The effect of different molarities of precursor Zn(NO$_3$)$_2$.6H$_2$O to the growth of ZnO by solution-immersion deposited on ZnO seeded template

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Abstract. ZnO films were grown on glass substrates by mist-atomization, with the growth temperature of 300 °C to form ZnO seeded template. The ZnO seeded template then undergo second deposition method, which is solution-immersion method to grow ZnO on the ZnO seeded template thin film. The thin films were immersed in different molarities of starting materials; which are zinc nitrate hexahydrate and HMTA. The molarities were varied from 0.05, 0.10, 0.20 and 0.40 M. As a control to the study, the ZnO seeded template which undergoes mist-atomization only, denoted as MA only is prepared for comparison studies to the other samples. The properties of the products were examined by photoluminescence (PL) spectrophotometer, Raman spectrophotometer, and ultraviolet-visible (UV-Vis) spectrophotometer. From the PL measurement, it shows that 0.40 M sample have highest UV emission and from Raman measurements, it was found that the sample immersed in 0.40 M precursor have high crystal quality. From UV-Vis measurements, sharp UV emission at ~378 nm is observed and 0.40 M ZnO thin film shows a better absorption properties.

1. Introduction
Zinc oxide (ZnO) is a semiconducting material with a wide and direct band gap of 3.37 eV at room temperature and high exciton binding energy of 60 meV. ZnO consists of two interconnecting sublattices of Zn$^{2+}$ and O$^{2-}$. Every of the Zn ions are surrounded by tetrahedral O ions, and vice versa. This semiconducting material received considerable interest due to its wide range of application such
as gas sensor [1], solar cells [2], UV photoconductive sensor [3], and biomaterial [4]. Diverse synthetic approaches have been introduced for ZnO nanostructures such as RF magnetron sputtering [5], electron beam evaporation [6], and pulse laser deposition [7]. Among these, mist-atomization and solution-immersion method are appropriate for the synthesis of ZnO nanostructures due to low cost, suitable for large production fabrication and environmentally friendly. To the best of our knowledge, our study is the first to grow ZnO nanostructures by the following two-step deposition techniques; (i) mist-atomization and (ii) solution-immersion method. First, ZnO nanoseed were deposited on Au-seeded glass substrate by ambient mist-atomization method. Next, ZnO nanostructure was grown by facile solution-immersion method on the ZnO seed layer. The influence of precursor solution molarity to crystal quality of ZnO thin films obtained is studied.

2. Experimentals

2.1. Preparation of ZnO seed layer by mist-atomization

The starting materials used in this study were zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O) and hexamethylenetetramine, HMTA (C$_6$H$_{12}$N$_4$). Zinc nitrate hexahydrate of Riedel-de Haën brand was used as the source of zinc for the growth of zinc oxide nanostructures. As the stabiliser in the starting solution, HMTA of same brand with 99-100.5 % pure analytical grade was used. Cleaned glass substrates with size of 2 x 2 cm$^2$ were sputter-coated with gold to form Au seed layer as in Figure 1. Then, ZnO nanoseed were grown on the Au seed layer by mist-atomization method as in Figure 2. The ZnO seed layer were prepared by mist-atomization technique as reported in our previous work [8].

![Figure 1](image1.png)  
Figure 1. (a) Deposition of Au seed layer and (b) Au-seeded glass

![Figure 2](image2.png)  
Figure 2. (a) Deposition of ZnO seed by mist-atomization method (b) ZnO/Au seeded glass
2.2. Synthesis of ZnO by solution-immersion method

![Figure 3](image)

**Figure 3.** (a) Deposition of ZnO by solution-immersion method and (b) ZnO/ZnO/Au template

Next, the ZnO seeded templates undergo deposition method to grow well-aligned ZnO nanostructure by solution-immersion as in Figure 3. The details for the method are as explained elsewhere [9]. The ZnO seeded templates prepared by mist-atomization were immersed in different molarity of precursor of 0.05, 0.10, 0.20 and 0.40 M.

2.3. Characterizations

The photoluminescence (PL) and Raman properties of the synthesized films were deliberated using Horiba Yvon-79 DU420A-OE spectrophotometer with a helium-cadmium (He-Cd) excitation laser source operating at 325 nm for PL and 514 nm for Raman. The UV-Vis spectroscopy was completed using a Varian Cary 5000 UV-Vis-NIR spectrophotometer with the wavelength range between 300 and 8000 nm with a data interval of 1 nm.

3. Results & discussion

3.1. Photoluminescence studies

Figure 4 and 5 present the PL spectra of the ZnO thin films prepared at various molarities. The luminescence of the ZnO thin films is closely related to the crystallinity of the film. As the crystallinity of the film is improved, the density of the defects decreases. The films were measured using room temperature (RT) PL emission spectra in the wavelength range of 330-900 nm at an excitation wavelength of 325 nm. In general, ZnO films exhibit two emission peaks, which correlate to the UV emission and the visible emission. The ~370 nm UV emission has been well understood to the association of direct recombination at near band edge of photogenerated charge carriers (exciton emission), meanwhile the green wavelength emission is due to the structural defects and intrinsic defects such as oxygen vacancies [10], zinc interstitials [11] and zinc vacancies [12].

As shown in Figure 4, the PL spectra in all samples show UV emission at the near band edge centred at 380 nm. The peaks appear at ~380 nm is due to excitation transition of ZnO. It is associated with the free-exciton recombination [13]. The higher the concentration of the precursor solution, the higher the UV intensity except for the sample deposited by mist-atomization (MA) only. The sample immersed in 0.05 M of Zn\(^{2+}\) solution shows the lowest intensity amongst all. The noticeable UV emission of ZnO thin film with 0.40 M shows that the thin film has a low level of defects compared to the other samples. The intense UV emission could be related to the much higher crystal quality [14] of the sample with molarity of 0.40 M in comparison to the other molarities. Figure 4 depicts that the intensity of UV emission of ZnO thins films increases with increasing molarity. As the molarity increased, the thickness of the ZnO films observed is thicker. M. F. Malek et. al [14] proposed that the thicker film contains more zinc particle which caused the increase in carrier concentration and hence improving the UV emission paragraphs are indented.

The red shift (shifted to the higher number of wavelength) and broader width of the UV emission as observed in Figure 4 could be attributed to the inhomogeneous strain distribution due to large lattice mismatch between the ZnO thin film and the ZnO seed layer [15]. The samples with lower molarities
showed red-shift properties and the range of UV emission is broader. From Figure 4, it can be concluded that ZnO thin film of 0.40 M molarity have lower lattice mismatch compared to ZnO thin films with other molarity.

Figure 4. UV emission PL spectra of ZnO thin films with the variation molarities of 0.4 M seeded ZnO (MA only), 0.05 M, 0.10 M, 0.20 M and 0.40 M.

Figure 5. Visible emission PL spectra of ZnO thin films with the variation molarities of 0.4 M seeded ZnO (MA only), 0.05 M, 0.10 M, 0.20 M and 0.40 M

Figure 5 shows the broad visible emission in the wavelength range of 500 to 800 nm was observed. The peaks for the deep-level emission were observed centred at about 610 nm. As stated before, the
green emission was attributed to structural or intrinsic defects of ZnO thin film. Some researchers reported below temperature of 1300 °C, Frenkel reaction occurs which result in zinc interstitials meanwhile at temperature above 1300 °C, there is Schottky reaction which led to oxygen vacancies [16, 17]. As the ZnO thin films in this work were annealed at 500 °C, it is show that Frenkel defects of zinc interstitials predominate the defects in the visible PL spectra.

Table 1 shows the UV emission to visible emission ratio, $I_{uv}/I_{vis}$ of ZnO thin films with varied molarity. ZnO thin film synthesized from 0.40 M molarity shows the highest UV to visible emission ratio. This indicates that the 0.40 M ZnO thin film exhibit good crystalinity with lower defects.

| Molarity, M | Ratio, $R = I_{uv}/I_{vis}$ |
|------------|----------------------------|
| 0.4 (MA only) | 0.07334 |
| 0.05 | 0.11786 |
| 0.10 | 0.12726 |
| 0.20 | 0.07529 |
| 0.40 | 0.24500 |

3.2. Raman studies

Raman scattering is an effective technique to investigate the crystallization, structure and defects in the nanostructure materials. From the group theory, hexagonal wurzite ZnO belongs to $C_{6v}^4$ space group and the point of the Brillouin zone are $A_1+2B_1+E_1+2E_2$; all will have two modes at the center of Brillouin zone [18, 19]. Generally, the polar $A_1$ (LO) mode is associated with oxygen deficiency of the film. Meanwhile, the non-polar phonon modes of $E_2$ symmetry have two frequencies, $E_2$ (high) and $E_2$ (low). $E_2$ (high) is related with the oxygen atom and $E_2$ (low) related with the vibration of the heavy Zn sublattice [20]. Some researchers reported that $E_2$ (high) shifted due to intrinsic defect in ZnO films and agreed that the shift of $E_2$ (high) can give information on stress for the thin films [21]. The film is under compressive stress when the $E_2$ (high) is up shifted, whilst a tensile stress will lead to its downshift [18, 22]. In the other hand, $E_2$ (low) determines the crytalinity of the films.

Figure 6 depicts the typical room temperature Raman spectra of ZnO growth by MA only, immersed in 0.05, 0.10, 0.20, and 0.40 M precursor. From the Figure 6, the sharpest and highest peak of $E_2$ (low) is owned by thin film prepared with 0.20 M. There is a small difference in intensity for the sample with 0.40 M. The thin film which undergoes deposition by mist-atomisation (MA) only shows the lowest Raman intensity, followed by the thin films immersed in 0.05 and 0.10 M of precursor solution. The presence of intense $E_2$ (low) peaks of thin films with 0.20 and 0.40 M precursor concentration portrayed the thin film exhibit best crystal quality with a hexagonal wurzite phase compared to the other samples with different molarities. According to the literature, the $E_2$ (high) wavenumber value for bulk ZnO is 437 cm$^{-1}$. From the Figure 6, the average Raman value for all of the samples is about ~432 cm$^{-1}$. All the samples showed downshift properties which revealed there is tensile stress exist in the films.
As stated before, $A_1$ (LO) is related with oxygen deficiency of the ZnO thin films. The $A_1$ mode is attributed to the vibration along the c-axis [23]. According to theoretical calculation, the $A_1$ (LO) wavenumber for bulk ZnO is 574 cm$^{-1}$. In this work, $A_1$ (LO) for ZnO thin films with 0.40 M has highest Raman shift (shifted to the right). A higher wavenumber proposed there is reduction in the defects of the ZnO films and better crystalinity of the films. The small and suppressed intensity of $A_1$ (LO) mode shows the reduction of oxygen deficiency effect on the ZnO films and the ZnO is grow along c-axis orientation. All the films generally and the thin film with 0.40 M precisely showed improvement in crystalinity compared to bulk ZnO and other set of samples.

Table 2. The resulting dataset for Raman energy compromises three main energies of ZnO thin films with varied molarity

| Molarity, M | $E_2$ (low) | $E_2$ (high) | $A_1$ (LO) |
|------------|-------------|--------------|------------|
| 0.4 (MA only) | 93.80 | 432.44 | NIL |
| 0.05 | 93.81 | 432.44 | NIL |
| 0.10 | 94.52 | 432.44 | 578.95 |
| 0.20 | 93.58 | 433.86 | 579.18 |
| 0.40 | 94.52 | 433.62 | 579.66 |
3.3. UV-Vis studies

Figure 7 represents the absorbance spectra of ZnO thin films with the variation molarities of 0.4 M seeded ZnO (MA only), 0.05 M, 0.10 M, 0.20 M and 0.40 M in the wavelength range of ~290 nm to 800 nm. The range of inter-transition is 370-390 nm. The absorption edges observed for all ZnO thin films were about ~378 nm, corresponding to the intrinsic band gap of ZnO which is 3.26 eV. At this wavelength, there are transitions of electrons from the valence band to the conduction band. The different molarity shows that there is great influence to the absorbance properties of the ZnO thin films by varying the molarity.

Commonly, there are three main factors that are able to manipulate the absorbance of the ZnO films; which are surface roughness, defect centres and oxygen vacancies [24]. The higher absorbance of the samples with higher concentration could be attributed to the multiple scattering of the incident light within the thin film. As the concentration increases, more ZnO nanostructures produced and hence there is no free space for the light to transmit. From Figure 7, it can be seen that ZnO thin film with 0.40 M shows the highest UV intensity amongst all. The high intensity at wavelength ~378 nm of higher molarity indicates that there are more activities of direct transition of electrons; between the edge of valence band and the conduction band. The intensity increases with increasing molarity because the thicker film contains more zinc particles, leading to an increase in the carrier concentration and enhancing the UV emission.

As compared to the ZnO thin film with 0.40 M, the ZnO thin film with 0.4 M (prepared by MA only), 0.05 M, 0.10 M and 0.2 M experienced lower UV light absorption which considered due to higher defects in the structural properties of the ZnO thin films. L.Y.Y. Bu reported that well ordered nanostructure effectively traps the light and reduces transmittance; which means the film has enhanced probability of absorption [25]. The ZnO thin film of 0.40 M has better orientation compared to the other films, which supported by the photoluminescence and Raman studies.

![Absorbance Spectra of ZnO Thin Films](image)

**Figure 7.** UV-Vis absorbance spectra of ZnO thin films with the variation molarities of 0.4 M seeded ZnO (MA only), 0.05 M, 0.10 M, 0.20 M and 0.40 M.
4. Conclusion
In the present paper, we have investigated good crystal quality with high absorption properties ZnO formed on ZnO seed layer. The ZnO seed layer was synthesized by mist-atomization method, whilst the ZnO nanostructure was deposited by solution-immersion method. From PL UV emission, it can be concluded that ZnO with 0.40 M have lower lattice mismatch compared to the other samples, which proved that the sample have lower defects. From PL visible spectra, it is believed that the defect-related green emission was governed by Frenkel defects of zinc interstitials. From Raman studies, all the samples showed that tensile stress exist in the films. Based on three main energies of Raman energy, it is proved that ZnO with 0.40 M has highest crystal quality amongst all. UV-Vis studies shows that ZnO with 0.40 M has highest probability of absorption which indicates the film has better orientation compared to the other films. These results suggest that a suitable precursor molarity should be used to obtain higher crystal quality ZnO thin films for applications in optoelectronic devices such as sensors and solar cells.

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