found to be at (111), (200), (220) and (311). Based on the results, the preferred orientation of Cu_2O thin films were (111) corresponding with the previous finding by Long Cheng Wang et al. that shown dominant orientation for n-type Cu_2O thin film was (111) at 36.45°[6]. Meanwhile, sample deposited at 150 minutes exhibited the highest intensity and crystallinity at 36.45° compared others. The longer the reaction time, the stronger and sharper the diffraction peaks of Cu phase [15]. The peak was also increase as the deposition time increase. The increment of the intensity indicated the structural improvement of Cu_2O where the crystallinity increase as the deposition time increase [16]. There were no others peaks corresponding to metallic copper or other impurities were observed which is matching with previous study by A. El-Shaer et al.[17]. XRD pattern for n-type TiO_2 / Cu_2O thin films deposited at 120 and 150 minutes were showed in Fig.3.

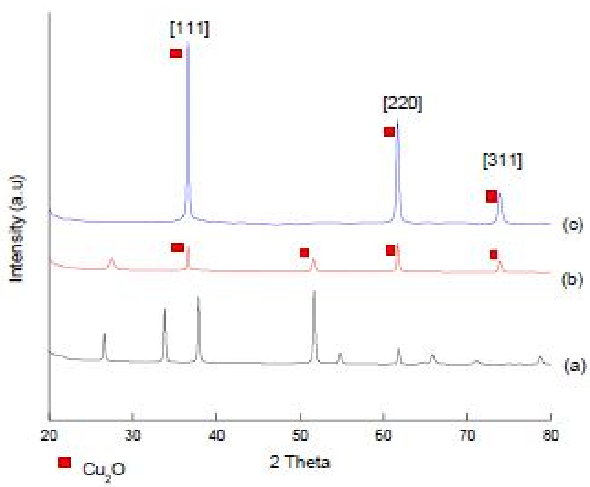

Figure 3: XRD pattern for (a) FTO substrate and Copper Dioxide with different deposition time (b) 120 and (c) 150 minutes, respectively

3.2.2 Morphological Properties

Based on the findings, the pyramid triangular shapes were started to form. This was due Cu_2O preferential orientation of (111) in structural properties was the pyramid triangular shape. All samples with pH 12.5 seem growth fully covered the n-type TiO_2 / FTO glass substrate. These results were consistent with XRD results where the increase intensity of Cu_2O peaks showed more compact and closer particles as the deposition time increase. However, the nanorod still can be seen from the images. This was because the nanorod have tall structures and the copper oxide were absorbed between the slits and spaces of the nanorod. FE-SEM morphological images for sample deposited at 120 and 150 minutes are showed in Figure 4, respectively

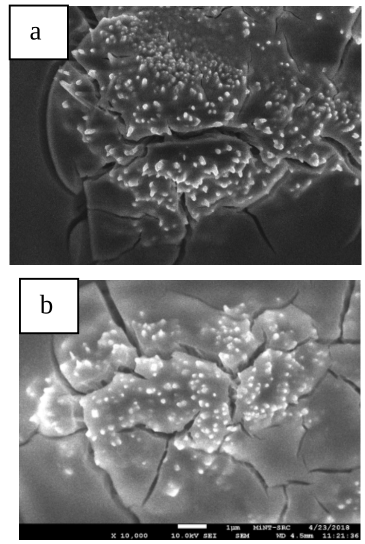

Figure 4: FE-SEM morphological images for sample at a) 120 and b) 150 minutes for magnification 10K

3.2.3 Topological properties

The average surface roughness of each sample was obtained for Cu_2O/ TiO_2 thin films which had been deposited using wide range of time from 120 to 150 minutes. From the results, samples deposited at 150 minutes showed the highest roughness which 22.67 nm compared to others. This results was corresponding with findings in [18] that the deposition time had a strong influence on the film growth. The longer deposition times were required for uniform coverage of the substrate. These results can be related to FE-SEM images where the surface of TiO_2 / FTO substrate started to become dense with the growth of Cu_2O as deposition time increase.

Sample deposited at 150 minutes with impeccable pyramidal structure and the highest roughness indicated the increment of grain size. Thus, it had high potential to absorb the light simultaneously. Corresponding to [19], increasing the grain size of the Cu_2O thin films will improve the charge transport through the film itself. The density of surface dangling bonds also decreased and lead to the improvement in device for solar cell. The average surface roughness for Cu_2O/TiO_2 thin film are presented in Table 7.

Table 7: The roughness of n-type TiO_2/ Cu_2O thin films corresponding deposition time

Deposition Time (minutes)	Average Roughness (nm)
120	10.72
150	22.67

3.2.4 Electrical properties

The sheet resistivity of the sample was obtained to find the resistivity for each of the sample. From Table 8, it shows that the sheet resistance of TiO_2/ Cu_2O thin film increased as the deposition time increase. As the deposition time increase, it tend to produce a Cu layer with (111) preferred orientation and results in relatively high sheet resistance and resistivity [20]. We believed that p–n junction was formed, with the Cu_2O was acting as a p-type semiconductor and TiO_2 was acting as an n-type semiconductor.

Table 8: Value of sheet resistance with different deposition time

Sample	Deposition time (minutes)	Sheet resistivity (Ω/sq) x 10^4
Sample 1	120	2.16
Sample 2	150	167

4. CONCLUSION

The fabrication of n-type TiO_2/ Cu_2O had been fabricated successfully using the hydrothermal and electrodeposition method. It was found that the optimum parameters for n- TiO_2 thin film are 16 hours of hydrothermal process, 0.05 mol TBOT volume with 130 ml HCL and 120 ml DI. The baking temperature is 150 ℃. Optimum parameters for electrodeposition had been discovered with pH of 12.5, deposition time of 150 minutes, and bath temperature of 40 ℃ and potential deposition of -0.4 V vs Ag/AgCl.

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