Optical Properties of Nano-Porous Structure ZnO Prepared by Catalytic-Immersion Method

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Abstract. This paper presents an efficient method to prepare ZnO nano-porous structure via immersion of Si substrate with catalyst assistance (gold) in the mixture of zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O) and urea (CH₄N₂O). Photoluminescence (PL) spectra of nano-porous ZnO revealed it had strong UV emission with low oxygen defect. Optical properties are found to be significantly affected by varying the Zn²⁺: urea ratio but from surface morphology observation, the porous structure was stable and seemingly unchanged.

1. Introduction
Nanosized ZnO, due to its unique properties such as chemical, structural, electrical, thermal and surface characteristics can be used in a wide range of applications depending on its shape-size controlled and material-dependent properties [1-4]. Being one of the dominant material for nanotechnology, ZnO versatility rise the range of application due to their structure, wide direct band gap (3.37 eV), large exciton binding energy (60 meV), size and thermal stability which make ZnO suitable for a wide range of devices [5, 6]. These unique properties of ZnO nanostructures attributed from its nanoscale shapes and size.

ZnO nanostructures is a versatile material that rich with various configurations such as nanorods, nanowires, nanotubes, nanoflower, nanosheet, etc. [5-9] which have been successfully fabricated by variety of growth condition. Due to all these properties, ZnO is one of the most promising materials for electronic applications such as light-emitting diodes (LEDs), UV photoconductive sensor, chemical sensors and solar cells [10-13]. Reported that, ZnO nanorods can be successfully achieved by various deposition techniques such as spray pyrolysis, chemical vapor deposition (CVD), thermal treatment, sol-gel spin coating process, immersion, etc. [14-18] that have been used to generate a structure of ZnO nanostructures. Among the aforementioned techniques, immersion technique is preferred due to its simplicity, faster operation, less power consumption, and lower cost than the other techniques. It is well known that the properties of ZnO produced by immersion method are dependent on its preparation parameter such as material concentration,
deposition temperature and time. Concentration plays an important role in controlling the morphologies and size of a ZnO nanostructure.

In this work, we study the influence of stabilizer molarity (urea) on the growth of ZnO using wet chemical approach on gold-seeded Si substrate and their properties were investigated. However, controlled synthesis of ZnO nanostructures using urea as a stabilizer still needs further investigation. But it is unfortunate that the papers on the synthesization of ZnO nanostructures are rarely reported to date.

2. Experimental details

2.1. Substrate preparation

One-side polished P-type silicon (Si) wafer (100) used as a substrate in this work was cut into 2 x 2 cm dimension or less for the growth of ZnO. It was ultrasonically cleaned with acetone, methanol, HF:water (1:10 ratio) and deionised (DI) water to remove organic and inorganic contamination that will affect the quality of ZnO. It was throughly dried with nitrogen gas before sputter-coated with gold for 60 s using gold target in argon plasma, which are similar to that described previously [18]. Then it was annealed at 500 °C for 30 min to ensure good adherence and improved crystallographic quality.

2.2. Synthesis of samples

The solution were prepared using a mixture of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$:6H$_2$O) (purify 99.9 %), and urea (CH$_4$N$_2$O) that previously dissolved separately in DI water. The molar ratio of Zn$^{2+}$: urea was varied from 2:1, 1:1, 1:2, 1:4, and 1:6. Gold-seeded Si substrates were then immersed in Zn$^{2+}$ aqueous solution at above condition in pyrex boiling tubes for 4 h at 90 °C. The deposited films on the substrates were annealed at 500 °C and the sample was subsequently taken out after cooling it down to room temperature. The chart of synthesization process is shown in figure 1.

![Figure 1. Chart of the research methodology](image-url)
2.3. Characterisation of samples

The obtained products were characterized with a field-emission scanning electron microscope (FESEM) using JEOL JSM-7600F, to determine the surface morphology of the samples. The optical properties were analyzed using photoluminescence spectroscopy (PL), PL-Raman Horiba Jobin Yvon HR800 using He-Cd laser source and UV-VIS-NIR spectrometer (Varian Cary 5000) using diffuse reflectance accessory (DRA).

3. Results and discussion

3.1. Surface morphology

From FESEM micrograph in figure 2(a), it is obviously noted that the samples consist of hierarchical nano-sheets with network pores structure (ZnO nano-porous) grow in all direction of the template surface. The irregular pores structure of ZnO thin films grow on gold-seeded Si substrate remained similar with the synthesized parameters whether in size or structure, similar with reported by Khusaimi et.al [19]. The diameter of ZnO pores is about 50 – 75 nm in all solutions even at higher molar ratios (higher concentration of urea). EDX spectrum show the composition of the sample consists of Zn and O element which show the purity of the samples produce. This composition consistent with PL spectra in figure 2 that show nano-ZnO porous ZnO thin films have low oxygen defect.
3.2. Optical properties

PL spectra of ZnO thin films growth at varying stabilizers ratio are presented in figure 3. The measurement was conducted at room temperature. PL spectrum for as deposited sample shows the existence of 2 peaks centered at UV emission is about 402 nm (3.09 eV) attributed to near band gap exciton emission and the broad emission in the blue-green region of 500 – 700 nm might be due to oxygen deficiency or due to zinc vacancy in ZnO films[20]. According to the PL spectra grown at higher concentration of precursor (Zn(NO$_3$)$_2$.H$_2$O) solution at 0.10 M with 0.05 M of urea (2:1), a weak violet emission with the lowest intensity of visible emission can be observed. As ZnO nanostructures grown at equal molar ratio concentration (1:1), a strongest PL emission at violet region and relatively weak visible emission were detected. As the concentration of stabilizer increase (1:2, 1:4 and 1:6), the violet emission intensity gradually decreased. It can be seen that the violet emission has much sharper peak which might be due to the crystallization perfection [20]. Figure 4 shows the intensity of UV over visible emission at 402 and 600 nm respectively. The result revealed that 1:1 ratio is the optimum parameter to prepare Zn$^{2+}$ solution to grow ZnO nano-porous due to highest intensity in UV/Vis intensity ratio graph that can led for further investigation to be promising material for optoelectronic devices.

![Figure 3. PL spectra of nano-porous ZnO](image)

Figure 5 shows optical and absorbance properties of nano-porous ZnO on gold-seeded Si substrate measured using external diffuse reflectance accessory (DRA). The transmittance spectra of ZnO nano-porous structure with 2:1 molar ratio solution exhibited highest transparency in the visible region (66%) followed by 1:1 (53%) and the lowest transmittance is 2:1 (50%). This spectra shows that the transmittance tend to increase with the increasing of stabilizer concentration. Since ZnO thin films in this work were deposited with different stabilizer solution concentration, the thickness and the
imperfect alignment of hierarchical ZnO nano-sheet with network pores structure of the films may attributed to the reduction of optical transmittance due to random scattering of incident light [21, 22]. However, the absorptivity of ZnO thin films 1:6 shows an improvement in absorption properties in UV region (below 400 nm) compared with the other molar ratio concentration. All these results indicated the optical properties of ZnO were highly dependent on the Zn$^{2+}$: urea solution concentration [23].

![Figure 4](image.png)

**Figure 4.** UV/Vis intensity ratio of nano-porous ZnO thin films

4. Conclusions

We have successfully grown ZnO nano-porous structure on Si substrate (100) with the assistance of gold act as a catalyst via immersion technique. FESEM image showed the morphology of nano-porous ZnO is stable and was not affected by variation of solution concentration. The diameter of pores is about 50 – 75 nm. The PL spectra show that 1:1 ratio concentration has a relatively stronger UV emission than the other samples. These nanostructures indicate that Zn$^{2+}$: urea solution plays an important role to determine the optical quality of the nanostructures. UV-Vis NIR spectra reveal that the highest optical transmittance achieved at higher solution concentration ratio.

![Figure 5](image.png)

**Figure 5.** (a) Transmittance and (b) absorption spectra of ZnO at varying stabiliser molarity.
5. References

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Acknowledgments
Authors would like to acknowledge Universiti Teknologi MARA (UiTM) (Research Management Institute, 600-RM/DANA 5/3/RIF (666/2012)) for their financial support.