

Growth Of Zinc Oxide (ZnO) Nanostructures By Thermal Chemical Deposition Method On Sputtered ZnO Seed Layer

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Abstract— We investigated the growth of zinc oxide (ZnO) nanostructures on a crystallized ZnO seed layer. The seed layer was deposited by RF magnetron sputtering and etched by HF solution before the deposition of ZnO nanostructures by thermal chemical vapour deposition. The HF etching was done to roughen the seed layer surface to enhance the growth of the ZnO nanostructure. We found that the shapes of the nanostructures on the HF-etched seed layer and those on un-etched seed layer are different. The ZnO nanostructure on the HF-etched seed layer also gave better photoluminescence spectra compared to those on un-etched seed layer. These suggest that the surface condition of seed layer has some effect on the growth of the ZnO nanostructure.

Keywords – Zinc oxide nanostructure; seed layer; HF etching

I. INTRODUCTION

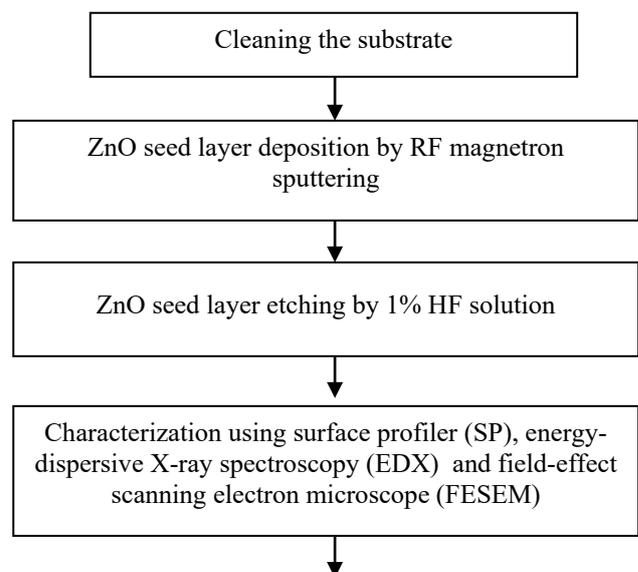
ZnO is a promising material for the realization and future of electronic devices. With its wide band-gap (3.37 eV), high excitonic binding energy, and high breakdown strength, ZnO can be utilized for electronic and photonic devices, as well as for high-frequency applications [1].

Researchers have been conducted extensively on zinc oxide because of its unique characteristics which has semiconducting and piezoelectric dual properties. These properties make ZnO very useful in various applications such as room-temperature and high-temperature ultraviolet (UV) lasers [2], light emitting diode [3], surface acoustic wave devices and gas sensors [4]. These unique nanostructures unambiguously demonstrate that ZnO probably has the richest family of nanostructures among all materials, both in structures and in properties. The nanostructures could have novel applications in optoelectronics, sensors, transducers and biomedical sciences [5]. Manipulation of ZnO nanostructure to be various structures such as prismatic, needle-like, tetrapods, nanorods, nanobelts, nanotubes, nanocombs by various physical and chemical techniques attracts researchers to study their still unknown properties. [6]. Tetrapods shaped whisker shows vibration insulation, microwave absorption, antibacterial effect, and anti static effect [7]. Xu et al. reported the synthesis of needle like morphology near the tip, such as nanopins of ZnO for field emitter cathod [6] of high emission efficiency; the nanowires

with high aspect ratio has been demonstrated to be good sensors [8].

The zinc oxide ZnO nanostructure has attracted great interest in ZnO-based heterojunction devices [9], chemical sensors [10], ultraviolet/blue-emission devices [11], and other devices. Recently, various synthesis techniques have been developed to fabricate ZnO nanostructure such as r. f. sputtering [12], thermal chemical vapor deposition (TCVD) [13], plasma enhanced chemical vapor deposition (PECVD) [14], and sol-gel spin coating [15]. In order to enhance the growth of the nanostructure, we propose the seed layer method. First, a crystallized ZnO seed layer is deposited by RF magnetron sputtering. Then the seed layer is etched by HF solution prior to the synthesise of ZnO nanostructure by thermal chemical vapor deposition (TCVD). The etching process is to prepare better nucleation sites for the ZnO nanostructure growth. In this paper we studied the effect of an etching time to the surface roughness of the thin films for further growth of ZnO nanostructures and characteristics of the ZnO nanostructure were investigated.

II. METHODOLOGY



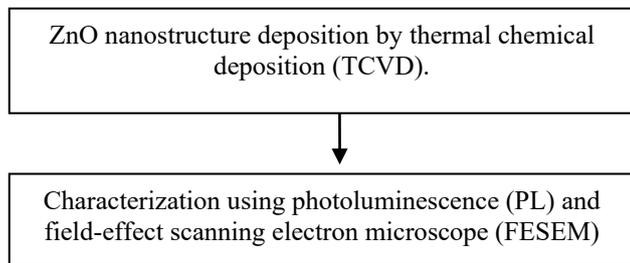


Figure 1 : Overall process flow chart.

Figure 1 shows the overall process flow in this work. ZnO seed layer were deposited on glass substrates by using RF magnetron sputtering using 99.99% ZnO as the target. The sputter chamber was pumped to the background pressure of 5×10^{-4} Pa using a turbo molecular pump. Before loading into the chamber, the glass substrate was cleaned using the standard organic cleaning method using acetone, methanol and deionized water in ultrasonic bath for 10 minutes, in sequence, and then blow dry using argon gas.

During the process of deposition, pure Ar gas (99.99%) at 45 sccm was inserted while maintain the pressure at 5mTorr. The depositions were done in 1 hour, to get ~500nm thick ZnO seed layer.

The surface of the sputtered ZnO seed layer is roughened by 1% HF etching solution before the thermal chemical vapour deposition of the ZnO thin films. The etching time was 1 and 10 seconds.

Next the ZnO nanostructure was deposited using Thermal Chemical Vapor Deposited (TCVD) in a two-furnace system shown in Fig. 2. The precursor is zinc powder. The temperature in furnace 1 is set to 700 °C while in furnace 2 is 500°C. There are two inlet gases which is oxygen and argon. The oxygen flow rate was set to 20sccm. Lastly are the characterization which contains surface morphology and optical properties.

The structural properties of the sputtered ZnO seed layer characterized by using surface profiler to measure the thickness of the surface and the field-effect scanning electron microscope (FESEM) for surface morphology. After TCVD process the sample were characterized by using FESEM and photoluminescence spectroscopy (PL).

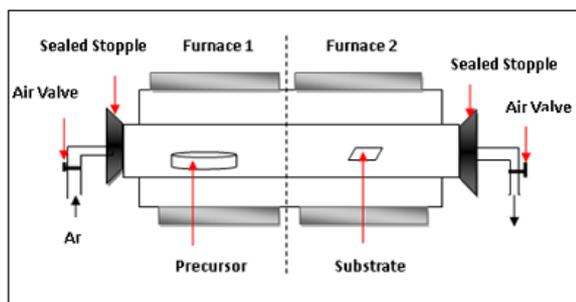


Figure 2 : TCVD setup for ZnO nanostructure deposition.

III. RESULTS AND DISCUSSION

A. ZnO seed layer

Thickness of ZnO seed layer

	Thickness (nm)
Before etching	442.83
Etching (1 seconds)	318.85
Etching (10 seconds)	125.49

Table 1 : Thickness of the surface before and after etching

Table 1 shows the thickness of the ZnO seed layer before and after the HF-etching process. As expected, the seed layer thickness decreases with longer etching time, showing that the ZnO layer was etched by HF solution.

Surface morphology

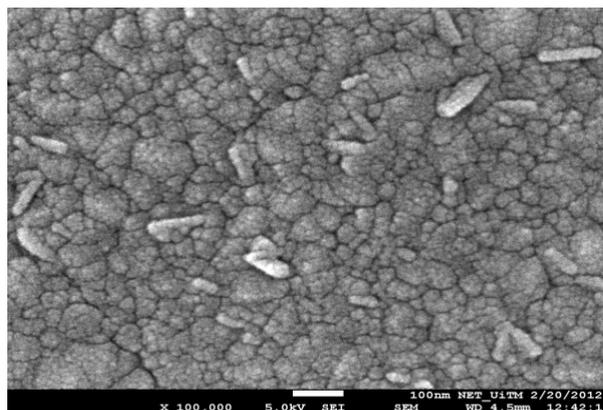


Figure 3 : FESEM images of deposited ZnO seed layer before etching

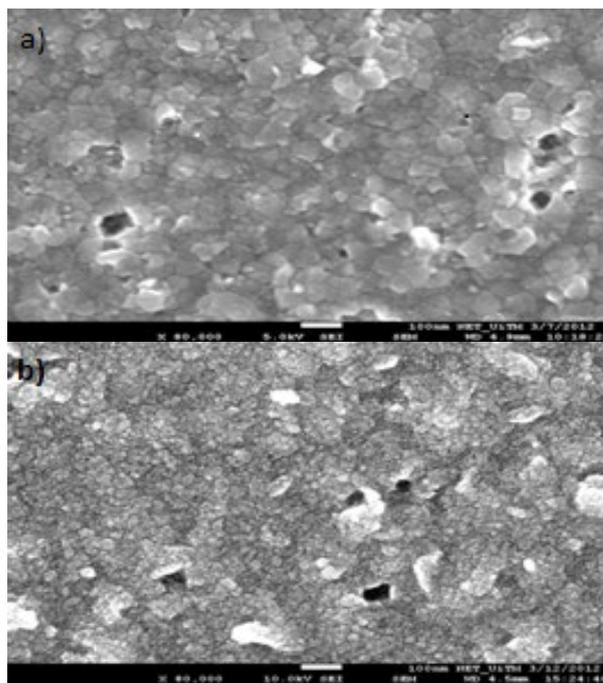


Figure 4 : FESEM images of an etched ZnO seed layer at different etching time (a) 1s (b) 10s

Figure 3 shows the FESEM image of the deposited ZnO seed layer. The deposited thin films consist of nano-sized particles. The morphology of ZnO grains was found to be continuous, dense but with non-uniform sizes.

Figure 4 shows the FESEM images of etched ZnO thin films at different etching time (a) 1s (b) 10s. After the etching the surface becomes rougher and with minimal porous structure. It shows that some of the seed layer of the thin films is etched away during the etching process causing the porosity to happen. The porous surface is expected to facilitate nucleation sizes for the ZnO nanostructures deposition.

EDX Characterization

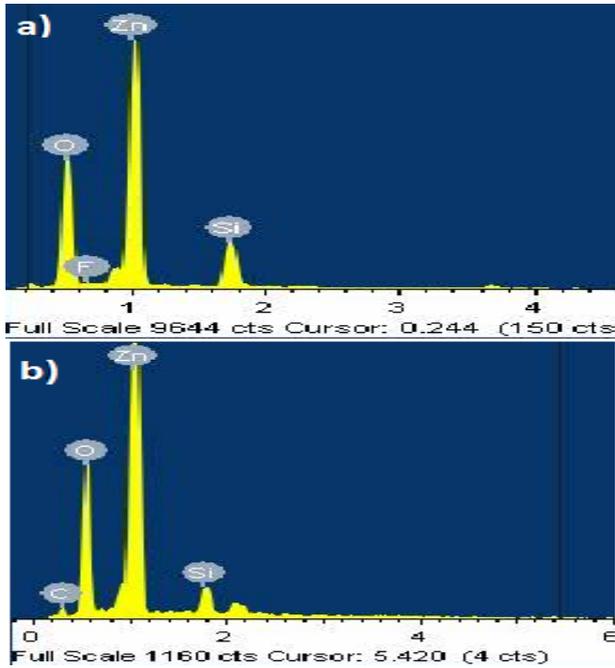


Figure 5 : EDX spectra of etched ZnO thin films at etching time of a)1s b)10s

Figure 5 shows the EDX compositional measurement result for the etched ZnO thin films with 1s and 10s etching time. The result shows peak corresponding to ZnO element in the sample indicating the presence of ZnO even after the etching process.

B. ZnO nanostructure Surface Morphology

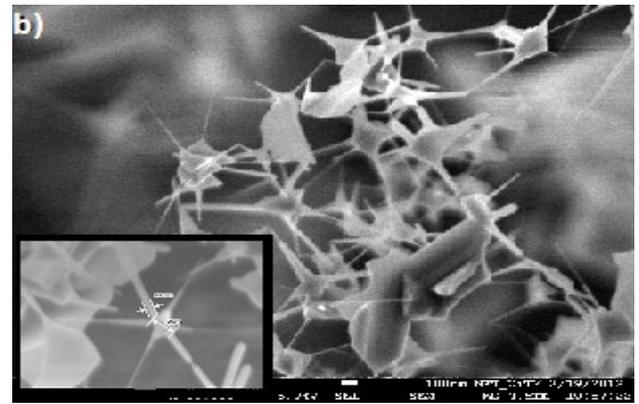
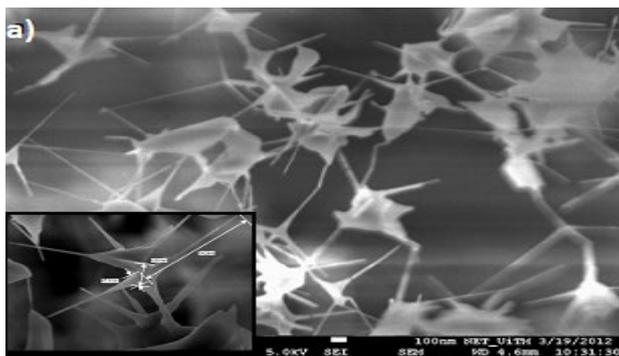


Figure 6 : FESEM images of ZnO nanostructure on ZnO seed layer etched for (a) 1s (b) 10s. The inset shows the enlargement of the nanostructure for better viewing.

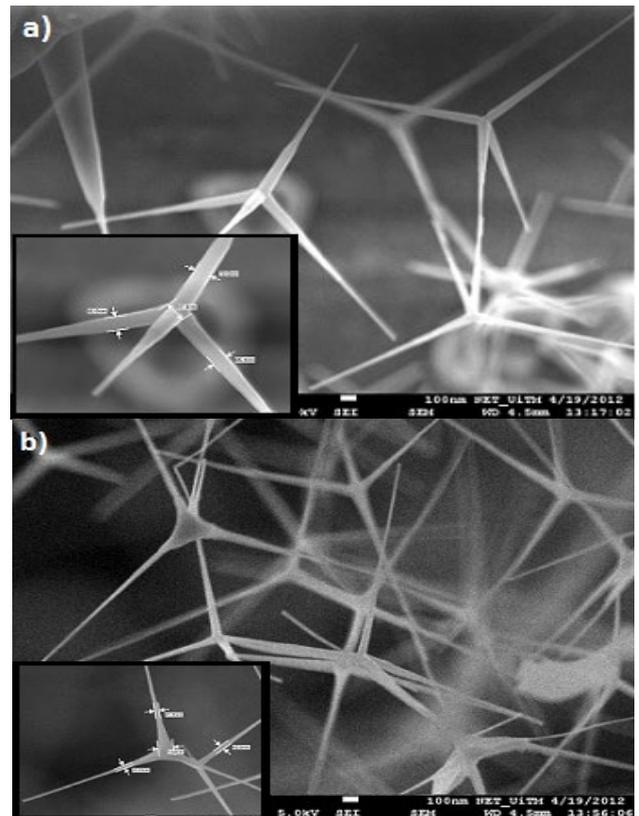


Figure 7 : FESEM images of ZnO nanostructure a) deposited on un-etched ZnO seed layer b) deposited directly on glass substrate. The inset shows the enlargement of the nanostructure for better viewing.

Figure 6 shows the FESEM images of ZnO nanostructure grown by the ZnO seed layer etched at different etching time (a) 1s (b) 10s. The shape of the nanostructure are almost in tetrapods forms. We can see that there is not much difference of the shape and sizes of the nanostructure, with regard to the etching time of the sputtered ZnO seed layer. The average thickness of the rod at 1s etching time is 42.6nm whereas for 10s etching time is 29.6nm. For comparison, we deposited ZnO nanostructures on un-etched ZnO seed layer, and directly on bare glass substrate (without ZnO seed layer).

Figure 7 shows the TCVD-ZnO nanostructures deposited on a) un-etched ZnO seed layer and b) glass substrate. Comparing Fig. 6 and 7, one can notice the difference of the nanostructure shape in which the nanostructures in Fig. 7 are clearly in tetrapods shape. The centre part of the tetrapods for those on etched seed layer are larger compared to those on un-etched seed layer and glass substrate. This suggest the different growth mechanism of the nanostructure, probably starting from the nucleation stage. However further investigation need to be done in order to understand and propose the growth mechanism.

Photoluminescence

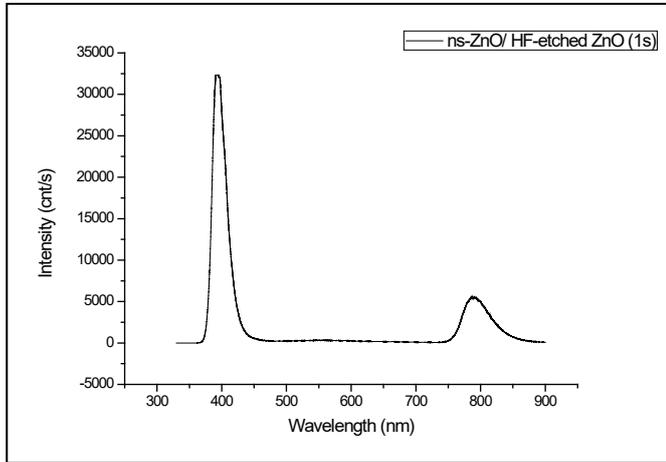


Figure 8: Photoluminescence spectra for ZnO nanostructure (ns-ZnO) on ZnO seed layer etched for 1s in HF solution

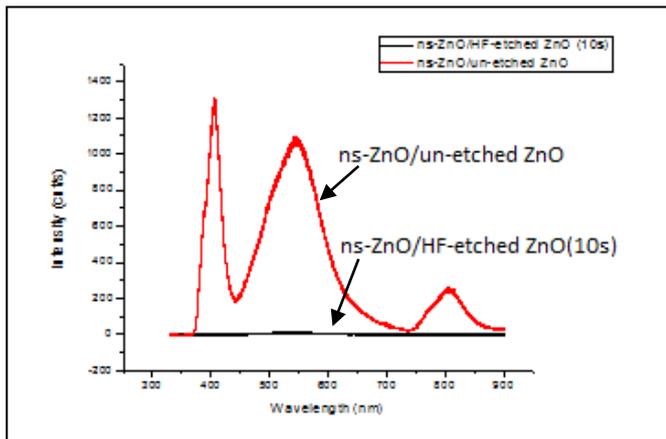


Figure 9: Photoluminescence ZnO nanostructure (ns-ZnO) on ZnO seed layer etched for 10s in HF solution and ns-ZnO on unetched seed layer.

Room temperature PL measurements of the ZnO nanostructure were obtained under excitation of He-Cd laser to study the light emitting properties of the samples. The PL spectra of the thin films in the range of wavelength from 330nm until 900nm are presented in Figure 8 and 9. PL spectra obtained from the ZnO nanostructures on the ZnO seed layer etched for 1s is shown in Fig. 8, whereas those on 10s-etched and un-etched seed layer are shown in Fig. 9.

From the spectra, a strong PL emission at 400nm for both samples with 1s etching time and from the un-etched ZnO layered which is a near-band edge UV emission is observed. This is due to the electronic transition from near conduction band to valence bands [16]. It can be seen that the sample of 1s etching shows the highest peak at 400nm. Another peak can be observed at around 800nm for the 1s etching sample. From Fig. 9 for the nanostructure on un-etched ZnO, beside the peak at 400nm, another broad peak can be observed at 540nm which belongs to the green emission. The most possible reason for the green emission of the ZnO thin film is caused by singly ionized oxygen vacancies[17]. The increased of oxygen vacancies will cause the increment of visible luminescence [18].

On the other hand, the PL spectra for the nanostructure on 10s-etched ZnO seed layer shows no emission peak. As for the nanostructures deposited directly on glass the measurement cannot be done due to extensive peeling. The nanostructures, were in form of a powder-like material on the glass substrate.

IV. CONCLUSION AND FUTURE RECOMMENDATION

ZnO nanostructures were deposited on ZnO seed layers. In order to enhance the nanostructure growth, the ZnO seed layers were etched by HF solution to roughen the surface in order to facilitate nucleation sites. From FESEM results, the sputtered ZnO seed layer consist of continuous and dense nano-sized grains but with non-uniform sizes. Due to the HF-etching the surface becomes rougher and some porosity were formed. The thickness of the ZnO layer decreased with the etching time, which is the evidence of ZnO removed by HF solution. The ZnO nanostructure deposited on the ZnO seed layers were observed by FESEM and we found that the shape of the nanostructure was different between the deposited on HF-etched ZnO seed layers and those deposited on un-etched ZnO seed layers. The shape of ZnO structure deposited on un-etched ZnO seed layer was similar to those deposited directly on glass substrate. These suggested that the surface condition of the ZnO seed layer played a role on the growth mechanism of the ZnO nanostructure. PL spectra of the nanostructure on 1s HF-etched ZnO showed better characteristics than those on 10s and un-etched ZnO seed layers.

For future recommendation, in order to further investigate the effect of the seed layer on the nanostructure growth, the etching parameters (HF solution concentration, post-etched rinsing method, etc) and ZnO seed layer crystalline quality can be considered.

ACKNOWLEDGMENT

The author is grateful to all staff and members of NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering; and Nano-Scitech Centre, Universiti Teknologi MARA (UiTM) Malaysia for their support, guidance, criticism and advices in completing this project. Then I also like to extend my gratitude and appreciation to Nur Sa'adah Muhamad Sauki, Nor Syahirah Kamorozaman, and Shafinaz Sobihana for all the guidance, support and advice provided to me throughout the study for the completion and success of this project.

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