Electrochemical Deposition of Zinc Oxide Thin Film using Two-terminal Setup

Amer Safri Hamidi
Faculty of Electrical Engineering
Universiti Teknologi Malaysia
Johor Bahru, Johor
amersafri@gmail.com

Mastura Shafinaz Zainal Abidin
Faculty of Electrical Engineering
Universiti Teknologi Malaysia
Johor Bahru, Johor
m-shafinaz@utm.my

***Abstract*—This paper reports on deposition process of Zinc Oxide (ZnO) using a simple electrochemical approach. The ZnO thin film was deposited on the Aluminium (Al) substrate in an aqueous solution of Zinc Chloride ($ZnCl_2$) at room temperature using two terminals electrochemical cell that consisted of positive and negative electrodes. Two types of Al substrate were used, which are Al foil and Al plate. Al foil or Al plate acted as the negative electrode (cathode) while Platinum (Pt) wire or Zinc (Zn) plate as the positive electrode (anode). A constant current density of 10 A/m^2 was applied in the experiment. 5mM $ZnCl_2$ and 0.1M potassium chloride (KCl) support solution used as the electrolytic solution. The experiment was carried out by varying the concentration of $ZnCl_2$ electrolyte solution and KCl supporting solution. Three different mixture of electrolyte solution and supporting solution, 125 ml of $ZnCl_2$ + 25 ml of KCl, 100 ml of $ZnCl_2$ + 50 ml KCl and lastly 75 ml $ZnCl_2$ + 75 ml KCl, were used . Each of the samples underwent 30 minutes of deposition process. At the end of the experiment, the morphologies and properties of ZnO were determined by studying the result from Single Electron Microscope (SEM) and Energy Dispersive X-ray spectroscopy (EDX). The structures of the ZnO were found as nanosheet-like network. The results evinced the potential of utilizing simpler setup of electrochemical approach in producing good characteristic of ZnO film for respective applications such as solar cell.**

Keywords— ZnO; thin film; electrodeposition; $ZnCl_2$; KCl

I. INTRODUCTION

Zinc Oxide (ZnO) is one of the widely used material in industry. ZnO mostly applied in the production of paints, rubber, plastics, catalysts, ceramic, pharmaceuticals and others [1]. In electrical and electronics industry, ZnO is used for ingredient of phosphors and as a transparent electrode. Since 1930s, ZnO became as one of the promising material for electronic for many decades. Physically, ZnO is a compound semiconductor with a wide bandgap of 3.37 eV [2]. Besides, ZnO thin films also had becoming as a key component and take a major part in most thin film solar cells. This is because the films can be produce in a large-scale without having to spend a lot of money. ZnO is one of the reactive material and deposition of this semiconductor can be performed under various mild condition. On the other hand, the improvement in properties of ZnO thin films become a challenge in the production and R&D of photovoltaics.

Nowadays, the world is facing critical issues such as climate changes due to greenhouse effect [3]. One of the answers to overcome this problem is to use renewable energies which can provide a long term solution to the world energy demand in a sustainable way. Solar energy carries the potential of becoming the largest renewable energy sources. The conversion of electricity from sunlight by photovoltaic (PV) solar modules has increased and the production cost have been reduced year by year. Currently, most of the solar cells used is crystalline silicon solar cells based on silicon wafers with a thickness of around 150–300 μm. However, high temperature is needed to produce thick silicon wafers and a very pure silicon is totally expensive as well as some of other materials [4]. Therefore, cost-effective thin-film solar cells may replace the current PV solar modules as it can absorb most of the sunlight with only a few micrometers of film thickness. The type of ZnO solar cells can become a huge prospect in the future because of low material consumption, effective energy conversion, simple production techniques and can produce efficiently by large areas deposition. Therefore, this paper reports on preliminary work of producing the ZnO film towards solar cell realization using a simple setup of two terminal electrochemical deposition cell.

II. METHODOLOGY

In this experiment, the configuration of two terminal electrodes in a 150 ml beaker was used to deposit the ZnO thin film on the Aluminium (Al) substrate. This configuration as shown in Fig. 1 comprises an Al substrate as the negative electrode (cathode) and Platinum (Pt) wire or Zinc (Zn) plate as the positive electrode (anode). A power source supplied the amount of current density needed during the deposition. Al was used because it is an active metal and easy to react during electrochemical deposition process. Moreover, the experiment process would be easier to be tested with Al as this was a preliminary prototype in ZnO deposition by electrochemical approach, before being implemented on different substrate types later.

Before starting the experiment, the surface of the substrate was cleaned first using deionized (DI) water to avoid any contamination because DI water are free from any mineral ions such as calcium, sodium and copper [5]. A mixture of $ZnCl_2$ aqueous solution and supporting electrolyte 0.1M KCl

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were used as the precursor. The major advantages of using $ZnCl_2$ aqueous solution as the electrolyte includes the solution are easy to handle, low cost and moderate toxicity. Varying the electrolyte concentration in electrochemical deposition possibly could alter the band-gap and lattice constant of the thin film. Basically, the deposition time was kept for 30 minutes with current density of 10 A/m^2. After the electrochemical deposition process, all of the samples were put in the petri dish before being kept in a closed container.

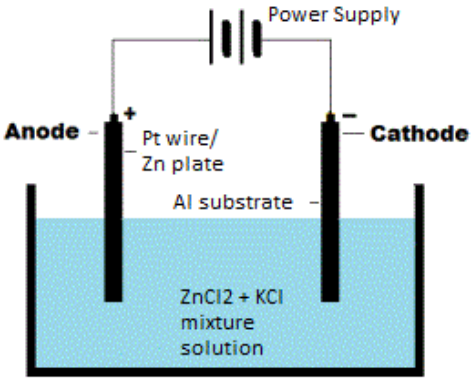


Fig. 1. The configuration of two terminal electrochemical cell

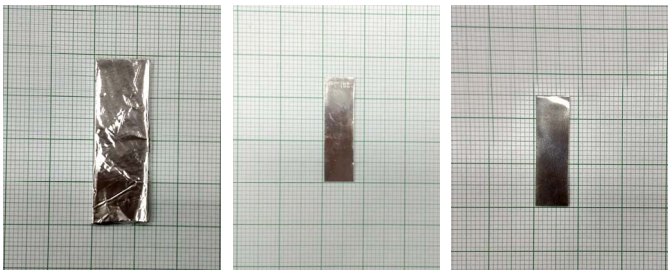
The characterization of surface morphology of samples was done by using Scanning Electron Microscope (SEM) while the Energy Dispersive X-ray (EDX) was used to identify the quantitative distribution of the elements presence.

A. Al Foil Negative Electrode and Pt Wire Positive Electrode

Firstly, Al foil was wrapped around a glass sides. The dimension of the glass slide was 25.4 x 76.2 mm in. The back side of the Al substrate was covered with cellophane tape which acted as insulator. Fig. 2(a) shows the Al foil sample before being deposited. Three Al foil samples with the same dimension were prepared to deposit the ZnO thin film on the substrate in three different mixtures of solution. The first solution was 125 ml $ZnCl_2$ + 25 ml KCl, the second was 100 ml $ZnCl_2$+50 ml KCl and the third solution was 75 ml $ZnCl_2$ + 75 ml KCl. All of the samples were soaked half of their size in the electrolytic solution for deposition. Therefore, the area of each dipped Al foil sample in the solution was 25.4 x 38.1 mm.

The total current density needed was 10 A/m^2. In other to obtain the desired current density, Equation (1) was applied where J is the current density, I is the current supplied by the power source and A is the area of dipped Al foil in the electrolyte.

$$J = \frac{I}{A} \qquad (1)$$



(a) (b) (c)

Fig. 2. (a) Al foil with 25.4 x 76.2 mm size sample (b) Al plate with 50 x 15 mm size sample (c) Zn plate with 50 x 15 mm size sample

B. Al Plate Negative Electrode and Pt Wire Positive Electrode

Basically, three Al plates with the approximate size of 50x15 mm were prepared. The backside of the Al plates were covered with cellophane tape. The Al plate sample used as shown in Fig. 2(b). The Al plates were soaked half of the size in three different mixture of solution, similar as described in section A. The total dipped area of each Al plate was 25 x 15 mm. Similar to experiment A, the current density was set to 10 A/m^2.

C. Al Plate Negative Electrode and Zinc Plate Positive Electrode

In this experiment, three Zn plates as in Fig. 2(c) with the size of 50 x 15 mm was used as the anode. The cathode was Al plate, as shown in Fig. 2(b). Same as previous experiment, the cellophane tape were attached at the back of the Al plates. This experiment still used the same mixture of solution, as mention in the previous section. The total dipped area of Al plate was 25 x 15 mm each.

The conditions applied for all samples prepared in this work were summarized in Table 1. The current density was kept for 10 A/m^2 and the deposition time was 30 minutes for all samples.

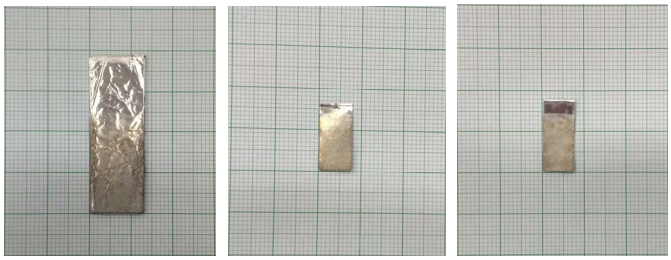
TABLE I. THE CONDITION FOR THE SAMPLES

Set	Sample	Anode	Cathode	Electrolyte
A.	A	Pt	Al foil	125 ml $ZnCl_2$ + 25 ml KCl
	B	Pt	Al foil	100 ml $ZnCl_2$ +50 ml KCl
	C	Pt	Al foil	75 ml $ZnCl_2$ + 75 ml KCl
B.	D	Pt	Al plate	125 ml $ZnCl_2$ + 25 ml KCl
	E	Pt	Al plate	100 ml $ZnCl_2$ +50 ml KCl
	F	Pt	Al plate	75 ml $ZnCl_2$ + 75 ml KCl
C.	G	Zn	Al plate	125 ml $ZnCl_2$ + 25 ml KCl
	H	Zn	Al plate	100 ml $ZnCl_2$ +50 ml KCl
	I	Zn	Al plate	75 ml $ZnCl_2$ + 75 ml KCl

III. Results and Discussion

A. ZnO growth on sample

After 30 minutes of electrodeposition process, the deposited ZnO could be seen on all of the Al substrate in each experiment using the naked eyes as it appeared in white-yellowish like colour. Fig. 3 shows the deposited ZnO thin film on all of the type of Al substrate.



(a) (b) (c)

Fig. 3. (a) Electrodeposited ZnO on Al foil (b) electrodeposited ZnO on Al plate for Pt wire as positive electrode (c) electrodeposited ZnO on Al plate for Zn plate as positive electrode

B. Morphology Study on Nanostructures of ZnO Thin Films

The formation of ZnO is mostly related to chemical reaction of elements in the electrolytic solutions. Generally, Zn presented in the solution would react with O element to form ZnO before it could be deposited on the substrate. When the oxygen is present as the precursor, ZnO electrodeposition would comply with the following equations:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

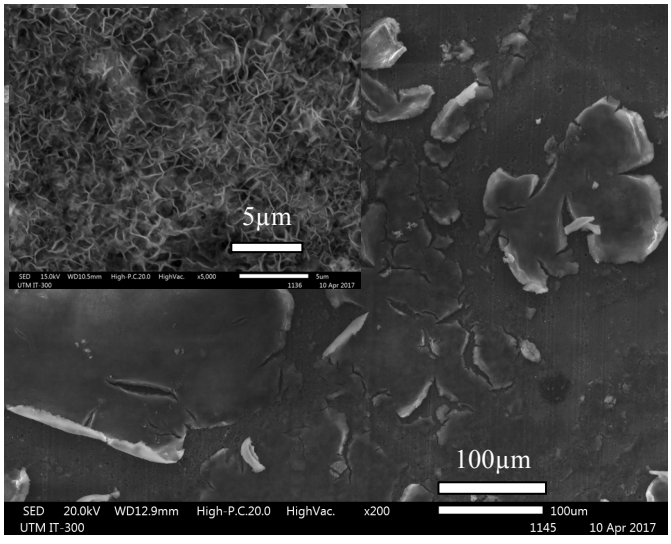


Fig.4. SEM image of ZnO thin film on Al foil (Sample A)

First, the electrolyte contains zinc cation and other anion. Then, the reduction of oxygen on the surface of the Al substrate leads to the adsorption of hydroxide ion. the precipitation of zinc hydroxide take places near the surface of the substrate generated by hydroxide ion. Finally, ZnO is formed and this process in known as the deposition of ZnO [6].

Many interesting features were unveiled from the SEM images. In this experiment, the SEM images were only captured for three samples according to the experiment's set. They were *A*. Al foil with Pt wire as positive electrode, *B*. Al plate with Pt wire as positive electrode and *C*. Al plate with Zn plate as the positive electrode. All of those three samples had shown similar structure behaviour which was ZnO nanosheet-like networks [7]. This networks were slightly curved and had an uneven surface morphology on a large scale.

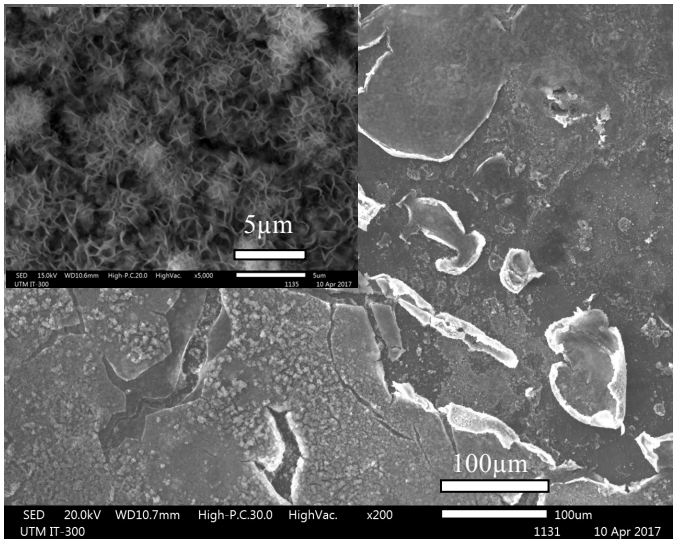


Fig.5. SEM image of ZnO thin film on Al plate (Sample D)

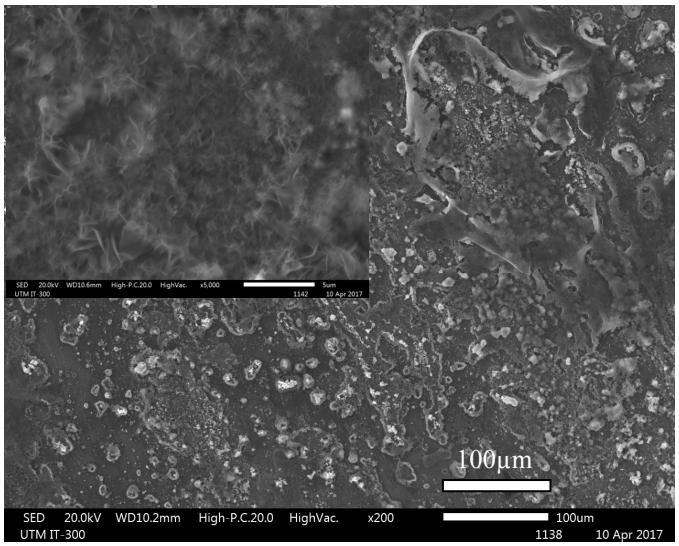


Fig.6. SEM image of ZnO thin film on Al plate for Zn plate (Sample G)

The SEM image of ZnO thin film grown on the Al foil in the mixture of 5mM $ZnCl_2$ and 0.1M KCl solution was shown in the Fig. 4. At low magnification scale, the crack and peeling morphology ZnO thin film aws observed. The electrodeposited ZnO on Al plate in Fig. 5 had shown even, uneven and crack morphology as well. Meanwhile, the thin film of ZnO in Fig. 6

had irregular shapes and separated into smaller parts. The real mechanism to explain the formation and growth of this ZnO structure is still under investigation and would not reported here.

C. Chemical Composition of the ZnO Thin Film

Using EDX, it could reveal the quantitative information and composition of deposited structures on the substrate which had been prepared. From the Fig. 7 and Table 2, it gave that Al has the higher weight percentage which was 36.69%. This was caused by the substrate type used in the experiment which was Al. The image from the EDX also proved the presence of ZnO thin film on the substrate surface. The weight percentage of Zn is 25.49% and O is 27.59%, indicated that the ratio of Zn:O is almost 1:1. The O percentage of 27.59% is slightly more than that of Zn as expected due to the existence of native oxides on the Al substrate. Therefore, the O percentage should in fact slightly more than that of Zn, as shown in the EDX results. There were also some other elements such as Cl and K presence on the surface of the surface due to the mixture of solution used in the experiment.

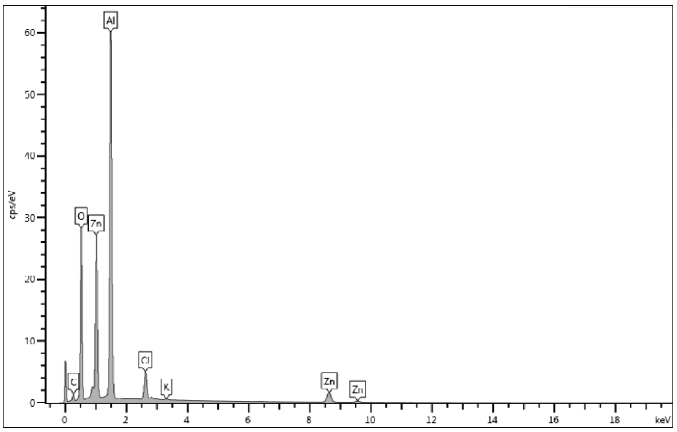


Fig.7. EDX result of electrodeposited ZnO thin film on the Al substrate

TABLE II. ELEMENT AND WEIGHT PERCENTAGE

Element	Wt%
C	6.09
O	27.59
Al	36.69
Cl	3.98
K	0.17
Zn	25.49
Total:	100.00

The electrical measurement test and optimization on the samples is still on-going. With the morphology characteristic observed, it is expected that the ZnO samples produced able to show good response (*ie* photoconductivity test) and probably suits well as a promising solar cell.

IV. CONCLUSION

ZnO thin film are formed by electrochemical deposition of $ZnCl_2$ with KCl as supporting solution. The nanostructure of the thin film was confirmed by using SEM and the composition of the elements presence in the deposited sample was done by using EDX. Another important part that need to be understand is the growth mechanisms of ZnO. The factor of the growth mechanisms also need to be studied more for better understanding of the electrochemical deposition process.

Acknowledgement

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