Properties of ZnO/TiO2 hetero-structures thin films grown by sol-gel with various zinc acetate dehydrated concentration

P L Gareso†, N Aeni, Musfitasari, N Rauf and E Juarlin

1Department of Physics, Faculty of Mathematics and Natural Sciences, Hasanuddin University, Jl. Perintis Kemerdekaan KM 10 Tamalanrea-Makassar 90245, Indonesia.

†pgareso@fmipa.unhas.ac.id

Abstract. We have investigated the structural and optical properties of ZnO/TiO2 hetero-structures thin film with various zinc acetate dehydrates concentration (0.5 M, 1.0 M, 1.5 M, and 2.0 M) grown by sol-gel method. Zinc oxide sol-gel were prepared by dissolving zinc acetate dehydrates as precursor into an ethanol. The solutions were added with triethanolamine as a stabilizer. For preparing the TiO2 sol-gel, titanium tetraisoproxide (TTIP) was used as precursor and it was dissolved into the ethanol and added with an acetic acid as stabilizer. A glass substrates were cleaned with acetone prior to the thin films was coated on it. The first layer was ZnO thin film and then followed by TiO2 were deposited into the glass substrates. The ZnO/TiO2 hetero-structures thin films were inserted into furnace for undertaking the heat thermal at the temperatures of 500°C for 60 minutes. X-ray diffraction was used to characterize the structural properties of ZnO/TiO2. The optical properties ZnO/TiO2 were characterized using the optical UV-Vis spectrophotometer measurement. Based on the X-RD results, the peak is clearly observed for ZnO thin films in the plane of (100), (002), and (101), indicating that ZnO in the crystalline phase, while TiO2 is in the amorphous phase. The optical band gap of the ZnO/TiO2 hetero-structures thin films for 1.0 M and 1.5 M is 3.150 eV, and 3.153 eV, respectively.

1. Introduction

Titanium dioxide (TiO2) material is an important material in semiconductor devices which is widely used in many semiconductor devices application such as photo catalysis, solar cell and photonic [1]. Also, TiO2 has unique properties in electric and crystal structures; therefore this material is used in many large area of device application [2]. In general, TiO2 can be grouped into three crystalline phases; they are anatase, rutile, and brookite phases. Among three crystalline phases of TiO2, rutile phase is well established phase among three crystalline phases in crystal structures of TiO2, and it is formed after annealing at temperature above 500°C [3]. Semiconductor ZnO is one of the II-VI compound semiconductors that have been received considerable attention since it has a wide band gap of 3.3 eV [4], and a large excitonic binding energy of 60 meV [5]. Also, ZnO is widely used in light emitting diodes (LED) [6], gas sensor [7], and photovoltaic devices [8]. Also, the ZnO has a good candidate for photo anode in dye sensitized solar cells (DSSCs) application due to its low cost and nontoxicity.

Several methods have been used to fabricate the ZnO and TiO2 thin films such as sputtering [9], chemical vapor deposition [10], and sol-gel process [11]. Among of these methods, sol-gel method...
offer several advantages including: inexpensive cost to study the properties in electric and optic characterization. Moreover, the sol-gel method is straightforward to control the chemical solution and deposition temperatures.

In this present study, we investigate the structural and optical properties of ZnO/TiO₂ hetero-structures thin films using sol-gel spin coating technique. The zinc acetate dehydrates were varied to the solvent solution. The samples were inserted to the oven to undertake the heat treatment at the temperature of 500°C during 60 minutes. After annealing, the samples were characterized the structural properties using X-ray diffraction measurements. For the optical characterization, the UV-Vis spectrophotometer was used to study the transmittance and the optical band gap of ZnO/TiO₂.

2. Experimental Set-Up
A Sol-gel method is essential technique to prepare a thin film, particularly for ZnO and TiO₂ thin films. For the case of ZnO thin films, the zinc acetate dehydrates precursor was dissolved in ethanol with different concentration. For TiO₂ sol-gel, the titanium tetraisoproxide (TTIP) was dissolved into ethanol. These sol-gel were stirred on the magnetic hotplate at temperature of 60°C for 15 minutes with a rotating speed of 1000 rpm. The ZnO and TiO₂ sol-gel were coated on a glass substrates using spin coating technique.

For a single layer, prior to the ZnO and TiO₂ sol-gel were grown on the glass substrates, they were cleaned with a pure water, a methanol and an acetone for 10 minutes into each solution to remove the unwanted particles. The ZnO and TiO₂ films were coated on the glass substrate with a speed rate of 2000 rpm during 30 seconds and were heated at 300°C for 5 minutes at rapid thermal processor (RTP). For ZnO/TiO₂ hetero-structures, the ZnO thin film was first deposited on the substrate and was heated at the temperatures of 300°C for 5 minutes. Next, the TiO₂ thin films were coated on the top of ZnO films and undertake the annealing processing which was similar heating process in ZnO thin films. Finally, all the samples were put into the furnace for annealing at the temperature of 500°C for 60 minutes.

The structural properties of ZnO/TiO₂ heterostructures films were studied using X-ray diffraction measurements with Cu Kα radiation (λ = 1.5406 Å). The scan range of diffraction angle between 20° and 70° and the speed rate of diffraction was 2°/min. The current and the voltage of diffraction measurements were kept a constant at 30 mA and 40 kV, respectively. The Debye-Scherrer formulation was performed to determine the structural parameters of ZnO/TiO₂ such as the crystalline size, and full width at half maximum (FWHM). In the case of the optical characterization of ZnO/TiO₂ samples, the single beam of UV-Vis spectrophotometer was used to study the transmittance/absorption and the optical band gap of the samples. The scan range of the wavelength was 250 – 800 nm.

3. Results and Discussion
3.1. Structural characterization
Prior to the structural characterization of ZnO/TiO₂ hetero-structures thin film, we first characterized the single layer ZnO and TiO₂ with aiming to observe the influence of ZnO and TiO₂ each in regard to the combination of ZnO/TiO₂ hetero-structures. Figure.1 reveals the X-RD curves of single layer ZnO and TiO₂ after annealing at 500°C during 60 minutes. For ZnO, it was obviously observed that the X-RD peak comes from the ZnO films. The X-RD peak appears at the diffraction angle of 31.53°, 34.61°, 36.31°, and 47.63° (JCPDS Card NO: 96-901-1663). These peaks angle correspond to the plane of (100), (002), (101), and (012) respectively. Based on the X-RD curves, the preferential orientation of ZnO single layer is (002) since the intensity of this peak is higher than that others X-RD peak intensity. These results are similar to the previous studies on the ZnO where the preferential orientation was (002) planes [12]. In the case of TiO₂ single layers, the X-RD curves of TiO₂ thin films appears at diffraction angle of 25.29°, 38.17°, and 48.43° (JCPDS Card NO: 96-500-0224) which correspond to the plane of (101), (004), and (200), respectively. The results of X-RD curves of TiO₂ thin films indicate that this film is categorised to the TiO₂ anatase phase.
Figure 1. X-ray diffraction (X-RD) spectra of single layer ZnO and TiO$_2$ thin films after annealing at 500°C for 60 minutes.

Figure 2 shows the X-RD curves of ZnO/TiO$_2$ hetero-structures thin films with various different zinc acetate dehydrates concentration of 0.5 M, 1.0 M, and 1.5 M after heat treatment at 500°C for 60 minutes. The X-RD results for 0.5 M reveals that there is no X-RD peak related to the ZnO and TiO$_2$ thin films, indicating that the film is amorphous phase. When the concentration of zinc acetate dehydrates was increased to 1.5 M, the X-RD peak that related to the ZnO and TiO$_2$ film can be clearly observed, although their intensity is still lower, indicating that the crystalline phase in these film take place at this condition. The X-RD curves were observed at diffraction angle of 32.18°, 34.88°, and 36.63° that correspond to the plane of (100), (002), and (101), respectively. These planes are represented to the ZnO thin film for 1.0 M zinc acetate dehydrates concentration. For 1.5 M zinc acetate dehydrates concentration, the X-RD curves were revealed at diffraction angle of 31.91°, 34.41°, and 36.56°, respectively which is shifted a little bit to the right of X-RD curves if compared to the zinc acetated concentration of 1.0 M. We also observed another X-RD peaks that are corresponded to the TiO$_2$ films. This peak emerges at diffraction angle of 25.51° with the crystalline plane of (011). It is important to note here that the X-RD peak for ZnO films is more clearly observed than TiO$_2$ peaks.

Figure 2. X-ray diffraction (X-RD) curves of ZnO/TiO$_2$ hetero-structures thin film with different zinc acetate dehydrates concentration of 0.5M, 1.0 M, and 1.5 M respectively after annealing at 500°C for 60 minutes.
**Tabel.1.** The structure parameters of ZnO/TiO₂ hetero-structures thin film for various different zinc acetate concentrations of 1.0 M and 1.5 M after annealing at 500°C for 60 minutes.

| Zinc acetate concentration | (hkl) | FWHM (deg) | 2θ (deg) | D(nm) |
|---------------------------|-------|------------|----------|-------|
| 1.0 M                     | (011) | 0.04       | 25.51    | 3.84  |
|                           | (100) | 0.12       | 32.18    | 1.36  |
|                           | (002) | 0.12       | 34.88    | 1.41  |
|                           | (101) | 0.08       | 36.63    | 2.16  |
| 1.5 M                     | (011) | 0.08       | 25.42    | 1.92  |
|                           | (100) | 0.09       | 31.91    | 1.82  |
|                           | (002) | 0.08       | 34.41    | 2.10  |
|                           | (101) | 0.08       | 36.56    | 2.15  |

The crystalline size (D) of the ZnO/TiO₂ hetero-structures thin film were determined using the equation of the Debye-Scherrer [13],

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the wavelength of X-ray diffraction (\(\lambda = 1.5406 \, \text{Å}\)), \(\beta\) is the full width at half-maximum (FWHM), and \(\theta\) is the Bragg angle, respectively. Based on Figure (2), the crystalline size of ZnO/TiO₂ film was determined using the plane structures in which only the plane having high intensity take into account. As shown in the Table.1, the crystalline size of ZnO/TiO₂ hetero-structures is 2.19 nm for 1.0 M concentration of zinc acetate dehydrates. The crystalline size decreases to 1.99 nm when the concentration of the zinc acetate increases to 1.5 M. These results indicate that decreases of the crystalline size can cause the increase the crystalline phase in the ZnO/TiO₂. As shown in the Figure.2, the X-RD peak shows high peak intensity of ZnO/TiO₂ for 1.5 M concentration of zinc acetate compared to the concentration of 1.0 M.

3.2. Optical characterization

The Optical transmittance spectra of ZnO/TiO₂ for various zinc acetate dehydrates concentration of 0.5M, 1.0 M, 1.5 M, and 2.0 M was depicts in Figure.3. As can be seen in this figure, the transmittance value of 0.5 M concentration of zinc acetate dehydrates is about 50%-60%. This value increases to around 75% at 1.0 concentration, indicating that there is enhancement of the crystalline phases in ZnO/TiO₂ hetero-structures. However, the transmittance value decreases as the concentration of zinc acetate dehydrates increased to 2.0 M. The transmittance value decreased from 75% (1.0 M) to 60% (2.0 M). Reducing the transmittance value at highest value of concentration (2.0 M) is probably due to the saturation of the crystalline phases take place in the samples. This means that, at high concentration, it is probably occurring that the defect can be generated into cluster or defect was agglomerated at the interface and as a result the transmittance value reducing.

The corresponding optical band gap of ZnO/TiO₂ hetero-structures thin films was estimated by extrapolation of the lienier relationship between \((ahv)^2\) and \(hv\) according to the equation [14].

\[
(ahv)^2 = A(hv - E_g)
\]
Figure 3. The transmittance spectra of ZnO/TiO$_2$ hetero-structures thin film with various different zinc acetate dehydrates concentration of 1.5M, 1.0 M, 0.5 M and 2.0 M respectively after annealing at 500°C for 60 minutes.

where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the optical band gap and $A$ is a constant. Equation (2) was used to estimate the optical band gap of ZnO/TiO$_2$ hetero-structures films by extrapolating the linear $(\alpha h\nu)^2$ in regard to $(h\nu)$. Figure 4 shows the plot of $(\alpha h\nu)^2$ as a function of photon energy $(h\nu)$ of ZnO/TiO$_2$ thin films for 1.0 M, and 1.5 M concentration of zinc acetate dehydrates. The optical band gap value of the ZnO/TiO$_2$ thin films for 1.0 M was estimated to be 3.150 eV. This value increases slightly to 3.153 eV as the concentration increases to 1.5 M, indicating that the optical band gap is shifted to the high energy (blue shift). Also this optical band is lower than the bulk of ZnO and TiO$_2$ semiconductor.

Figure 4. Plot of $(\alpha h\nu)^2$ vs photon energy $(h\nu)$ of ZnO/TiO$_2$ hetero-structures thin films for 1.0 M and 1.5 M zinc acetates concentrations after annealing at 500°C for 60 minutes.
4. Conclusion
The structural and optical properties of ZnO/TiO$_2$ hetero-structures thin films with various different zinc acetates dehydrates concentration after heat treatment at the temperatures of 500°C during 60 minutes have been investigated using sol-gel technique. The X-RD results show that the ZnO thin films indicate in the preferential orientation of (002) plane due to high peak intensity compared to other peaks. For TiO$_2$ thin films, the X-RD peak is not clearly observed since the film is in the amorphous phase. The optical band of the samples is 3.510 eV for 1.0 M concentration of zinc acetates dehydrates. This optical band gap value increases slightly to 3.513 eV as the concentration increased to 1.5 M. Also, the optical band gap of ZnO/TiO$_2$ is shifted to high energy. By combining of two different semiconductors of ZnO and TiO$_2$, the device performance could be enhanced especially in DSSC device performance with the utilizing of the TiO$_2$ as an absorbing material.

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