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Depositionof TiO_2/ZnO Thin Films using Spin-Coating Method

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ABSTRACT. Thin film technology is important to semiconductor devices, optical coatings, and corrosion protection and also important within physical science. Thin films commonly used in metal oxide material as a layer or bilayer to improve the performance of films. In this study, TiO_2 and ZnO were synthesized by using sol-gel method and deposited using spin coating technique by using glass substrate. The sol-gel TiO_2 has been produced by using titanium (IV) butoxide, N-butanol, acetic acid and distilled water in molar ratio 2:20:1:1 meanwhile zinc acetate dehydrate, iso-propanol, diethanolamine and distilled water with molar ratio 1:20:1:1 was used to produced sol-gel Z The calcination temperature were used for first layer of TiO_2 from 400°**C** to 600°**C** and for the second layers of ZnO are 500°**C** and 600°**C**. A combination of characterizations such as X-ray diffraction (XRD), atomic force microscopy (AFM), field-emission scanning electron microscope (FESEM), and ultraviolet-visible spectrophotometry (UV-Vis) were used. The XRD analysis confirmed that TiO_2 with anatase structure and ZnO with hexagonal wurtzite were present. The XRD intensity increases with increasing of calcination temperature. The surface roughness analysis by AFM shows the TiO_2/ZnO thin films surface was improved with increasing the calcination temperature. All the result suggested that the use of bilayer thin films effectively enhanced the quality of films crystallinity and optical properties as compared to a single layer thin films.

Keywords: *Thin films, Bilayer, Multilayer, Titanium dioxide (TiO_2), Zinc Oxide (ZnO), Sol-gel;*

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1. INTRODUCTION

A thin film is a thickness layer of films where the metal oxide material has been used as a layer and deposited onto the substrate. Generally, the deposition of thin films used metal oxide material as a layer or bilayer thin films because it improved the performance of films. The layer of thin films has been deposited with different substrate such as glass [1,2], quartz [3] and silicon wafers [2]. Moreover, chemical composition widely used for thin film application such as sol-gel [4,5], electro-deposition [6], chemical vapor deposition (CVD) [1,7], impregnation [8] and atomic layer deposition [9].

In this study, titanium dioxide (TiO_2) and zinc oxide (ZnO) has been used as bilayer thin films. Generally, TiO_2 is a white solid organic and also known as titania. TiO_2 is a one of semiconductor material widely used to improved the performance in film thickness such as crystallite size [10], morphology [10,11], and optical properties. Moreover, transmittance in visible region, chemical stability and high reflective index actually good for optical thin films [4]. Generally, TiO_2 have three different phase crystalline structures such as rutile, anatase and brookite. Generally, anatase and brookite in metastable form and by using calcination process, the phase able to transform both structure into stable rutile form [12]. Zinc oxide (ZnO) is one of metal oxide widely usedin thin films proces. The advantages of using this semiconductor as additive for our case study because this material are cheap [13], non-toxic [13] and low cost attractive material [8]. Zinc oxide (ZnO) was used as additive because also used in electrical and optical application where it improve the optical absorption property [14] and excellent in ultraviolet photosensitivity [9].

Sol-gel method is one of liquid chemical mixture to formed TiO_2 and ZnO solution. Generally, this method widely used in thin films because these technique effective for bilayer and multilayer thin films surface structure, low cost [5,6,10], high purity [5,13] and easy to control the reaction condition structure at low temperature [6]. These method actually suitable for combined metal oxide because it increased the thickness layer and also the porosity of the thin films. Besides that, deposition technique widely applied for thin films such as spin coating [2,5,15] and dip coating [1,16]. Spin-coating defined as method to produced uniform organic films in large areas on the substrate by using spinning process and dip-coating is one of coating process and usually this process used for complex shape substrate. The methods was used to characterize the structure and optical properties of bilayer TiO_2/ZnO thin films by using X-ray diffraction (XRD),atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM).

2. MATERIALS AND METHODS

The TiO_2/ZnO thin films were prepared by sol-gel method with pre-deposited TiO_2 at different calcination temperatures from 400°C to 600°C. The sol-gel of TiO_2 was prepared by using titanium (IV) butoxide and n-butanol at room temperature. Then, acetic acid and distilled water were added dropwise into the precursor under continuous stirring at room temperature for 2 hours to produce homogenous TiO_2 sol-gel. The ZnO sol-gel was prepared using zinc acetate dehydrate and isopropanol. The diethanolamine and distilled water were added into the ZnO precursor solution under strong stirring and heated at 60 °C for 2 hours. The resultant of both TiO_2 and ZnO sol-gel were kept ageing at room temperature for 24 hours. The microscope glass slides were used as substrates. The substrates were cleaned using ethanol and acetone then rinsed with deionized water. The bilayer TiO_2/ZnO thin films with pre-deposited TiO_2 were deposited using spin coater (MTI; VTC-50A). The deposition of thin film was started with deposited TiO_2 pre-deposited layer on substrate. The spinning of coating speed used was 3000 rpm for 30 s. After that, the film was dried at 100 °C in oven. The TiO_2 pre-deposited layer then calcined at 400 °C, 500 °C, and 600 °C before deposited with ZnO sol-gel. By using the same glass substrate coated with pre-deposited TiO_2, the glass was placed again on spin coater to deposit with ZnO sol-gel to forming TiO_2/ZnO thin film. Then, the TiO_2/ZnO thin film was post-calcined at temperature 500 °C and 600 °C. The TiO_2/ZnO thin films were characterized and analyzed in detail as follow. The crystalline phases of the thin films were identified through XRD (Bruker AdvanceD8). The surface roughness and morphology of the grain sizes were studied by using AFM(XE-100) and FESEM, respectively.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis of TiO_2/ZnO Thin Films. Bilayer of TiO_2/ZnO thin films was deposited using glass substrate and the crystal structures of bilayer were analysing by XRD. All XRD analyses confirmed that TiO_2 was present with an anatase crystal structure and ZnO was present with wurtize crystal structure. No other phase rutile or brookite was determined in the result. XRD peak of TiO_2 matched with anatase of JCPDS 00-021-1272 and ZnO pattern matched with the wurtzite of JCPDS 00-036-1451.

Fig. 1 shows XRD pattern of TiO_2/ZnO thin films where the calcination temperature of first layers TiO_2 increased from 400°**C** to 600°**C** and for second layers of ZnO maintain at 500°**C**. The results show increases of peak intensity after calcination process. It reveal the intensity of anatase peak of 2θ = 25.28°, 37.80°, 62.69°, and 68.76° are attributed to the (101), (004), (204), and (116). For hexagonal wurtzite intensity peak of 2θ = 31.77°, 34.42°, 36.25°, 47.53°, 56.60° and 67.96° are assigned to (100), (002), (101), (102), (110) and (112), respectively. It shows that the crystallinity of the TiO_2 film improved with deposition ofMechiakh et al.[10] and Xu et al.[17] also found the similar result where the calcination temperature has influenced the intensity on the diffraction peaks.

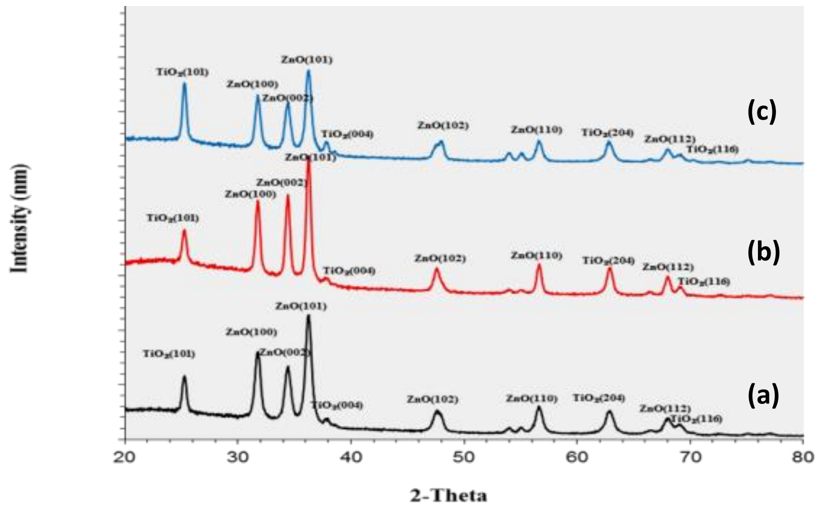


Fig. 1. XRD pattern of TiO_2/ZnO thin films (a) TiO_2 (400°**C**)/ZnO (500°**C**), (b) TiO_2 (500°**C**)/ZnO (500°**C**) and (c) TiO_2 (600°**C**)/ZnO (500°**C**)

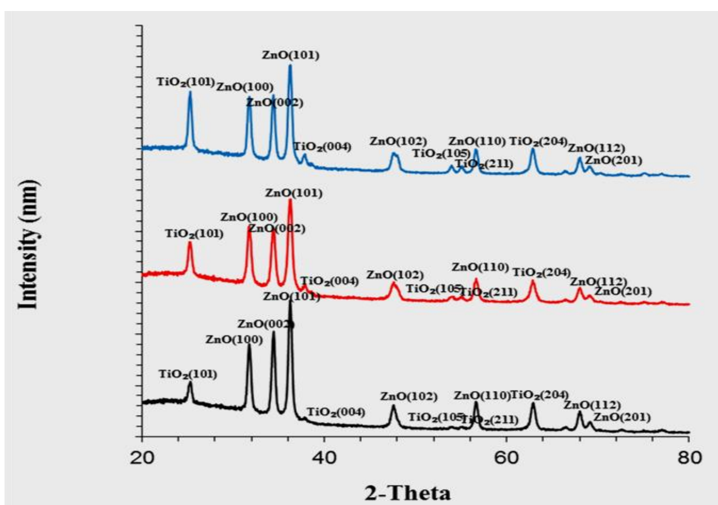
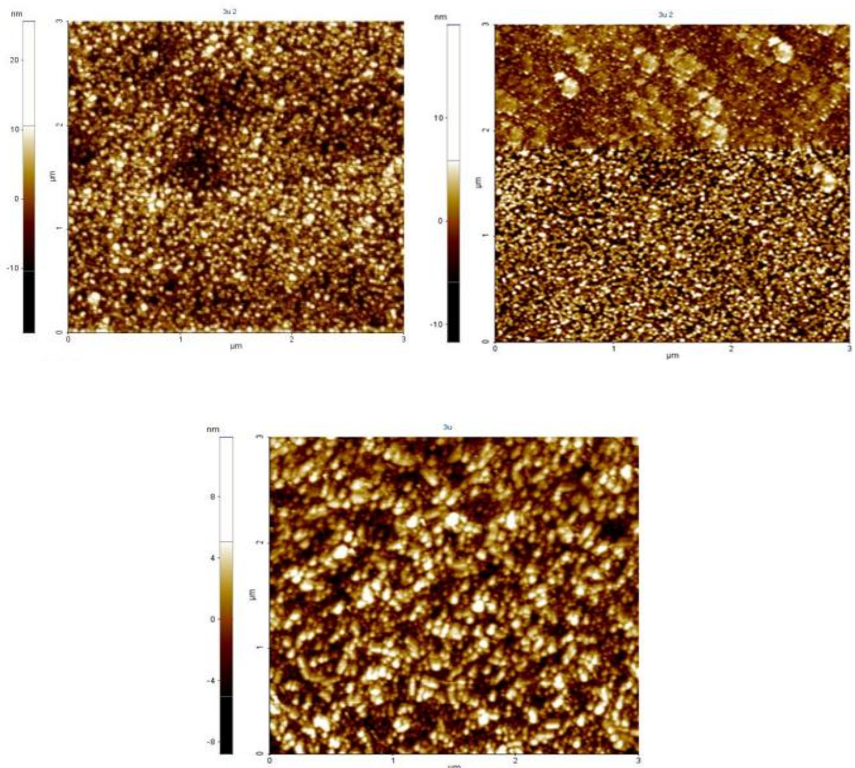


Fig. 2. XRD pattern of TiO_2/ZnO thin films (a) TiO_2 (400˚C)/ZnO (600°**C**), (b) TiO_2 (500°**C**)/ZnO (600°**C**) and (c) TiO_2 (600°**C**)/ZnO (600°**C**)

Fig. 2 shows XRD pattern of TiO_2/ZnO thin films for TiO_2 layers at 400°**C**, 500°**C**, and 600°**C** and ZnO at 600°**C**. It shows that the XRD pattern is similar with Fig. 1 and the intensity is significantly enhanced by increasing the annealing temperatures. Fig. 2 shows the intensity of anatase peak of 2θ = 25.28°, 37.80°, 53.89°, 55.06° and 62.69° are attributed to the (101), (004), (105), (211), (204) and (116), respectively. For hexagonal wurtzite intensity peak of 2θ = 31.77°, 34.42°, 36.25°, 47.53°, 56.60°, 67.96° and 69.1° are assigned to (100), (002), (101), (102), (110), (112) and (201), respectively. The highest intensity peak for $TiO_2$are at 2θ = 25.28° (101) and for ZnO at 36.25° (101). It shows when the calcination temperature increases, the intensity of some peak also increase. In addition, Shi et al.[18] also has similar result where the intensity improved when temperature increase and the crystallinity quality of ZnO film has been improved where TiO_2 film used as a buffer layers. In addition, Hussin et al.[19] was observe with increases the crytallite size also improved crytalline quality of TiO_2/ZnO bilayer. Moreover, crystallization of thin film shows thickness deposition and annealing process play important roles to improve the performance of thin films.

3.2 Surfaces Morphology of TiO_2/ZnO Thin Films. The AFM characterization was carried out on bilayer TiO_2/ZnO thin films with different calcination temprature. Fig. 3 shows the images of single layer TiO_2 and bilayer TiO_2/ZnO thin films. It can see that the surfaces roughness become smoother after applied the calcination process. The lower roughness value represents good homogeneity of the TiO_2 particles on the surface. The layer of TiO_2 show smooth surfaces but with bilayer, the roughness of thin films becomes more smooth. The result shows the decrease of RMS valuesingle layer TiO_2 (600**°C**) from 5.333nm to 2.578nm for bilayer TiO_2 (600**°C**)/ZnO (600**°C**).The grain size and average surface roughness perfomance increases when the buffer layer has been used significant with enhancement in crystallinity. In addition, the calcination temperature influences the decreasing of surface roughness. Ibrahim et al.[20] also concluded that the annealing temperature strongly affects the structure of thin films.



(a) RMS 5.3nm (b) RMS 3.0nm (c) RMS 2.6nm

Fig. 3. AFM morphology (a) single layer TiO_2 (600**°C**), (b) TiO_2 (600**°C**)/ZnO (500**°C**) and (c) TiO_2 (600**°C**)/ZnO (600**°C**)

Based on the result show in Fig 3, RMS values slightly decrease after single layer TiO_2 films was deposited with ZnO layer. Hussin et al.[19] founds the similar results, which the value of RMS and grain size improved when applied bilayer thin films and the particle size reaction also depend on deposition temperature and impurities from the grain boundaries.

The FESEM images in Fig. 4 shows the effect of calcination process on the TiO_2/ZnO thin films. The particle and boundary clearly show in the images with different size of grain boundary. It shows when the temperature increase, the size of particle become bigger and the gap between boundaries becomes smaller. Xu et al.[21] have similar result where the calcination temperature influences the size of particle.

AFM results for grain size also has significant result with FESEM result where surface roughness improved and grain size reduced from 22.228 nm for TiO_2 (400°C)/ZnO (500°C) to 9.114nm for TiO_2 (600**°C**)/ZnO (500**°C**). TiO_2 (600**°C**)/ZnO (600**°C**) grain size also reduced from 16.673nm of TiO_2 (400**°C**)/ZnO (600**°C**) to 5.886nm TiO_2 (600**°C**)/ZnO (600**°C**). The calcination process influences the growth of particle size significantly with AFM result of surfaces roughness becomes smoother. The particles for single TiO_2 thin films show the homogeneous particle and after deposition with ZnO, the grain size becomes irregular and increases the particle size of TiO_2/ZnO thin films.

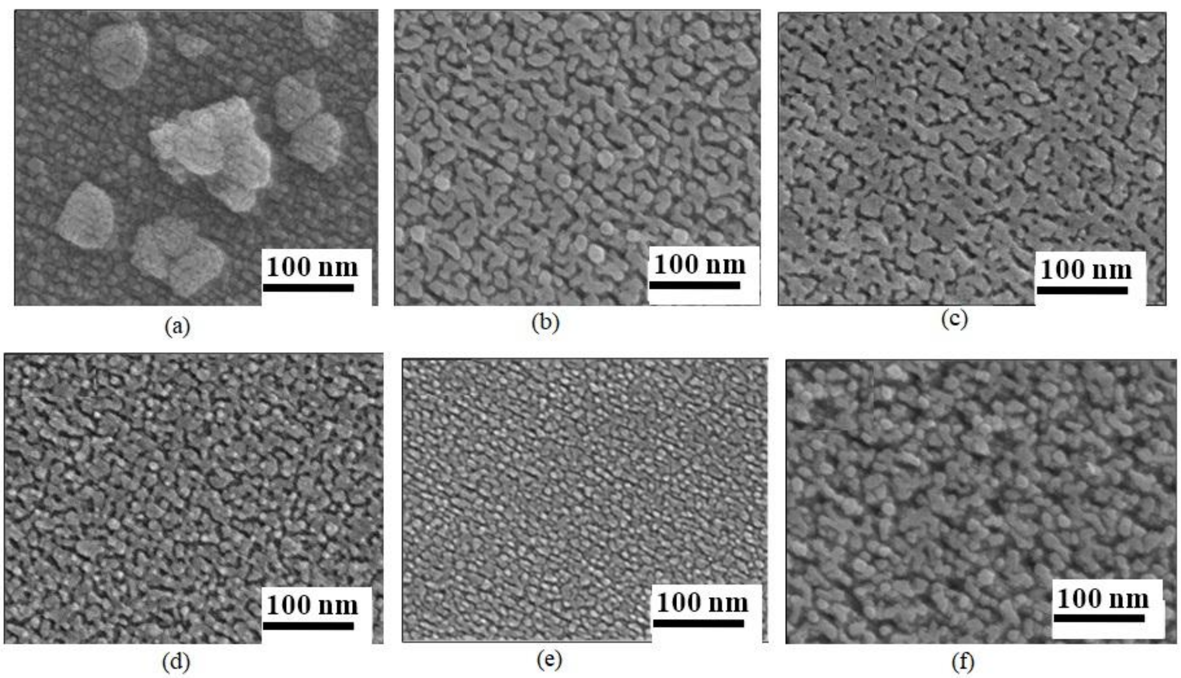


Fig. 4. The effect of calcination process on the surface morphology of bilayer TiO_2/ZnO thin films (a) TiO_2 (400**°C**)/ZnO (500**°C**), (b) TiO_2 (500**°C**)/ZnO (500**°C**), (c) TiO_2 (600**°C**)/ZnO (500**°C**), (d) TiO_2 (400**°C**)/ZnO (600**°C**), (e) (b) TiO_2 (500 **°C**)/ZnO (600 **°C**) and (e) TiO_2 (600 **°C**)/ZnO (600 **°C**)

4. SUMMARY

TiO_2/ZnO thin film had been succesfully growth on the glass substrate using spin coating method. XRD result shows the intensity of peak improved with bilayer TiO_2/ZnO thin film. The RMS value decrease for single layer TiO_2 (600**°C**) from 5.333nm to 2.578nm for bilayer TiO_2 (600**°C**)/ZnO (600**°C**). It shows the surface morphology become smooth with deposition with ZnO layer. The transmittance spectra of TiO_2/ZnO thin film shows the improvement of transmittance after applied the calcination process. High transmittance and good conductivity makes TiO_2/ZnO thin film widely used in optical application especially in solar cell.

Bilayers TiO_2/ZnO thin films show better properties compared with single layers of thin films. It proved that, TiO_2 thin films improved the crystallinity strucuture, surfaces roughness, grain boundary size and transmittances by using ZnO as bilayer of the thin films.

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