ISSN 2278-3091
Volume 9, No.3, May - June 2020
International Journal of Advanced Trends in Computer Science and Engineering
Available Online at http://www.warse.org/IJATCSE/static/pdf/file/ijatcse100932020.pdf
https://doi.org/10.30534/ijatcse/2020/100932020

# The Etching of ZnO/Glass by Hydrogen Peroxide Solution: Surface Morphological, Structural, and Optical Properties

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## ABSTRACT

This research was conducted to study the surface morphological, structural and optical properties of the samples after applying hydrogen peroxide ($H_2O_2$) etching on Zinc Oxide ZnO/glass substrates. In order to fabricate ZnO thin film on the soda lime glass substrate, RF sputtering machine was used. The deposited layer of the ZnO thin film thickness was measured to be 1.218µm. The ZnO/glass samples were then immersed by the percentage of the hydrogen peroxide ($H_2O_2$) concentrations which were 5% and 30% at the different time treatments. After immersing the samples into 30% concentration of $H_2O_2$ for 50 seconds, the result in SEM images showed the formation circles that resemble ZnO islands. The thickness of ZnO layer is reduced when the immersion time increases.

**Key words :** Zinc Oxide (ZnO), chemical wet etching, surface structure, hydrogen peroxide ($H_2O_2$)

## 1. INTRODUCTION

Zinc Oxide (ZnO) is one of the tremendous semiconductor materials that are widely used in most of the electronic industry, for example, solar cells, photodetector, piezoelectric, LEDs, and lasers. Apart from that, ZnO is also used in the production of cosmetic, rubber, health supplements and many more [1]. As for the transparent ZnO film, it is one of the metal oxides in a part of semiconductor material groups and the bandgap of this inorganic sample is measured within an ultraviolet wavelength [2]. It consumes high energy bandgap, 3.37 eV and larger binding energy. As for the 60meV of ZnO thin film, it is the key element of the great workable devices [3]. Various kind of glass substrates can be used in this kind of research such as quartz, fused silica, and soda lime glass. The soda lime glass is selected in this particular research due to its high optical transparency. Besides that, it is also a good insulator and cost-effective material [4]. Hydrogen peroxide ($H_2O_2$) is generally used in the ZnO and GaN samples cleaning. Wang *et al.* (2014) reported that the enhancement of UV emission and surface uniformity of the etched-ZnO attributed to the various concentrations of $H_2O_2$ etchants [5]. While, Chen *et al.* (2005) revealed that the effects of luminescent characteristic and deep-level emission of ZnO are related to the 30% of the $H_2O_2$ concentration and ZnO surface, respectively [6]. Meanwhile, the immersion of ZnO nanorods on silicon substrate into the 30% hydrogen peroxide concentrations resulting in the oxygen desorption effect, luminescent characteristics increased, and moderately changed the structural property of the sample [7]. Meanwhile, for this study, $H_2O_2$ was selected due to its high availability. A part of, $H_2O_2$ being the high availability, it is also one of the good oxidizing agent with an excellent etching rate [5]. However, a report of $H_2O_2$ etching on ZnO/glass substrate is rarely found from the literature review. Hence, the surface morphological and structural qualities of the etched ZnO were investigated and the relationship between the resultants and etchant concentration was revealed. In this research, we reported that the fabrication of ZnO on a glass substrate was completed by RF sputtering machine. The etched ZnO islands were successfully formed by a simple $H_2O_2$ etching method.

## 2. EXPERIMENTAL WORK

In this particular research, the fabrication of the ZnO thin film on the soda lime glass was done using the RF sputtering machine. The glass substrate was cleaned by dipping the substrate into deionized water for 15 minutes and was dried by nitrogen blowing. The RF power and base pressure were set at 150W and $3.54\times10^{-3}$ mbar, respectively. The $H_2O_2$ wet etching process was conducted to form etched ZnO/glass substrate. The deposited ZnO samples were dipped into $H_2O_2$

solution at different concentration (5% and 30%). The unwanted chemical moisture on the etched ZnO samples was rinsed and dried by a nitrogen air gun. The bandgap, the structural and the surface morphological were characterized by UV-spectroscopy, X-ray diffraction, scanning electron microscope (SEM), respectively. The captured SEM images were evaluated using ImageJ® software for determining the diameter of each ZnO islands.

## 3. RESULTS AND DISCUSSIONS

The non-uniform shapes and sizes of ZnO islands were detected from all the samples as shown in Figure 1. The 30%/100s sample showed the lowest decrement on the ZnO thickness compared to the other samples. The etched ZnO value had decreased simultaneously with the increasing of $H_2O_2$ concentration. The stable gas of $H_2O_2$ found continuously reducing the thickness of ZnO thin films. Non-uniform thicknesses of films were spotted from all samples. The average thickness of the samples (Figure 1) was calculated to be 1.218µm (as-deposited), 0.989µm (5%/50s), 0.411µm (30%/50s) and 0.386µm (30%/100s). It can be seen that the thicknesses of the etched ZnO layer had decreased which is due to the $H_2O_2$ etching effect. The lower thickness of the etched ZnO layer is found from the sample 30%/100s. The ImageJ® software was used to estimate the diameter of the ZnO islands formed on the glass substrate. Figure 2 indicates the filtered images of the ZnO islands on the glass substrate by using the ImageJ® software. Meanwhile, Table 1 shows the average diameter of ZnO islands on a glass substrate. Sample 5%/50s, 30%/50s, and 30%/100s indicated the average diameter of ZnO islands as 1.477, 1.062, and 1.872 µm. The lowest diameter of ZnO islands is obtained from the sample 30%/50s, while the sample 30%/100s showed the largest diameter of ZnO compared to the other samples.

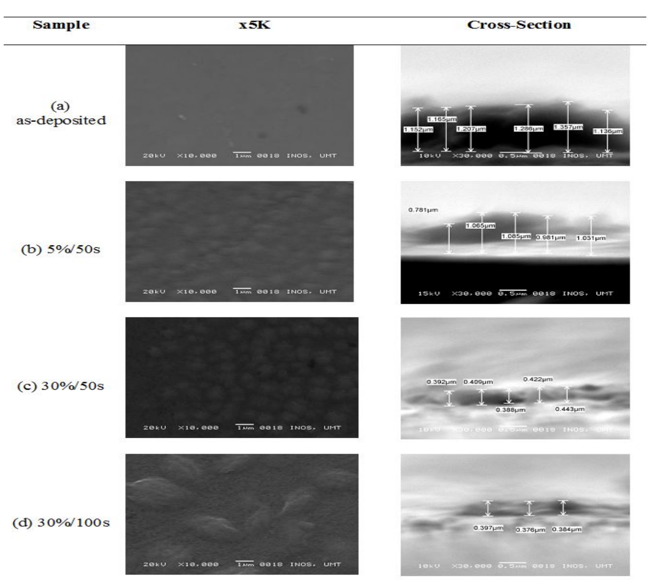


**Figure 1:** Top view and Cross-sectional SEM Images of ZnO films at different concentration.

For ImageJ® analysis, well-formed ZnO islands were spotted from sample 30%/50s with larger spacing between islands. $H_2O_2$ is believed to generate more defects which relate to oxygen element [8]. After introducing an oxidizer for $H_2O_2$, the oxide layer is formed on the ZnO surface [9]. The etching mechanism of O-terminated surface is faster and uniform compared to the Zn-terminated [10]. Moreover, at the ZnO surface, an oxidizer of $H_2O_2$ is reported to effectively remove Zn interstitials, Zn or $O_2$ vacancies [11].

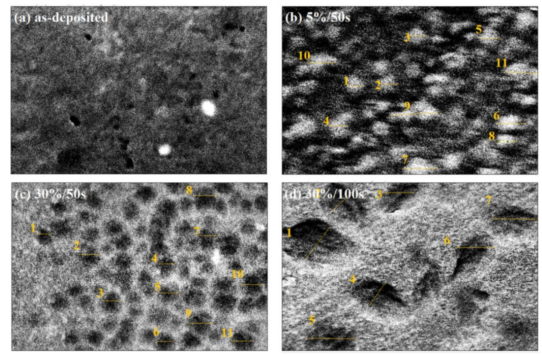


**Figure 2:** ZnO film images analyzed using the ImageJ software at different concentration.

**Table 1:** Average diameter of ZnO islands grown on glass substrate based on ImageJ analysis

| Sample | Average Diameter (µm) |
|---|---|
| as-deposited | - |
| 5%/50s | 1.477 |
| 30%/50s | 1.062 |
| 30%/100s | 1.872 |

The broad single peak at around 35.3$^{o}$ was observed on all samples, showing that the ZnO films tended to grow on 101 crystal plane (refer Figure 3). The crystallite size of the samples was determined using the Scherrer's equation.

$$D = 0.94\lambda/(\beta\cos\theta) \quad (1)$$

where $\lambda$ is the X-ray wavelength, $\theta$ is the diffraction angle and $\beta$ is the full width at half maximum (FWHM) of the ZnO peak value. The crystallite size value of 43.54, 51.21, and 48.37 nm were obtained from the sample as-deposited, 30%-50s, and 30%-100s. A wide broader XRD peak of ZnO, no crystallite size is calculated from the sample 5%-50s. Sample 30%-50s showed the highest crystallite size value compared to the other samples. The highest crystallite size value was reported from the well-formed ZnO islands on the glass substrate. Figure 4 indicates the optical transmittance of samples at different etching condition. All samples show the transmission of 80% and above in the visible range wavelength (400-700 nm). The transmittance of ZnO is increased with the decrement in ZnO thickness [12]. It can be observed that the sample 30%/100s resulted in the highest transmission after the 550 nm wavelength due to the decrement of ZnO thickness.

From the transmittance graph, the direct bandgap of ZnO is calculated by the Tauc equation as the following below.

$$\alpha h v = A\,(h v - E_{bg})^{1/2} \quad (2)$$

where $\alpha$, $h$, $v$, $A$ and $E_{bg}$ are the optical absorption coefficient, the Planck's constant, the frequency of the incident photon, the constant for a direct transition (absorbance value) and the bandgap energy, respectively. In addition, the bandgap energy of ZnO films is calculated by considering the linear graph of an extrapolation $(\alpha h v)^2$ versus energy $hv$, as shown in Figure 5. The bandgap energy of ZnO films was measured to be 3.85 eV (as-deposited), 3.83 eV (5%/50s), 3.29 eV (30%/50s) and 3.28 eV (30%/100s). The 30%/100s sample showed the lowest bandgap energy compared with other samples. Ismail *et. al* reported lower bandgap energy of ZnO prepared by sol-gel method at around 3.27 eV using the same calculation method [13]. On the hand, Azzafeerah *et. al* used potassium hydroxide (KOH) to fabricate porous gallium nitride (GaN) on a sapphire substrate [14]. As for future work, potassium hydroxide (KOH) chemical etching will be used to make porous ZnO on a glass substrate. This future work is considered since the ZnO bandgap energy (3.37 eV) is very close to GaN bandgap energy (3.39 eV) and the structural property for both samples are similar.

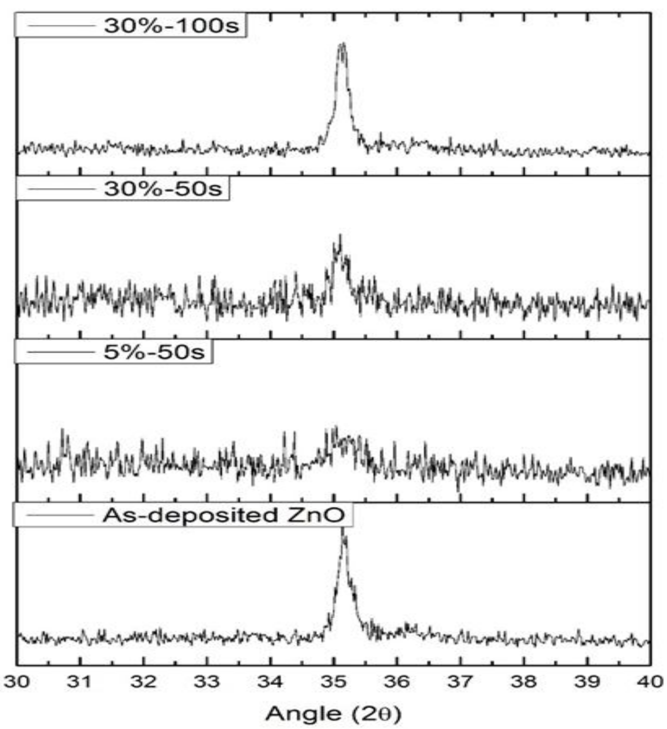


**Figure 3:** XRD diffraction of the studied samples for different $H_2O_2$ concentration.

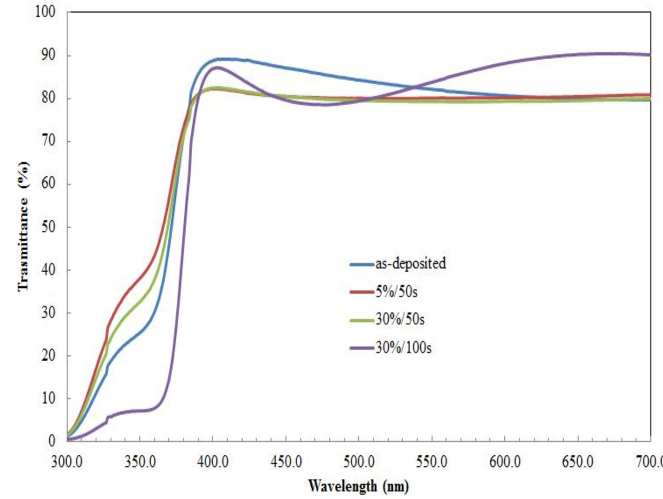


**Figure 4:** Optical transmittance spectra of the studied samples for different $H_2O_2$ concentration.

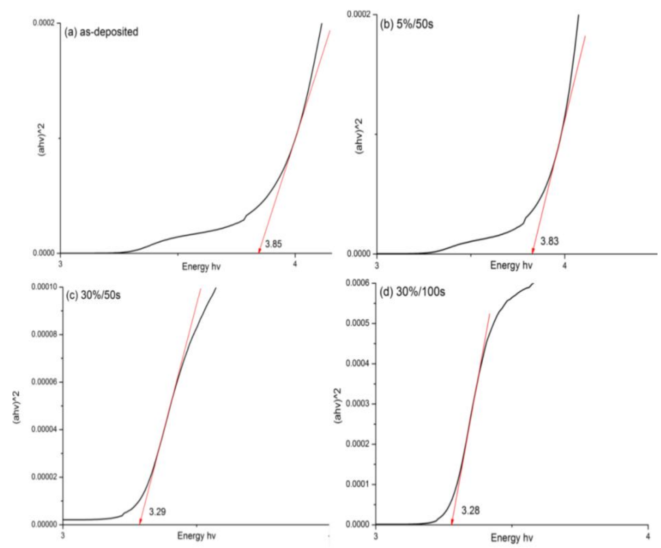


**Figure 5:** The Tauc plots of $(\alpha h v)^2$ versus energy $hv$.

## 4. CONCLUSION

The ZnO islands have been successfully formed with a simple wet chemical $H_2O_2$ etching. The SEM characterization showed that the higher $H_2O_2$ concentration had significantly reduced the average thickness of the ZnO thin film but had the largest ZnO islands grown on the glass substrate. Meanwhile, the XRD characterization had confirmed that all the studied ZnO samples were grown on 101 crystal plane. Furthermore, the highest $H_2O_2$ concentration resulting in the highest transmittance value due to the decrement of ZnO thickness. As for the calculated bandgap energy, the thinnest ZnO film (highest $H_2O_2$ concentration) gave the lowest value which was 3.28 eV.

**ACKNOWLEDGEMENT**

Mohd Zaki Mohd Yusoff would like to thank Universiti Teknologi MARA (UiTM) Cawangan Pulau Pinang, Malaysia that supports this work. Meanwhile, Muhammad Syarifuddin Yahya would like to thank Universiti Malaysia Terengganu for the support and the equipment provided.

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