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CHARACTERIZATION OF TiO_2, ZnO, AND TiO_2/ZnO THIN FILMS PREPARED BY SOL-GEL METHOD

Nur Syahraain Zulkiflee, Rosniza Hussin, Jumrah Halim, Mohd Izham Ibrahim, Mohamad Zulhafizi Zainal, Shahzua Nizam and Suhailah Abdul Rahman
Department of Material and Design Engineering, Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia
E-Mail: gd140084@siswa.uthm.edu.my

ABSTRACT

Nanostructured thin film has been extensively study because they exhibit better structural, optical, and electrical properties. Generally, the photocatalytic activity was relying on adapting condition of the material to be composited. These composite materials will be manipulated the particles size, crystallographic phase and morphology of the nanocrystallite according to condition of method preparation. Thin films of TiO_2, ZnO, and TiO_2/ZnO were deposited on microscope glass slides by sol gel dip coating technique. The titanium dioxide (TiO_2) solution was obtained from titanium (IV) butoxide and butanol as the precursor, while zinc oxide (ZnO) solution was obtained from zinc acetate dehydrate and isopropanol as the precursor. Both of solution was ageing for 24 hours and different calcination temperatures used to calcined the thin films (400 ^oC, 500 ^oC, 600 ^oC). The thin films were characterized by X-ray Diffraction (XRD), and Atomic Force Microscopy (AFM). In this study, the effect of temperature show difference results of single layer and bilayer thin films. The result of XRD shows when the temperature increase, the thin films provide a good crystallization phase in which the structure of the diffraction peaks higher. From the AFM analysis, the surface roughness and the grain size increases as the temperature increase. Based on the characterization was carried out, the increase in temperature has influenced the distribution on the phase structure. The intensity of nanostructure thin films and also the smooth and compacted surface roughness were controlled by the temperature.

Keywords: ZnO, TiO_2, thin film, Sol-Gel dip coating.

INTRODUCTION

Scientifically, the thin film produced by decomposing the scale of atoms / molecules and the scale of it physical or chemical properties (Sundaram *et al*, 2004). In addition, the thin film is low-dimensional materials have produced through the process of condensation at all levels of atoms and molecules depend on the quantity or layer of coating to be produced (Hans and Dieter, 2003). TiO_2 has attracted significant attention of researchers because it show the most promising prospect in environmental purification for example as the photocatalytic degradation of pollutant (Sundaram *et al,* 2004), photoelctrochemical solar energy conversion, dye sensitized solar cells (Mathews *et al*, 2009), gas sensor, hydrogen by water photoelectrolysis and optical coating application (Foll, 2010), (Anderson and Chris, 2009) (Marcelo *et al*, 2006), (Jiaguo *et al*, 2001) (Bing *et al,* 2005). TiO_2 known to be one of the most important semiconductors with high photocatalytic activity, absence of toxicity and excellent chemical stability under various conditions (Tian *et al*, 2009), (Dong *et al*, 2002), (Morteza and Alireza, 2008). While, ZnO is a photonic property with wurtzite crystalline structure. ZnO has wide direct band gap (3.37 eV) and a large exciton binding energy (60 meV). Zinc oxide (ZnO) is the most active and extensively studied as a very attractive material for electronic, photovoltaic and optoelectronic applications (Wang *et al* 2004), (Naseri *et al,* 2011), (Patcharee *et al,* 2012), (Firdaus *et al*, 2012).

Thin films can be deposit using several techniques such as atomic layer deposition (ALD) (Hussin *et al*, 2014), chemical vapor deposition (CVD) (Kwang-Sik *et al,* 2003), magnetron sputtering (Chung *et al,* 2008), spray pyrolysis (Raut *et al*, 2011), and sol-gel (Naseri *et al,* 2011) method. Among these methods, sol-gel methods have been notable advantages including uniformity of the thin film microstructure, low synthesis temperature and low cost. Sol-gel method has emerged as one of the most promising process as it is particularly efficient in producing thin, transparent, homogenous layers on various substrates at low cost and it allows the choice of refractive index and thickness of the layer by changing elaboration conditions. The sol-gel process is known as dispersion of solid particles in liquid form (Vomvas *et al*, 2007), (Sakti, 2010), (Tian *et al*, 2009), (Mathews *et al* 2009), (Firdaus *et al,* 2012). Hence, in this study bilayer TiO_2/ZnO and single layer of TiO_2 and ZnO have been synthesis using sol-gel route to obtained the surface roughness and crystalline structure.

TiO_2, ZnO, and TiO_2/ZnO thin films crystalline size was controlled by calcinations at various temperatures and were analyzed by using atomic force microscopy (AFM), and X-ray Diffraction (XRD).

EXPERIMENTAL

TiO_2, ZnO, and TiO_2/ZnO thin films was prepared by the sol-gel dip coating method at different calcinations temperature. In this synthesis, the precursor of TiO_2 was prepared by using Titanium (IV) butoxide and butanol. The titanium (IV) butoxide was dissolved in butanol and stirred for 1 hour. Then acetic acid and distilled water was added dropwise into the precursor under continuous strong stirring at room temperature for 1

hour to produce sol-gel TiO_2. The resultant solution was kept ageing at room temperature for 24 hours.

The precursor solution for ZnO was prepared using zinc acetate dehydrate and isopropanol. The zinc acetate was mixed with isopropanol. Then DEA and distilled water were added into the precursor sol under strong stirring and heated at 60 ºC for 1 hour.

Glass slide were used as substrates. The substrate were cleaned with ethanol and acetone then rinsed with deionized water. Then, the glass substrate was dried at 70°C for 15 min. After cooling the substrates were dipped in the solution, and then withdrawn at speed 20 mm/min. After that, the film was dried at 100°C for 10 min. The substrate was dip 10 times into the sol to obtain the uniform layer. To growth bilayer TiO_2/ZnO nanostructured thin film, the cleaned microscope slide glass was firstly dip-coated into TiO_2 sol and dried at 100 ºC to form TiO_2 thin film. By using the same glass with TiO_2 thin film, the glass then continuously dip-coated with ZnO sol and dried at 100 ºC. Finally, the films were calcined for 1 hour at different temperature (400 ˚C, 500˚C, 600 ˚C).

The TiO_2, ZnO, and TiO_2/ZnO nanostructured thin films were characterized and analyze in detail as follow. The crystalline phase of the thin films was identified through X-Ray Diffraction method (XRD. Model D8 Advance, Bruker) with diffraction patterns scan used at 2θ from 20° to 65°. The surface roughness and morphology of the grain size was studied by using Atomic Force Microscope (AFM, XE-100).

Thickness of the thin films was measured by using surface profiler. The thickness of thin films can be control through controlling times repeating of coating sol-gel on substrate. The thicknesses of thin film were from 3900 nm to 4400 nm for both single and bilayer thin films. All the sample were coated with 10 times dipping.

RESULTS AND DISCUSSIONS

Crystallization of TiO_2, ZnO, and TiO_2/ZnO thin film

The crystal structure of TiO_2, ZnO, and TiO_2/ZnO thin films was analyze through X-ray diffraction (XRD) in order to identify the phase and crystallinity of thin films. Figure-1 (a), (b), and (c) show the XRD diffraction pattern of TiO_2 thin film calcined at different temperature. While Figure-1 (d), (e), and (f) show the XRD diffraction pattern of ZnO thin film also calcined at different temperature. Figure-1 (g), (h), and (i) show the bilayer TiO_2/ZnO thin film. The XRD measurement revealed that a single layer of TiO_2 and ZnO thin films and bilayer TiO_2/ZnO thin films showed TiO_2 phase with an anatase structure (JCPDS File 00-021-1272) and zincite phase for ZnO (JCPDS File 00-036-1451). The X-ray diffraction spectrum of single layer TiO_2 and ZnO also bilayer TiO_2/ZnO thin films calcined at 400 ºC, 500 ºC, and 600 ºC are shown in Figure-1.

The diffraction pattern of TiO_2 indicates the presence of anatase at the highest peak in $2\theta = 25.28^o$ (1 0 1). There are also weak diffraction peak of TiO_2 at $2\theta = 36.95^o$, 48.05^o, and 53.89^o which attribute to (1 0 3), (2 0 0), and (1 0 5) respectively. The formation of hexagonal ZnO with zincite phase at $2\theta = 31.8^o$, 34.3^o, 36.3^o, 47.5^o, 56.6^o, and 62.9^o which are attributed to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), and (1 0 3) planes, respectively resolved clearly when calcination temperature increased.

When the temperature increased, the diffraction peak also increased. The TiO_2/ZnO thin films pattern can be seen in Figure-1 (g), (h), and (i) with increasing of peak TiO_2 and ZnO when calcination temperature increased. The XRD results demonstrated that the TiO_2/ZnO thin film in Figure-1 (i) has sharp and narrow diffraction of the peaks demonstrated that the crystallinity of thin films improved when TiO_2 incorporated with ZnO. The deposition of ZnO with TiO_2 improve the crystallinity of TiO_2 thin film (Naseri *et al*, 2011). In addition, the formation of larger particle size and degree of crystallinity is found in the structure of TiO_2 thin films with increasing calcination temperature.

From the Figure-1, shows that the relative intensity of the peaks increases with calcination temperature and the preferred orientation for all sample was (1 0 1) peaks.

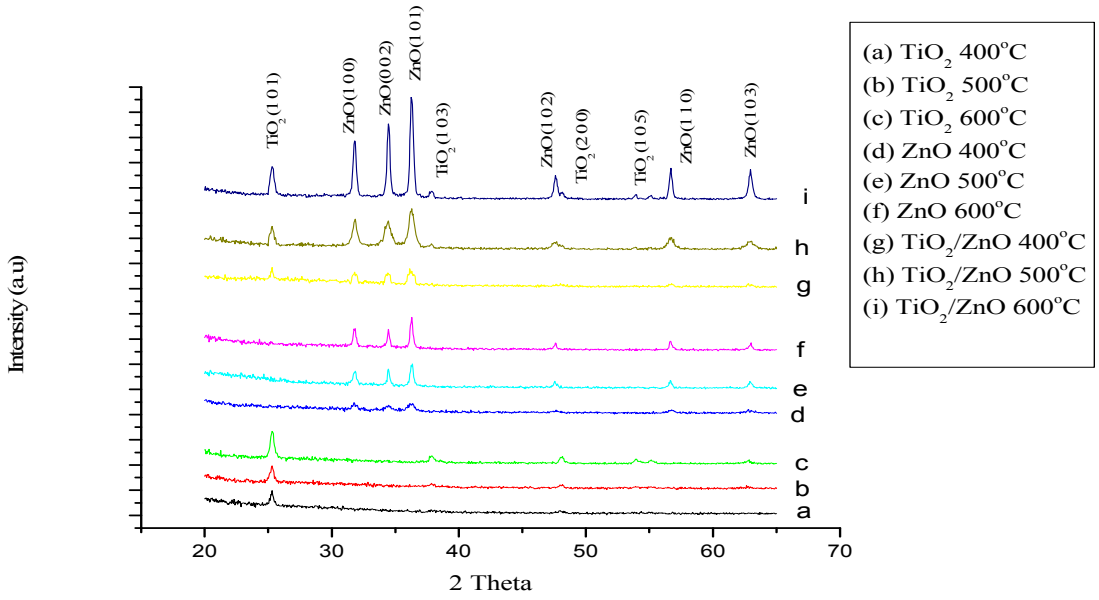
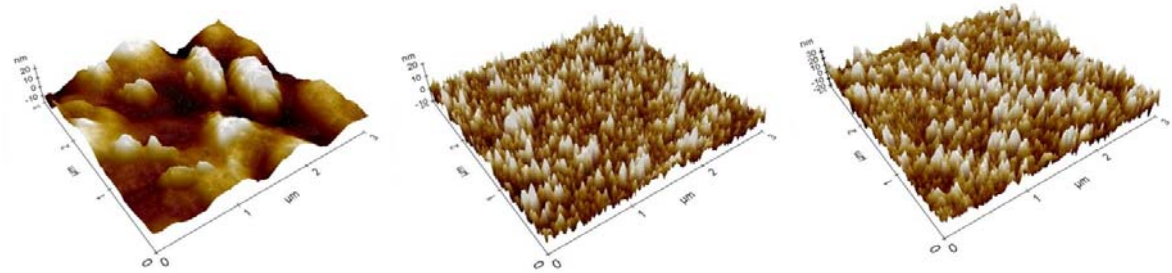


Figure-1. X-ray diffraction pattern of the TiO_2, ZnO, and TiO_2/ZnO thin films calcined at different temperatures.

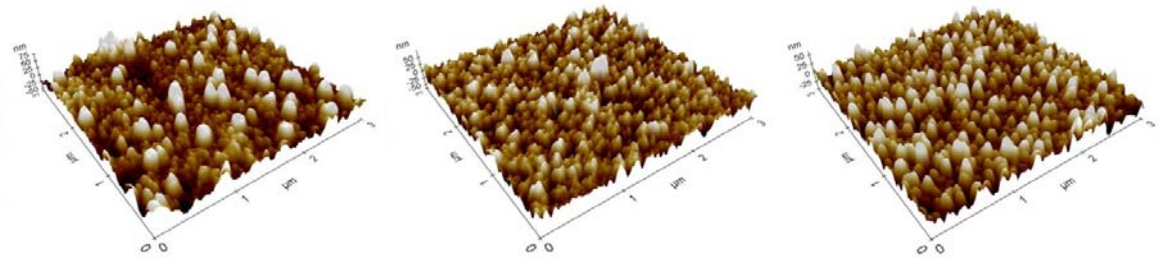


(a) TiO_2 400 ºC
RMS = 2.35 nm

(b) TiO_2 500 ºC
RMS = 2.87 nm

(c) TiO_2 600 ºC
RMS = 5.77 nm

Figure-2. Morphology and surface roughness of TiO_2 thin films calcined at different temperatures.

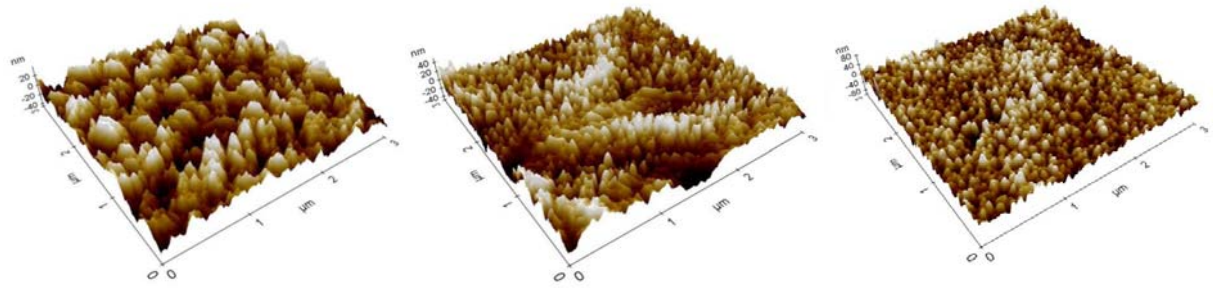


(a) ZnO 400 ºC
RMS = 2.64 nm

(b) ZnO 500 ºC
RMS = 3.35 nm

(c) ZnO 600 ºC
RMS = 4.47 nm

Figure-3. Morphology and surface roughness of ZnO thin films calcined at different temperatures.



(a) TiO_2/ZnO 400 ºC RMS = 5.14 nm (b) TiO_2/ZnO 500 ºC RMS = 8.67 nm (c) TiO_2/ZnO 600 ºC RMS = 9.63 nm

Figure-4. Morphology and surface roughness of TiO_2/ZnO thin films calcined at different temperatures.

Surface roughness of TiO_2, ZnO, and TiO_2/ZnO thin films

Various forms of particles morphology of TiO_2 thin film which has clearly found using the sol-gel synthesis. Figure-2, Figure-3, and Figure-4 show the morphology of thin films surface roughness with different calcination temperatures for all the samples. The calcination temperature used are 400 ºC, 500 ºC, and 600ºC that influence in the spread of particles.

Figure-2 shows the surface morphologies of 3 samples TiO_2 thin film with different calcination temperature (a) 400 ºC with RMS = 2.35 nm, (b) 500 ºC with RMS = 2.87 nm, and (c) 600ºC with RMS = 5.77 nm. While Figure-3 shows the surface morphologies of 3 samples of ZnO thin film with different calcination temperature (a) 400 ºC with RMS = 2.64 nm, (b) 500 ºC with RMS = 3.35 nm, and (c) 600ºC with RMS = 4.47 nm. Figure-4 shows the surface morphology of TiO_2/ZnO thin film, (a) 400 ºC with RMS = 5.14 nm, (b) 500 ºC with RMS = 8.67 nm, and (c) 600 ºC with RMS = 9.63 nm. All the morphologies of TiO_2, ZnO and TiO_2/ZnO thin films show the increasing in RMS value.

As can be seen, the morphology of TiO_2 thin films forming sharp particles on the surface in Figure-2. While Figure-3 shows the AFM morphology of ZnO thin films with rounded particles on the surface. The particles are not clearly visible and not fully homogenous against low calcination temperature as can be seen in Figure-2(a), Figure-3(a), and Figure-4(a). The difference in particle size can be clearly seen at all sample of thin films with different calcination temperatures.

From Figure-4, the thin films were clearly visible form on the surface layers with incorporation of TiO_2 and ZnO. The crystallization for bilayer formed better as assisted by coating TiO_2 on TiO_2/ZnO (Hussin *et al*, 2012). Whereas when the calcinations temperature increased, the densed and compacted particles were formed on the layers as shown in Figure-2 (c), Figure-3 (c) and Figure-4 (c). This is because the layer structure of thin film growth homogenously on substrate if the calcination temperature used was increased.

The particles are formed more closely and dense when the calcination temperature is increased. As shown in the Figure-2, Figure-3, and Figure-4 above, the effect in shape and agglomerate particle is affected by the different calcinations temperatures and by incorporating TiO_2 with ZnO. This is because when the calcinations temperature increase, the particles are formed and found to be compacted with each other. Hussin (Hussin *et al,* 2012) states that if the number of increasing calcinations temperature, the surface roughness will increase at each temperature applied respectively. However, the surface becomes smoother and RMS values are increased when the calcinations temperature increased. It is proved that when the calcinations temperature is higher, surface roughness and particle size are also increasingly created and formed. The morphology of thin films clearly show that the particle formation increased and the structural morphology become compact therefore the surface of the film become smoother.

CONCLUSIONS

TiO_2, ZnO, and TiO_2/ZnO nanostructured thin films have been successfully deposited on glass substrate by sol-gel dip coating method. Their structural properties have been studied as a function of temperatures (400 ºC, 500 ºC, and 600 ºC). XRD analysis shows that the intensity of nanostructure thin films controlled by the temperature. The highest intensity form at TiO_2/ZnO calcined at 600 ºC. The surface roughness of TiO_2/ZnO thin films are compared with TiO_2 and ZnO single layer through AFM. TiO_2/ZnO nanostructured thin film show the smooth and compacted surface roughness than TiO_2 and ZnO single layer.

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