Optical and Structural Characterization of ZnO/TiO₂ Bilayer Thin Films Grown by Sol-Gel Spin Coating

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Abstract. Structural and optical properties of ZnO/TiO₂ bilayers thin films have been investigated using x-ray diffraction (X-RD), scanning electron microscopy (SEM), and optical transmittance UV-Vis measurements. ZnO thin films were prepared by dissolving zinc acetate dehydrated into a solvent of ethanol and then added triethanolamin. In the case of TiO₂ layers, tetraisoproxide was dissolved into ethanol and then added an acetate acid. The layer of ZnO was deposited first followed by TiO₂ layer on a glass substrate using a spin coating technique. The ZnO/TiO₂ bilayers were annealed at various temperatures from 300°C until 600°C for 60 minutes. The X-ray diffraction results show that there was an enhancement of the x-ray spectra as annealed temperature increased to 600°C in comparison to the samples that were annealed at 300°C. Based on the optical measurement of UV-Vis, the band gap energy of ZnO/TiO₂ bilayer is around 3.2 eV at temperature of 300°C. This value is similar to the band gap energy of ZnO. SEM results show that there is no cluster in the surface of ZnO/TiO₂ bilayer.

1. Introduction

The optical properties of semiconductor can be enhanced by coupling of two semiconductors in the terms of hetero-structures than a single semiconductor. The two semiconductors that are combined in this study ZnO and TiO₂. Zinc oxide thin film is one of the II-VI compound semiconductors that has been received considerable attention for many researchers due to its application in thin film sensors [1], light emitting diodes [2], spintronic devices [3], and nanolasers [4, 5]. Also, ZnO thin films used as a solar cell window since it has high optical transmittance in the visible region. ZnO has a wide band gap of 3.3 eV, large excitonic binding energy of 60 meV, and high carrier mobility at room temperature.

Titanium dioxide (TiO₂) is important semiconductor having a huge application in photo catalysis, solar cell and photonic devices [6]. Moreover, TiO₂ can be applied in optical filters, antireflection coatings, sensors and catalysts [7]. This wide range of the application of TiO₂ is due to its unique electronic and structural properties. TiO₂ can be classified into three crystalline phases: anatase, rutile, and brookite. Rutile is the most stable phase and it is usually obtained after annealing at temperature above 500°C [8]. Also, TiO₂ is in the visible light region and its band gap is 3.0 eV for rutile and 3.2 eV for anatase crystalline phase.

In this present work, we investigate the optical and structural characterization of ZnO/TiO₂ bilayers thin films grown by sol-gel processing. For these purposes, the samples of ZnO/TiO₂ were deposited using spin coating method and the samples were annealed at various temperatures from...
400°C to 600°C for 60 minutes. The films were characterized by optical transmittance UV-Vis, and X-ray diffraction (X-RD) measurements, scanning electron microscopy (SEM).

2. Experimental Set-Up
ZnO/TiO₂ bilayers were prepared using sol-gel spin coating method with the speed rate of 300 rpm for 15 second. The first layer was ZnO thin films followed by TiO₂ layers. For ZnO layers, Zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O) was dissolved with ethanol of 1.5M, and diethanolamine (DEA) as starting material, solvent, and stabilizer, respectively. For preparing TiO₂ precursor, 1.5 ml titanium tetraisoproxide was dissolved into 10 ml ethanol and then added 0.1 ml acetate acid. These solvent were stirred on the magnetic hotplate at 80°C during 5 hours with the speed rate of 1100 rpm.

The glass substrate was cleaned with HCL to remove the unwanted particles prior to the ZnO layers were coated on it. The first layer of ZnO solution was deposited on the glass substrate and then it was heated at 300°C for 10 minutes. After that, TiO₂ dissolution was coated on the top of ZnO and then it was heated at 300°C for 10 minutes. Finally, the ZnO/TiO₂ bilayers were annealed at various temperatures from 300°C to 600°C for 60 minutes.

X-ray diffraction measurement were carried to investigate the structural characterization using a single scan diffractometer with Cu Kα (λ = 1.5406 Å) radiation and scanning range of 20 between 20° and 50°. During the measurement, the current and the voltage of X-RD were maintained at 30 mA and 40 kV, respectively, and the scan speed was 2°/min. Optical transmittance measurements were performed to characterize the optical properties using a single beam UV-Vis spectrophotometer with a wavelength range of 250 – 800 nm.

![X-ray diffraction patterns of ZnO/TiO₂ bilayer thin films after annealing at various temperatures from 300°C to 600°C during 60 minutes.](image)

3. Results and Discussion
3.1 Structural characterization
The structural characterization of ZnO/TiO₂ bilayer thin films were taken place used the X-ray diffraction measurements. Figure 1 shows the X-ray diffraction pattern of bilayer ZnO/TiO₂ after annealing at various temperatures from 300°C to 600°C during 60 minutes. As shown in this figure that, after annealing the samples at 300°C, the X-ray diffraction peak were observed in the very small intensity. Annealing the samples at 400°C shows the increase in the peak intensity. As the annealing temperature was further increased, the peak intensity of X-ray diffraction pattern becomes higher and narrower in comparison to the samples that were annealed at 400°C. These results indicate that there is an improvement in the crystalline of the films after annealing. In addition to this, the X-ray diffraction
patterns of ZnO/TiO₂ bilayer after annealing at 400°C (see figure 1) appears at diffraction angles of 31.2°, 34.8°, and 36.6° which corresponds to the plane of (100), (002), and (101) respectively. These peaks were shifted to higher diffraction angle of 32.4°, 35.1°, and 36.9°. Also, the plane of (100), (002), and (101) are corresponded to the ZnO layers. Meanwhile, the X-ray diffraction peak which are related to the TiO₂ layers were not clearly observed after annealing at 300°C and 400°C, but this peak emerged when the samples were annealed at 600°C although its intensity too small.

The lattice parameters of ZnO/TiO₂ layers are determined with Crystallography Open Database (COD) that are confirmed from the X-ray diffraction patterns of ZnO/TiO₂ bilayer. Based on the database, the lattice parameter of both ZnO and TiO₂ layers after annealing at various temperatures from 300°C to 600°C during 60 minutes are tabulated in table 1. As can be seen in table 1, the lattice parameters of TiO₂ layers are higher than that of ZnO layers. Also, the lattice parameters of ZnO and TiO₂ layers are higher after annealing at 600°C than that annealing at 300°C. The increase of the lattice parameters of ZnO/TiO₂ bilayer thin films after annealing the samples at 600°C is probably due to the contribution from X-ray diffraction peak appears in the TiO₂ layers after annealing at 600°C. Annealing the samples below 600°C results the x-ray diffraction pattern was not clearly observed.

| Table 1. The lattice parameters of ZnO/TiO₂ at various temperatures from 300°C to 600°C during 60 minutes based on COD data. |
|---|---|---|---|---|
| Annealing Temperatures | ZnO layers | TiO₂ layers |
| | a(Å) | c(Å) | a(Å) | c(Å) |
| 300°C | 3.205 | 5.122 | 3.797 | 9.579 |
| 400°C | 3.219 | 5.149 | 3.797 | 9.579 |
| 500°C | 3.219 | 5.149 | 3.797 | 9.579 |
| 600°C | 3.219 | 5.149 | 3.804 | 9.614 |

From the XRD data measurements, the grain size (D) of the ZnO/TiO₂ bilayer thin films can be estimated using the Debye-Scherrer formula,

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

where \( k \) is a constant, \( \lambda \) is the x-ray wavelength (Cu Kα, \( \lambda = 1.5406 \) Å), \( \beta \) is the full width at half-maximum (FWHM), and \( \theta \) is the Bragg angle, respectively. Based on figure 1, the plane of (002) and (101) are preferred orientation for ZnO layers, while the plane of (011) is belong to TiO₂ layers; therefore we used these planes to calculate the grain size (D) of the ZnO/TiO₂ bilayer thin films. Base on the Debye-Scherrer formula, the grain size and FWHM are tabulated in table 2.

As shown in table 2, the grain size of the ZnO/TiO₂ decreased as the annealing temperatures increased. However, when the annealing temperature was further increased up to 600°C, the grain size of the ZnO/TiO₂ increased significantly. The grain size is reflected to the X-ray diffraction patterns of the samples. It can be seen in figure 1, the x-ray diffraction peak from TiO₂ was not clearly observed after annealing the samples at 300°C to 500°C. This TiO₂ peak would contribute the grain size of the ZnO/TiO₂ bilayer, although there was an improvement in the ZnO diffraction peak at these temperatures range. After annealing the samples at 600°C, the TiO₂ diffraction peak was observed. Also in table 2, the grain size of the samples annealed at low temperature is higher than annealed the samples at high temperature, although the X-ray diffraction peak did not show the ZnO or TiO₂ layers, these indicates that at the lower annealing temperatures the samples were amorphous. Thereby, we must rely on the samples annealed at 500°C and 600°C. Increase the grain size of ZnO/TiO₂ bilayers that is followed by increase of the intensity indicates that there is an improvement in the crystalline of the films after annealing at 600°C. Previous studies were also observed the improvement of crystalline of the films after annealing in the ZnO samples [9].
Table 2. Parameters crystal of ZnO/TiO₂ bilayers includes crystal planes, FWHM, diffraction angle, and the grain size of the crystal.

| Annealing temperatures (°C) | Crystal planes (hkl) | FWHM | Diffraction angle (2θ) | Grain Size (D) (nm) |
|-----------------------------|----------------------|------|------------------------|---------------------|
| 300                         | (002)                | 0.082| 34.60                  | 202.47              |
|                             | (101)                | 0.120| 36.50                  | 139.50              |
| 400                         | (002)                | 0.083| 34.77                  | 201.83              |
|                             | (101)                | 0.120| 36.66                  | 139.50              |
|                             | (011)                | 0.127| 25.71                  | 128.04              |
| 500                         | (002)                | 0.179| 34.93                  | 93.32               |
|                             | (101)                | 0.198| 36.74                  | 84.78               |
|                             | (011)                | 0.120| 25.33                  | 164.35              |
| 600                         | (002)                | 0.120| 35.11                  | 154.04              |
|                             | (101)                | 0.099| 36.93                  | 139.72              |

Figure 2. The transmittance spectra of ZnO/TiO₂ bilayers after annealing at different temperatures from 300°C to 600°C for 60 minutes.

3.2. Optical characterization

Figure 3 displays the optical transmittance of ZnO/TiO₂ bilayer thin films after annealing at different temperatures from 300°C to 600°C during 60 minutes. The transmittance value of the samples after annealing at 300°C is around 40 - 50%. After annealing at 500°C, it is around 55-60% in the transmittance value. This value slightly increased to 65-70% when the annealing temperature was further increased to 600°C. The increase of the transmittance value after annealing indicates the improvement of the crystalline of the films which is also confirmed in the X-ray measurements. In addition to this, there was a sharp absorptions edge was observed that located at 340-360 nm.

The optical band gap of ZnO/TiO₂ bilayer thin films are determined by extrapolation of the linear relationship between \((\alpha h\nu)^2\) and \(h\nu\) according to the equation [10] \((\alpha h\nu)^2 = A(h\nu - E_g)\), where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy, \(E_g\) is the optical band gap and \(A\) is a constant. The optical band gap of ZnO/TiO₂ bilayer thin films are obtained using this equation by plotting \((\alpha h\nu)^2\) in regard to photon energy (\(h\nu\)). Figure 3 depicts the plot of \((\alpha h\nu)^2\) versus photo energy (\(h\nu\)) for ZnO/TiO₂ bilayer at various annealing temperatures from 300°C to 600°C for 60 minutes. The optical band gaps of ZnO/TiO₂ bilayers thin films were determined by extrapolating the linear portion of \((\alpha h\nu)^2\) in regard to (\(h\nu\)) abscissa. After annealing the samples at 300°C, the optical band gap of...
ZnO/TiO$_2$ is 3.24 eV. This optical band gap slight decreased to 3.17 eV and 3.14 eV after annealing the samples at 400°C and 500°C, respectively. Narrowing the optical band gap as annealing temperatures increased indicates that there is a reduction of the amorphous phase in the annealed samples at these temperatures range [11].

**Figure 3.** Plot of $(\alpha h\nu)^2$ vs photon energy $(h\nu)$ of ZnO/TiO$_2$ bilayer thin films after annealing (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C.

**Figure 4.** (a) SEM image of ZnO/TiO$_2$ bilayer annealing at 600°C (b) Cross-sectional of SEM images of ZnO/TiO$_2$ bilayer.
The surface of ZnO/TiO₂ bilayer can be observed using scanning electron microscopy (SEM). Figure 4(a) shows the micrographs SEM of the morphology surface of ZnO/TiO₂ bilayer. It was clearly observed that the surface is smooth without any cluster forming at the surface. However, there is a crack on the surface that is due to the high temperature annealing to the substrate. Figure 4(b) displays a cross-section of SEM images of ZnO/TiO₂ bilayer to measure the thickness of the films. From the figure 4(b) the thickness of the film was 20 µm.

4. Conclusion

We have studied the structural and optical characterization of ZnO/TiO₂ bilayer thin films after annealing at various temperatures from 300°C to 600°C for 60 minutes. The ZnO/TiO₂ thin films were coated on the glass substrate using sol-gel method. Based on the X-ray diffraction measurements, the grain size of the ZnO/TiO₂ decreases as annealing temperature increased, but it decreases after high annealing temperatures. The transmittance value of ZnO/TiO₂ increases with increasing the temperature that indicates that the improvement of the crystalline of the films. SEM results show that there is a crack on the surface due to high annealing temperature.

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