Optical measurements on tailored zinc oxide thin films under optimal conditions

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Abstract

ZnO is synthesized by using conventional chemical route which is known as the “sol – gel” method and deposited on glass and silicon substrate. Morphological and optical properties have been investigated using XRD, AFM, FESEM and UV – vis test. In order to optimize the synthesized ZnO thin film, the ZnO thin film is coated with thin film of different thickness associated with various annealing temperature. Thicknesses of ZnO thin film coated for 3, 5 and 9 coating cycles of coating are 40 nm², 60 nm² and 200 nm², respectively. The data report that the grain size of the seed solution increases from 80 nm to 110 nm as the thickness of ZnO thin film increases. As the thin film is treated with annealing temperature from 200 °C to 450 °C, the grain size of thin film also increases from 100 nm² to 450 nm². The RMS value of thin film also increases due to intense surface roughness on ZnO thin film. The band gap value of thin film decreased from 3.26 eV to 3.18 eV for coating ZnO thin film with thickness 40 nm² – 200 nm².

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1. Introduction

Development of nanotechnology has lead to many novelist finding for fabricating biosensors which is associated with tailored transducer for fast response of the sensor. Development of tailored transducer in a respective optoelectronic application is very critical due to various criteria that need to be achieved such as size dimension of the nanostructure, stability, sensitivity etc. Recent interest for the development of transducer for biosensor application has utilized transition metal oxide due to its unique morphological and electrical characteristic. In present years, ZnO has become a remarkable choice as a platform for various applications such as photovoltaic, solar cell, optoelectronic biosensor [1–5] etc due to large band gap which is 3.37 eV [6] and bio compatibility [7].

Intensive reviews have proven that ZnO has become an emerging choice for environmental purpose due to considerable cost, non-toxic and high reactivity. Studies focused on morphological properties of ZnO material which is prepared by the sol – gel method has lead to novel application as sensing material for biosensor development. ZnO seed solution which is indexed to the wurtzite structure and associated with high crystalline characteristic have high tendency to synthesis quasi 1D nanowires of ZnO by using bottom up approach or growth process such as VLS mechanism, pulsed laser, hydrothermal [8–10] method etc. Prior to the formation of ZnO nanostructures, close studies regarding the crystallographic and the morphological properties of ZnO thin film is conducted by adjusting various parameters of the seed solution to form tailored thin film for respective application. Parameters which are involved in synthesizing ZnO thin film are the thickness, annealing temperature processing, pre-annealing temperature, post-annealing temperature, sol seed concentration, annealing period time processing etc. In this study, ZnO seed solution is synthesized by using chemical route, which is the sol – gel method and the thickness of the seed solution is altered to investigate the optical and structural properties of ZnO thin film coated on glass and silicon substrate. In order to further optimize ZnO thin film, the coated thin film is annealed with different annealing temperature.

2. Experimental

2.1. ZnO thin film preparation process

Chemical route is used to synthesis ZnO thin films, which is known as the sol – gel method. The sol – gel method involves three main essential chemicals which are the precursor, solvent
and sol-stabilizer. The precursor used for synthesizing ZnO seed solution is zinc acetate dihydrate or \([\text{Zn(CH}_3\text{COO})_2\text{2H}_2\text{O}]\) powder, which is purchased from Sigma-Aldrich (98%; Sigma-Aldrich).

The solvent used is isopropanol (IPA) and the sol-stabilizer is monoethanolamine (MEA; 99%; Merck). Zinc acetate powder was measured and ensured that 1632 mg of zinc acetate powder is dissolved in 40-ml IPA solvent to obtain 0.2 mol of ZnO seed solution. The solute solution is then stirred with speed rotation of 1000 rpm for 20 min. The heating temperature is maintained at 60 °C. The volume of the sol stabilizer, MEA will be measured to ensure that the ratio between the solvent and sol stabilizer is 1:1. After stirring the solvent for 20 min, the MEA is added subsequently for the next 120 min until the solution becomes a stable ZnO seed solution. The prepared ZnO seed solution was left for ageing at room temperature for more than 24 h.

### 2.2. ZnO coating procedure

Prepared ZnO seed solution is then coated on silicon and glass substrate. The size sample of silicon substrate and glass substrate are both 2 × 2 cm². Both the silicon and glass substrates initially undergo standard cleaning procedure process before being coated with ZnO seed solution. Prepared ZnO seed solution is coated by using the coating method. The coated samples is heated at temperature 60 °C for 20 min. Then the temperature is ramped up to 150 °C and kept constant for 10 min. After 10 min, the samples where cooled down till the temperature drop to 50 °C. The purpose of heating the sample after coating is to remove the residue moisture and enhance the adhesion force between the surface of the silicon/glass substrate and ZnO seed solution. The step is repeated for coating another layer of ZnO solution on the samples [11–13].

### 2.3. Sample characterization

ZnO samples undergo morphological and optical characterization to investigate the effect of different thicknesses of ZnO thin films. The morphology of the ZnO thin films was examined using field emission scanning electron microscopy (FESEM; Carl Zeiss AG-ULTRA 55, Gemini). Crystallization and micro-structures of the ZnO thin films were characterized using an atomic force microscope (AFM; SPA400–SPI3800, Seiko Instruments Inc., Japan) and X-ray diffraction (XRD; Bruker D8) with Cu-Kα radiation from 30° to 80° 2θ operated at 40 kV and 40 mA. Optical transmittance measurements were carried out using an ultraviolet – visible – near infrared spectrophotometer (UV – vis – NIR; Perkin-Elmer Lambda 950) with a slit width of 2 nm at normal incidence. All measurements were carried out at room temperature.

### 3. Results and discussion

#### 3.1. AFM characterization

Atomic force microscopic (AFM) analysis is conducted to investigate the morphology characteristic of coated ZnO thin film which is prepared by conventional the sol – gel method. In this studies, six main samples which are labeled as samples a,b,c,d,e and f are prepared to monitor the surface morphological properties. Initially, samples a, b, and c are prepared based on different thickness layer of ZnO thin film which is coated on glass substrate.

Fig. 1 illustrates 2D AFM image ZnO thin film which is obtained by utilizing tapping mode with the scan area of 500 × 500 nm². The scan speed is synchronized to a speed of 2 MHz to obtain the desired image of the grain particles on ZnO thin film which can be visualized clearly. From the observation in Fig. 1, the grain size of ZnO thin film is increasing proportional as the thickness of thin film is increased. At lowest thickness of ZnO thin film, the island structure of grain is exhibited. Hence, the number of grains observed in lowest thickness of ZnO thin film is largest and the amount of grain is reduced as the thickness of ZnO thin film is increased which shows that the coalescence of grains are merging together to form larger grain size. The uniformity of the ZnO thin film can be observed based on the surface analysis in Fig. 1(a – c). The surface roughness of the thin film is measured based on the different height (H – H₁) of the grain thickness. As obtained from Fig. 1(a – c), the differential height of grain for ZnO thin film for samples a, b and c are 7.29 nm, 13.96 nm and 23.87 nm, respectively. As the value of different height of grain increases, the roughness intensity of the surface increases gradually. This shows significantly that the roughness of the surface thickness is influenced by the thickness of the thin film. The roughness intensity value of ZnO thin film surface with different thickness layer is consistent with the RMS (Root Mean Square) value which is illustrated in Fig. 3. The RMS value is increased as the thickness of the ZnO thin film increases. The ZnO of sample b which has thickness of 60 nm² is further characterized with different annealing temperature to investigate the influence of annealing temperature of ZnO thin film.

Fig. 2 shows the morphological effect of ZnO thin film which is treated with different annealing temperature. ZnO thin film samples which is treated with annealing temperature of 200 °C, 350 °C and 450 °C is labeled as samples d, e and f. All the samples d, e and f has identical thin film thickness of 60 nm². As the temperature of annealing process is increased from 200 °C to 450 °C, the grain size of ZnO thin film is increased gradually. The increment of grain size occurred when the thin film is treated with higher
temperature due to the formation of crystallite when the nucleus of ZnO gel film is pre-heated. As the crystallite is further treated with higher temperature, the neighboring crystallite will coalescence to form large grain crystal [14]. Hence, larger grain will be formed at higher temperature annealing due to sufficient activation energy of individual zinc and oxygen atoms which will tend to re-bond with the adjacent grain to form larger grain size [12]. Drawbacks of excessive re-bonded mechanism between zinc and oxygen atoms at higher annealing temperature treatment will lead to structural defect of wurtzite hexagonal structure of ZnO due to co-existence of biaxial stress which is contributed by imbalance of Zn:O ratio [15]. Low temperature annealing will also cause defect due to insufficient grain size of ZnO thin film, which in turn will cause voids on the structure, and the dislocation density defect will be increased. Hence, suitable annealing temperature is essential to treat thin film to form a stable thin film which is associated with 1:1 ratio of Zn:O.

According to the results obtained in Fig. 3, the RMS value for ZnO thin film increases as the samples is treated with higher temperature of annealing process and high thickness of coated thin films. Hence, the surface roughness of the thin film is strongly influenced by the thickness and annealing temperature. Previous studies have mentioned that the increase of grain crystal size also will cause enhancement in surface roughness of ZnO thin [16]. From Fig. 3, the effect of ZnO thin film thickness has stronger influence in altering the surface roughness of thin film compared to the treatment of increased annealing temperature which is consistent with XRD data whereby the grain size of ZnO thin film increased more rapidly when the sample is coated with higher thickness compared to the treatment of annealing at different annealing temperature. As the thickness of thin film increases, the number of grain in the homogeneous thin film is increased and shorter time is required for the grain to coalesce to form larger grain compared to when thin film is treated with higher annealing temperature which require time for each individual grain to obtain sufficient activation energy to coalescence to form large grain size. Rough surface of thin film is tailored for sensor application due to large surface area to volume ratio. Based on the result of AFM and XRD, the scattering effect in ZnO thin film is reduced when it is treated with larger thickness and higher annealing temperature [17].

3.2. SEM characterization

Fig. 4(i) and (ii) represent the FESEM image of ZnO thin film which is coated with 40 nm² and 100 nm² thickness. It is clearly illustrated that as the thickness of thin film increases the grain size of the ZnO thin film also increases, the result of which is consistent with XRD data which is illustrated in Fig. 6. The uniformity of ZnO thin film also reduces as the thickness of coated ZnO thin film increases. Fig. 5(i) and (ii) represent FESEM image of ZnO thin film which is treated with annealing temperature of 200 °C and 450 °C. From the observation, it clearly illustrates that the grain size of ZnO thin film gradually increased as it is treated with higher annealing temperature. Hence, from results of Figs. 4 and 5, the grain size of ZnO thin film can be altered easily when the thin film is treated with different annealing temperature.

3.3. XRD characterization

Fig. 6 illustrates the X-ray Diffraction data of ZnO thin film which is coated with different thickness layer of thin film on glass substrate. The relative peak intensity exhibited is (100), (002), (1 0 1), (1 0 2) and (1 1 0). This shows that pure ZnO thin film is coated which is in agreement with standard data (JCPDS36-1451). According to the value of lattice structure “a” and “c”, the ZnO thin film is indexed to hexagonal wurzite structure. Table 1 also shows that the parameter lattice “c” is larger than “a” which significantly indicates that the preferential growth of ZnO thin film is c-axis. The value of lattice structure “a” and “c” is calculated based on the following formula:

\[ a = \sqrt[1]{\frac{\lambda}{3 \sin \theta}} \]

(1)
Table 1
Morphological characteristic of ZnO thin film coated with various thickness layer and treated with different annealing temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm²)</th>
<th>Annealing temperature (°C)</th>
<th>Grain size, D (nm)</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>40</td>
<td>200</td>
<td>50</td>
<td>3.22</td>
<td>5.00</td>
</tr>
<tr>
<td>b</td>
<td>60</td>
<td>200</td>
<td>50</td>
<td>3.00</td>
<td>5.21</td>
</tr>
<tr>
<td>c</td>
<td>100</td>
<td>200</td>
<td>100</td>
<td>3.00</td>
<td>5.21</td>
</tr>
<tr>
<td>d</td>
<td>60</td>
<td>350</td>
<td>100</td>
<td>2.98</td>
<td>5.17</td>
</tr>
<tr>
<td>e</td>
<td>60</td>
<td>450</td>
<td>140</td>
<td>3.00</td>
<td>5.19</td>
</tr>
<tr>
<td>f</td>
<td>60</td>
<td>500</td>
<td>420</td>
<td>3.01</td>
<td>5.21</td>
</tr>
</tbody>
</table>

Fig. 7. XRD result of ZnO thin film treated with different annealing temperature.

\[
c = \frac{\lambda}{\sin \theta}
\]  (2)

where, \(\lambda\) represent the X-ray wavelength of the incident Cu Kα radiation (0.154056 nm). The preferential growth orientation for ZnO thin film with various thickness is (002) peak which shows peak (0 0 2) is exhibited at highest intensity. Hence, the grain size is measured by utilizing Scherrer’s equation based on (0 0 2) peak intensity, since (0 0 2) plane is the dominant plane which shows highest peak intensity in the XRD data [17]. ZnO thin film has preferential growth at c-axis due to sufficient kinetic energy of individual Zn and O atoms which will be situated on the lattice position [18]. With the references of Table 1, the grain size of individual ZnO thin film increases as the thickness of ZnO thin film in increased. Enlargement of grain size of ZnO thin film with different thickness is consistent with the AFM data obtained in Fig. 1. Hence, thicker thin film of ZnO contributes larger grain due to reformation of individual Zn and O atoms. Hence, the dislocation density of the lattice structure of ZnO is improved as the thickness of ZnO thin film increases. Dislocation density, \(\delta\), of ZnO thin film is calculated based on the formula:

\[
\delta = \frac{1}{D^2}
\]  (3)

Fig. 8 illustrate the UV – vis transmission peak of ZnO thin film which is coated with different thickness layer. The transmisison peak is exhibited at the visible wavelength range of 380 nm – 700 nm. More than 60% of transmission is exhibited at visible wavelength. From the observation of Fig. 6, the transmission percentage of ZnO thin film deteriorates as the thickness of ZnO thin film reduces. The reduction factor of transmission percentage is due to increase of grain crystal size of ZnO thin film as the thickness of coated ZnO thin film is increased. Previous literature has mentioned that the transmission spectra of respective thin film are strongly affected by surface scattering, grain-boundary scattering and thickness of coated thin film [19]. From these studies, it is revealed that as the thickness layer of coated ZnO thin film increases the grain size of thin film is increased which is consistent with XRD data in table one. Hence, at larger thickness layer, the transmission peak intensity is reduced due to larger grain size. It also can be concluded that ZnO which is associated with large grain size has high absorption UV-light properties which is tailored for solar cell application [20].

Fig. 9(a – c) illustrate the band gap value of ZnO thin film which is coated with thickness of 40 nm², 60 nm² and 100 nm². The band gap, Eg value is obtained by plotting the taut plot graph which is \(h v\) versus \((ahv)^2\) where \((ahv)^2\) represent the absorption coefficient [21]. Absorption coefficient derives from the following formula:

\[
a = \frac{A(hv - Eg)^{1/2}}{hv}
\]  (4)

where, \(A\) is constant, Eg is the energy band gap, \(v\) represents the frequency of the incident radiation and \(h\) is the plank’s constant and \(1/2\) is referred as the direct allowed transition which is the parameter associated for electronic transition. From Fig. 7, a significant decrement in band gap, Eg, is shown as the thickness of ZnO thin film increases. The band gap value obtained for ZnO thin film with thickness of 40 nm², 60 nm² and 100 nm² is 3.26 eV, 3.23 eV and 3.18 eV, respectively. According to the previous AFM and XRD data for ZnO thin film with various thickness, the main factor which affects the reduction of band gap value of thin film is due to the increase in grain size of ZnO thin film [22]. Quantum size effects (QSE) is occurred due to electron confinement perpendicular to the surface of grain boundaries. Hence, when the grain size of ZnO thin film is increased, the grain boundaries in thin film is reduced, which in turn reduces the quantum size effect. The main factor which influences the reduction of effective band gap, Eg, due to increase in grain size, is elimination of quantum size effects [23,24].

3.4. Optical characterization

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Following formula will explain the mechanism of relative quantum size effect with various grain size:

\[ E_{\text{gap, nanocrystal}} = E_{\text{gap, bulk}} + \frac{\pi^2 h^2}{2 R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - 0.248E_R \]

where, ZnO bulk band gap, \( E_{\text{gap, bulk}} \) value is 3.20 eV [20] and \( E_R \) is the bulk binding energy, which is 60 meV. The electron and hole effective masses are taken as \( m_e = 0.24 m_0 \) and \( m_h = 2.31 m_0 \). Besides that \( h \) represents the plank constant and \( R \) is the radius of the grain crystal. According to the band gap equation, increment of radius of grain crystal will cause reduction in effective band gap of the respective thin film and vice versa for reduction of radius of grain crystal. Hence, as the intensity of quantum size effect deteriorates, the band gap value of the respective thin film will tend to reduce.

4. Conclusions

Investigations of the morphological and optical properties of ZnO thin film have been conducted and several objectives have been achieved from the conducted studies. Gradual changes in the morphological and optical properties of ZnO thin film, which is associated with thickness ranging from 40 nm to 200 nm, have occurred. AFM data reports that the RMS value of thin film increase from 4.908 nm to 82.25 nm as thickness of thin film is enhanced. RMS value of thin film is further increased when ZnO thin film is treated with elevated temperature. Surface roughness becomes more intense and the grain size obtained from AFM and XRD result exhibits elevated grain size of thin films. FESEM results also show that the grain size of ZnO thin film is increased when the thin film is treated with higher annealing temperature and the grain size of thin film is increased when higher thickness of ZnO thin film is coated on substrate. Optical transmission of ZnO thin film exhibits highest transmission percentage for glass substrate coated with lowest thickness value of ZnO thin film. Hence, the studies can contribute for optimization procedure to synthesize desired size dimension of ZnO nanowires through bottom-up approach. Alteration of band gap energy of thin film can also be done by adjusting the thickness layer of thin film. Studies also reveal that increment of different annealing temperatures has stronger influence in changing the grain size of ZnO thin film compared to coating of different thickness of ZnO thin film.

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References


