The Influence of Immersion Time to the Optical properties of ZnO Growth on PMMA-coated Substrate by Solution-Immersion Method

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Abstract. We present the growth of ZnO on PMMA-coated substrate under influence of different immersion time by solution-immersion technique. PMMA polymer was coated on the substrate by spin-coating method. The PMMA-coated substrate was then prepared for non-immersed and immersed for four (4) and six (6) hours in zinc solution. The optical properties of the film obtained were characterized using Photoluminescence (PL), Raman Spectra and Ultraviolet-Vis (UV-Vis) spectroscopy. It was found that shorter time of immersion (4 hours) produced higher intensity of PL and Raman. However, the reverse was found for UV-Vis measurement. The low absorption that was shown from the film immersed for 4 hours may correspond to the random distribution and orientation of ZnO particle growth on PMMA-coated substrate.

1. Introduction
In recent years, the synthesis of zinc oxide has received considerable attention owing to the many interesting and unique properties like a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV[1-3]. So far, there have been many of studies the ZnO in the form of thin films. This is due to the ZnO thin films that is highly transparent in the visible region [1]. Transparent ZnO thin films are well-known for the application in electronic and optoelectronic devices like transparent thin film transistor (TTFTs), optical filters, transparent electrodes, back-reflector in solar cells thin film and space applications [2, 4]. There are various types of methods to fabricate ZnO such as
thermal oxidation, chemical vapor deposition, RF sputtering, sol-gel, spray pyrolysis and others [5, 6]. Among these methods, sol-gel has advantages due to its ability to tune the size of ZnO to µm and nm level, low-cost, lower crystallization temperature and large surface area coating capability [7].

Polymers have been used in various applications like power tool handles, cable, jackets, capacitor films, electronic packaging materials and others. Recently, the electrical and optical properties of polymers have been extensively investigated due to their application in optical devices [8]. The polymer that be chosen in this work is poly (methyl methacrylate) (PMMA). PMMA is a transparent polymeric materials, which possesses many desirable properties such as light weight, high light transmittance, chemical resistance, high rigidity, good tensile strength and hardness, colorless, resistance to weathering corrosion and good insulating properties [8, 9]. Furthermore, PMMA has extensive application in the field of sensor, coating and others due to its good optical transparency and processability[10]. Commonly, the spin-coating methods has always been used to fabricate PMMA as the method is easy, fast, low-cost, controllable [11] and produced uniform thickness of PMMA.

Organic-inorganic combinations are of great interest, owing to their excellent structural and optical properties [12, 13]. Introducing ZnO on PMMA surface mainly focuses on improving the optical properties of the films that was acting as multifunction materials in UV shielding, antibacterial or bactericides [10]. Furthermore, there have been reports that the free surface energy of the films will be enhanced by introducing metal films into polymer [10].

Have been reported that 4 hours of immersion time successfully obtained to growth ZnOnanorods on the substrate. However, the ZnO was grown on the other seed layer like a gold or ZnO-seed [14]. Therefore, due to the optimization of 4 hours have been done before, we are increasing the immersion times until about 6 hours and on different seed layer. Thus, in this work we are investigating the growth of ZnO on PMMA-coated substrate where PMMA-coated substrate acting as a seed layer. Further, we are focused on the effect of different immersion times to the growth of ZnO on PMMA-coated substrate and the optical properties of the films were being studied.

2. Experimental work

![Flow chart for the growth of ZnO on PMMA-coated substrate](image-url)

Figure 1. Flow chart for the growth of ZnO on PMMA-coated substrate
2.1. Substrate preparation
The glass substrate was prepared by cutting into 1.5 cm x 2 cm of dimension. After cutting process, the glass substrate was cleaned by using three different solutions; methanol, acetone and distilled water. The glass substrate was placed in the beaker and the solution was filled up until all the substrate fully immersed. Then, the beaker was placed in the sonicator bath for 10 minutes. The process was repeated for two times for each of the solutions. Finally, the clean substrate was dried by using argon gas and ready to be used.

2.2. Material preparation
The ZnO sol-gel was prepared as follows: zinc nitrate hexahydrate Zn(NO$_3$)$_2$·6H$_2$O and hexamethylenetetramine (HMTA) (CH$_4$N$_2$O) was dissolved in distilled water, and the both of the solution were mixed together at room temperature. At the same time, PMMA solution was prepared by dissolving PMMA powder with average molecular weight of 120,000 in a toluene solution. Toluene was acting as the solvent in order to prepare PMMA solution. All of the solutions prepared were stirred for 24 hours at 60 °C for aging process to make the solution homogeneously mingled.

2.3. Growth deposition
2.3.1. Spin coating. PMMA was deposited on the glass substrate using the spin - coating technique. The spin-coating time was 50 s. In the beginning 10 s, the spin-speed of the glass substrate was 3000 rpm, in the middle 30 s, the spin-speed was 6000 rpm and in the latter 10 s, the spin-speed was 2000 rpm. After coating, the sample was dried at 100 for 10 minutes.

2.3.2. Immersion. For non-immersion, the substrate with PMMA on it was not immersed in the zinc solution. The process continues for the PMMA-coated substrate that was immersed in a zinc solution by immersion method for 4 hours and 6 hours at temperature of 90 °C. After immersion, the films was annealed for 20 minutes at 100 °C. Subsequently, the samples were cooled at room temperature before taken to the characterization stage. The schematic diagram for growth deposition of ZnO on PMMA-coated substrate can be seen in Figure 2 and Figure 3 and the parameter was stated in Table 1.
Table 1. Parameter of ZnO growth on PMMA-coated substrate at different times of immersion

| No. of sample | Time of immersion | Temperature of immersion (°C) | Annealing temperature (°C) | Annealing time (minutes) |
|---------------|------------------|-----------------------------|--------------------------|-------------------------|
| (a)           | Non-immersion    | 90                          | 100                      | 20                      |
| (b)           | 4 hours          | 90                          | 100                      | 20                      |
| (c)           | 6 hours          | 90                          | 100                      | 20                      |

2.4. Characterizations
The optical properties were synthesized by using Photoluminescence Spectrometer, Raman Spectra and Ultraviolet-Visible (UV-Vis) Spectroscopy.

3. Results and discussions
The optical properties of ZnO growth on PMMA-coated substrate were analyzed by using Photoluminescence Spectrometer (Horiba JobinYvon), Raman Spectra (Horiba JobinYvon) and UV-Vis (Carry 5000 UV-Vis-NIR Spectrophotometer).

3.1. Photoluminescence (PL) spectra

Figure 4. PL spectra of ZnO growth on PMMA-coated substrate at different time of immersion (a) non-immersion, (b) 4 hours and (c) 6 hours
Figure 4 demonstrated the PL spectra of ZnO growth on PMMA-coated substrate at different immersion times; 4 hours and 6 hours in the range wavelength of 300 - 800 nm. The spectra also show for the film that was non-immersed as shown in figure 4(a). In case of non-immersed, the film was prepared without ZnO growth on it. Therefore, the film present as pristine PMMA-coated on the substrate. In general the PL spectrum consists of two characteristic parts: a short-wavelength region located in the ultraviolet region and broad spectral bands in visible region [15]. The spectrum shows for the non-immersed film, two peaks of emission appeared centred at 286 nm and 441 nm of wavelength. After the films immersed for 4 hours and 6 hours, the peak of emission shifted to the longer wavelength, centred at 412 nm and 578 nm. The shifted wavelength may indicate that the films immersed in different immersion times were dominated by larger domains [16]. The peak in UV region called the UV emission or near band edge (NBE) which contributed to the free exciton recombination, while the visible emission originates from the defects[17].

The ZnO growth on PMMA-coated substrate at 4 hours immersion time depicts good intensity and sharp peak in the UV emission. As be reported that the appearance of sharp and strong the UV emission indicates the ZnO may have good crystalline structure in the samples[15]. However, after immersion time enhanced to 6 hours, the intensity reduced with broad and wide peak as shown in both UV and visible emission. The reason may due to the crystalline structure of the ZnO have possibility changes and defected. The longer periods of immersion time probably causing the ZnO underwent crystal restructuring during the immersion process in the aqueous solution [7]. As a result the films might be affected and have defect in its structure which give the lower intensity and broad band emission [18]. Therefore, 4 hours of immersion time present the films have good intensity and better crystalline structure of ZnO compared to the films that are non-immersed and immersed for longer immersion times.

3.2. Raman Spectra
Raman spectroscopy provides information on the vibrational properties of ZnO growth on PMMA-coated substrate [19]. The Raman spectra of ZnO growth on PMMA-coated substrate under influence of different immersion time are depicted in Figure 5.
Figure 5. Raman spectra of ZnO growth on PMMA-coated substrate at different time of immersion (a) non-immersion, (b) 4 hours and (c) 6 hours.

The spectra present the films figure 5(a) non-immersed and two different immersion times; figure 5(b) 4 hours and figure 5(c) 6 hours. The spectra covered in the range 200 – 900 cm\(^{-1}\) of Raman shift. Non-immersion represents the film of PMMA-coated substrate without ZnO as mentioned in the PL spectra analysis before. In the spectra, non-immersion film was observed as the lowest intensity with obvious peak appeared at 311 cm\(^{-1}\), 376 cm\(^{-1}\), 503 cm\(^{-1}\), 632 cm\(^{-1}\) and 860 cm\(^{-1}\) of Raman shift. After the films were immersed, the spectra exhibit two peaks at 600 cm\(^{-1}\) and 811 cm\(^{-1}\) of Raman shift. It can be seen the film that was immersed for 4 hours give the higher Raman intensity compared to others. After the immersion time increase to 6 hours, the Raman intensity of the films decrease and no shifting peak is observed.

There are strong and weak peak present in the spectra shown in both graphs. A peak appeared at 600 cm\(^{-1}\) were contributed to the \(A_1\) (LO) mode. This vibrational mode of \(A_1\) (LO) was caused by defects such oxygen vacancies, zinc interstitials, the complexes or free carrier [16, 19, 20]. Furthermore, peak appeared at ~600 cm\(^{-1}\) probably indicates the films consists of c-axis of wurtzite ZnO are parallel to the sample surface [15, 19]. However, a weak peak was observed as the \(A_1\) (LO) mode in the spectra. As be reported by M. F. Malek et al, the weakest intensity was contributing to the minimization of the effect of oxygen deficiency on the growth of ZnO[19]. Therefore, it means the structure of ZnO growth on PMMA-coated substrate for 4 hours of immersion time is better and crystalline compared to the film that was immersed for 6 hours as well as for non-immersion film. Thus, the spectra analysis is consistent with the PL result in figure 4 where the ZnO growth PMMA-coated substrate at 4 hours immersion time gives better intensity.

3.3. Ultraviolet-Vis (UV-Vis) spectroscopy

Figure 6 presents the absorption spectra of ZnO growth PMMA-coated substrate under influence of different immersion times in the wavelength range of 280 - 900 nm. All the samples showed high absorption in the UV region and transparent in the visible region with the absorption edge around at ~330 nm.
Figure 6. UV absorption of ZnO growth on PMMA-coated substrate at different immersion times (a) non immersion, (b) 4 hours and (c) 6 hours

From Figure 6, the ZnO growth on PMMA-coated substrate at 6 hours of immersion time gives good absorption. It can clearly see in the UV region, non-immersion film present higher absorbance than the film that was immersed at 4 hours. However, the absorbance intensity decreased and the film highly transparent in the visible region. The absorption of the film increased with the increasing of immersion times and the absorption edge shift to the lower wavelength. It has been reported that when the absorption edge shifted into the lower wavelength, the absorbance increase with decreasing size of particles [21, 22]. 6 hours of immersion time present higher absorption and the film probably contains...
the small particles size of ZnO in the sample. However, the analysis inconsistent with the PL and Raman result previously where the films that was immersed for 4 hours exhibit good PL and Raman intensity.

In the case of UV absorption, the reason may be due to the distribution and orientation of ZnO particles contains in the sample that was immersed for 4 hours were randomly scattered. The random distribution of ZnO particles caused the scattering of light not effectively scattered on the rough surface and low absorbance are produced. As a result, the UV absorption of the films that was immersed for 4 hours exhibit low absorbance compared to the films that was non-immersed and immersed for 6 hours in UV region. Even 6 hours give a better absorption, have been reported that the longer immersion time will be produced larger of ZnO nanorods[23]. The good absorption showed probably caused from the distribution of ZnO in this sample is better. However, 4 hours of immersion will be chosen in this UV measurement because the sample is more crystalline and may have small size of ZnO as shown in another analysis previously. From that, it can be seen that the optical properties was significantly affected by the surface morphology and the scattering light efficiently is very dependent on particle distribution of the films [24]. Therefore, further study need to be done to improve the morphology as well as the optical properties of the sample that was immersed for 4 hours.

4. Conclusion
In summary, the ZnO growth on PMMA-coated substrate under influence of immersion times was successfully prepared by the solution - immersion method. PL analysis and Raman spectra exhibit the film that was immersed for 4 hours have good intensity and might form better crystalline of ZnO particles on the PMMA-coated substrate. However, UV absorption of the film immersed for 4 hours give low absorbance due the sample may have a random distribution and orientation of ZnO particles. It was shown that the optical properties are significantly affected by the surface morphology and the scattering of light efficiency dependent on particle distribution. Thus, further studies need to be done to improve the distribution of particles as well as optical properties of ZnO growth on PMMA-coated substrate for the sample that was immersed 4 hours.

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