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EFFECTS OF ANNEALING TEMPERATURE ON STRUCTURAL, MORPHOLOGY AND OPTICAL PROPERTIES OF TiO_2 THIN FILM

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ABSTRACT

This paper reports on the effects of Titanium dioxide (TiO_2) thin films which were deposited by sol-gel spin coating technique with different annealing temperatures at 300°C, 400°C and 500°C for a period of 1 hour. The precursor used was 2 ml of Titanium (IV) Butoxide. The research is focusing more on the uniformity of TiO_2 thin films. TiO_2 films were characterized by structural properties, surface morphological, surface topological and optical properties. For 500°C annealed film, transparent TiO_2 thin film were deposited more uniform than the others. The surface morphologies of the TiO_2 thin film were observed by a field emission scanning electron microscope (FESEM).The surface topologies and roughness were characterized by an atomic force microscope (AFM). The structural properties were characterized by an X-ray diffractometer (XRD). The optical properties were characterized with an ultraviolet-visible spectrometer (UV-Vis). The results indicated the optical transmittance of TiO_2 thin films were elevated with higher annealing temperature.

Keywords: annealing temperature, titanium IV butoxide, anatase.

INTRODUCTION

Titanium dioxide (TiO_2) has good physical properties such as high dielectric constant, good mechanical resistance and good insulation properties [1]. TiO_2 is an n-type semiconductor with 3.2 eV band gap and has a range of utilization for the applications of photocatalytic [2], antireflection coatings [3], solar cells [4] and gas sensor [5]. The physical, optical and structural properties of titanium dioxide (TiO_2) depend on crystalline phases of the material. TiO_2 is a material with three crystalline phases; anatase, rutile and brookite are commonly observed in this thin films [6]. Rutile is the most stable at all temperatures in very acidic or basic. In addition, it has high refractive index (2.5 ~ 4.5) [7], [8]. Stoichiometry of rutile TiO_2 is greatly dependent on parameters of deposition, particularly in condition of annealing and the environment. The melting point of rutile is 1850℃ associated with purity titanium dioxide. Anatase and brookite are more stable at lower temperature, but both react to rutile at high temperatures (915℃ to 750℃ of anatase and brookite). Moreover, lower annealing temperature at lesser than 350℃, the structural of TiO_2 on thin film becomes amorphous [6], [9],[10].

TiO_2 thin films can be synthesized using various techniques, including sputtering [11], electrophoretic deposition [12], sol-gel [13],[14], dip coating [15] and spin coating [16]. Spin coating is extensively used in the fabricate of TiO_2 thin films due to fast growth, capacity for handling large sample size, mass production capacity and high yields. However, spin coating technique involves a process of subsequent annealing, which is known to increase the spread of impurities from the substrate of glass coating. This process tends to restrict the grain growth in the film and also increases the number of lattice defects, which decreases the photocatalytic activity of the TiO_2 thin films.

The intention of this work was the optimization process of Titanium (IV) Butoxide concentration to produce uniform and transparent TiO_2 thin films using sol-gel spin coating and to determine the optimum annealing temperature, which would produce the best performance of thin film.

EXPERIMENTAL

Figure-1 indicates the research methodology of the optimization of TiO_2 thin film for solar cell application. The glass substrates were cleaned with acetone in an ultrasonic bath for 5 minutes at 50°C and purged to dry with nitrogen gas.

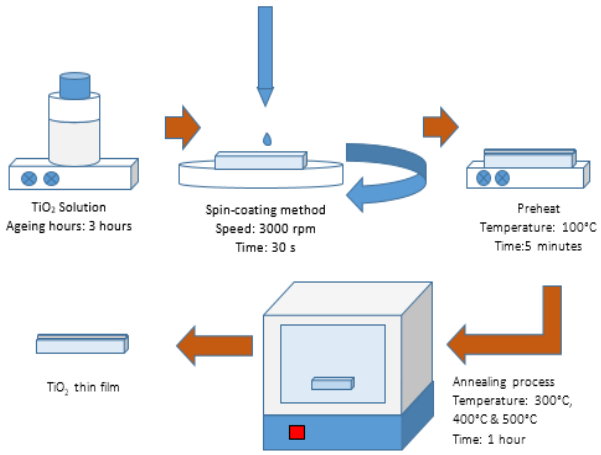


Figure-1. Schematic diagram of sol–gel process and deposition of TiO_2 thin film.

The starting materials used were titanium butoxide as precursor, ethanol as solvent, deionised water as a function of adding the oxygen (O), acids and triton X-

100 as a stabilizer to avoid precipitation in solution and at the same time used to increase the conductivity of films. The type of acids were glacial acetic acid and hydrochloric acid. For solution preparation, titanium butoxide mixed with ethanol, acid catalysts and triton X -100 were stirred for 3 hours for ageing process at room temperature**.** TiO_2 solution used for the deposition of thin films by spin-coating method was obtained by the partial hydrolysis and condensation.

TiO_2 films were deposited by spin coating method (3000 r.p.m for 30s) for 5 layers. TiO_2 solution was dropped up to 10 times onto the substrates. Each layer was preheated at 100°C for 5 minutes. The thin films were annealed at 500°C for 1 hour. Annealing also produces better physical attachment which improves the electronic contact between all the particles of the thin films. After annealing at 500°C for 1 hour, the thin films were underwent slow cooling at room temperature. Then, thin films were coated with gold electrode by using sputter coater. The sputter coater was set to 20mA for 30 seconds. Then, TiO_2 thin films were physically characterized.

The surface morphology of the TiO_2 thin film was observed by a field emission scanning electron microscope (FESEM). The magnification of the images is 50K times. The thickness of each sample was characterized using KL Tenko surface profiler. The optical transmittance spectra were recorded in the wavelength range of 300-1000nm using a Shimadzu Ultra Violet-Visible Spectrometer (UV-Vis). The structural properties were characterized by PAnalytical Smartpowder X-ray diffractometer (XRD). XRD is used to identify the crystallinity and phases of the TiO_2 film. The measurement was obtained at 2θ degree by Cu Kα radiation. The surface topologies and roughness were characterized by an Atomic Force Microscope (AFM), XE-100 Park system at room temperature. With noncontact cantilever and non-contact mode, this characterization method promises a non-destructive testing. Other than that, it also capable to give the information on grain size and roughness of TiO_2 thin film.

The estimation of the crystal grain size, D according to Scherrer's equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ is the light wavelength, β is the full width half maximum and θ is the degree of diffraction.

RESULTS AND DISCUSSION

Surface morphology

Figure-2 shows the cross-sectional view of TiO_2 thin films annealed at 500°C. For sample deposited using 1.5 ml, 2.0 ml and 2.5 ml of Titanium (IV) Butoxide, the thicknesses are 41.3 nm, 88.1 nm and 98.4 nm, respectively. It shows the inceasing of thickness when the concentration of Titanium (IV) Butoxide was increased. Figure-3 shows that 2ml of Titanium (IV) Butoxide, the TiO_2 thin film is more uniformity than the others.

Figure-4 shows three types of sample that annealed at 500°C, 400°C and 300°C. In this research, annealing of TiO_2 thin film at 500°C shows the particles size between 15.9 nm to 49.1 nm. On the other hand, annealing at 300°C and 400°C had grown particles ranging from 12.7 nm to 14.0 nm and 14.1 nm to 15.5 nm. It was found that the particle size increases as the annealing temperature increased.

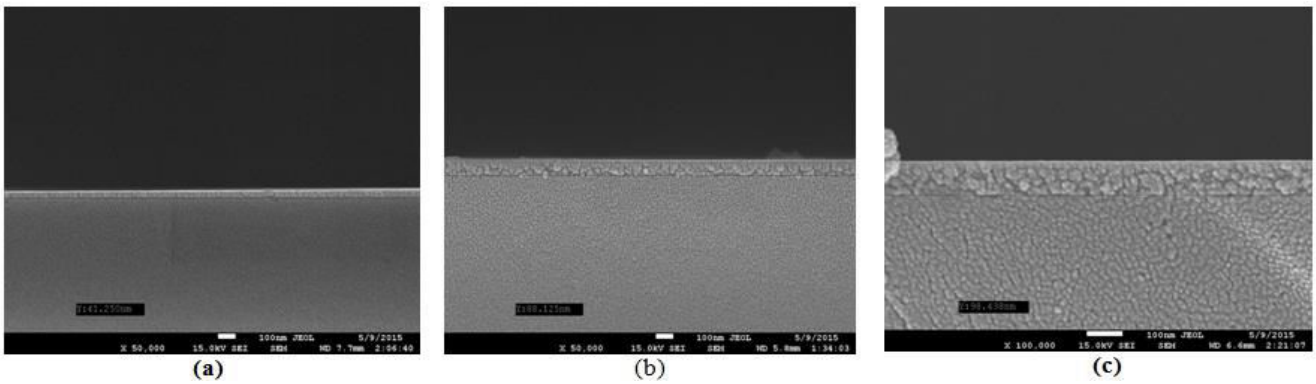
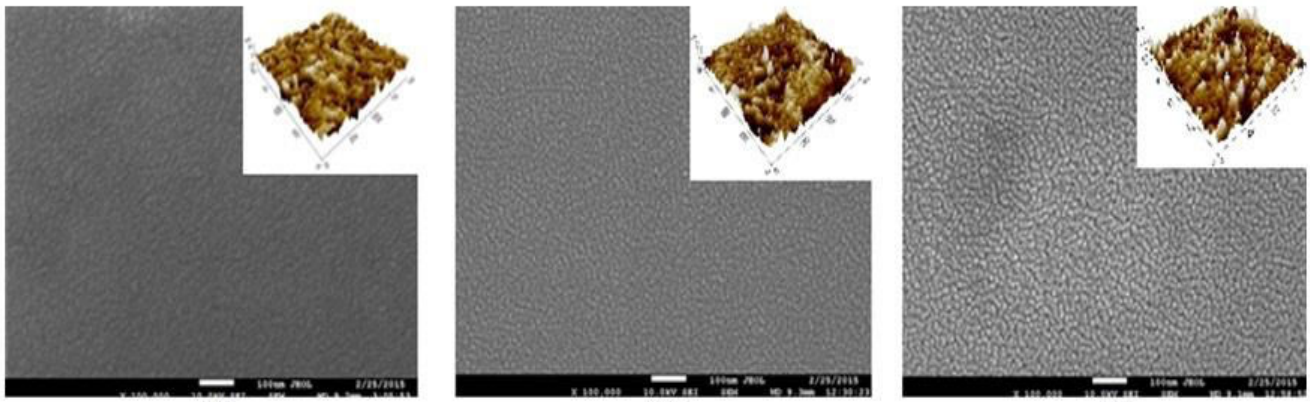


Figure-2. Cross section of TiO_2 thin film for diffrent titanium butoxide concentration (a) 1.5 ml (b) 2.0 ml and (c) 2.5 ml.

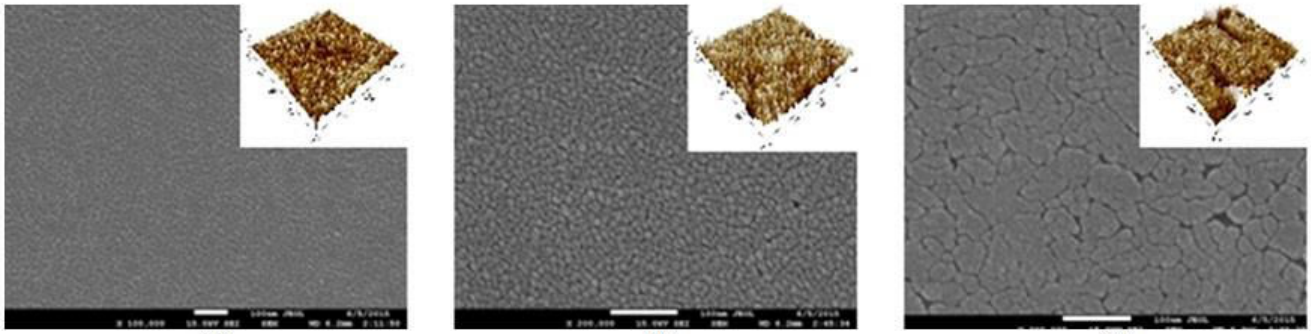
Surface topology

Figure-4 shows two dimensional AFM images of the deposited films annealed at 300°C, 400°C and 500°C. When the annealing temperature was increased, the grain size was decreased. The grain size for annealing temperature of 300°C, 400°C and 500°C are 91 nm, 56 nm and 49 nm, respectively. Furthermore, the AFM roughness analysis also presented the value of the roughness parameters. The lower roughness value represents good homogeneity of the TiO_2 particles on the surface. AFM image at 500°C has the lowest roughness. Table-1 shows the grain size and surface roughness of TiO_2 thin film. The average particle size lies in the range of nm, which is slightly larger than that obtained from the XRD results.



(a) (b) (c)

Figure-3. Surface morphology of TiO_2 thin film for different titanium butoxide concentration (a) 1.5 ml (b) 2.0 ml and (c) 2.5 ml.



(a) (b) (c)

Figure-4. Surface morphology of TiO_2 thin film for different annealing temperature (a) 300°C (b) 400°C and (c) 500°C.

Table-1. Grain size and surface roughness with different annealing temperature.

Annealing temperature	Grain size	Surface roughness
300°C	91 nm	0.383 nm
400°C	56 nm	0.811 nm
500°C	49 nm	1.349 nm

Structural Properties

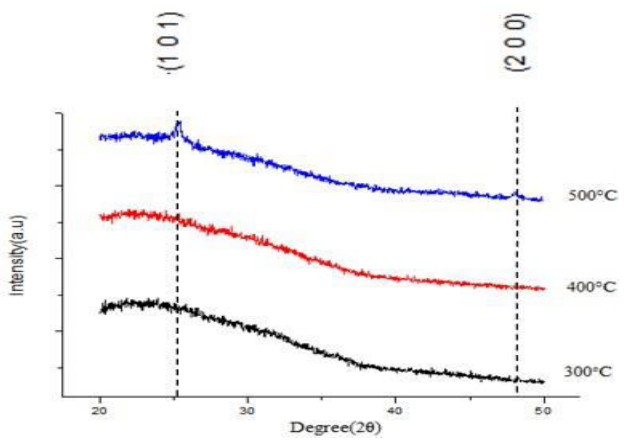


Figure-5. X-ray diffraction patterns of the TiO_2 thin film at various annealing temperature.

XRD is essential in the determination of the crystallinity. Figure-5 shows the XRD spectra of the TiO_2 thin films, as-deposited at different annealing temperature namely 300°C, 400°C and 500°C. As-deposited samples were basically polymorphs and characteristic peaks were visible corresponding to TiO_2 which major anatase phase at 500°C. The thin film was in anatase crystalline state with a better orientation of (101) at 25.32° Besides that, XRD peaks at 48.14° corresponded to the anatase orientation (200) peak also shown in the annealed samples which could be indexed as standard tetragonal stable anatase crystalline state. However at 300°C and 400°C, annealing temperature, no peaks were visible because of small size of the crystal and very low intensity of the diffracted X-rays. In anatase phase that the orientation (101) surface was the most stable and dominant peak with the highest intensity. The intensity of TiO_2 thin film existed with annealing temperature. The weak intensity of diffraction peaks for the as-deposited film indicates the presence of amorphous phase.

The temperature dependence of XRD patterns can be described by the mobility of atomic species in thin films at various annealing temperature. At low annealing temperature, the evaporated species possess small energy and a low surface mobility causing a less controlled surface structure. The low mobility of atoms avoids full

crystallization of the films. Nevertheless, at high annealing temperature, and high temperature, atoms acquire high sufficient mobility to organize themselves in more crystalline arrangement.

Optical properties

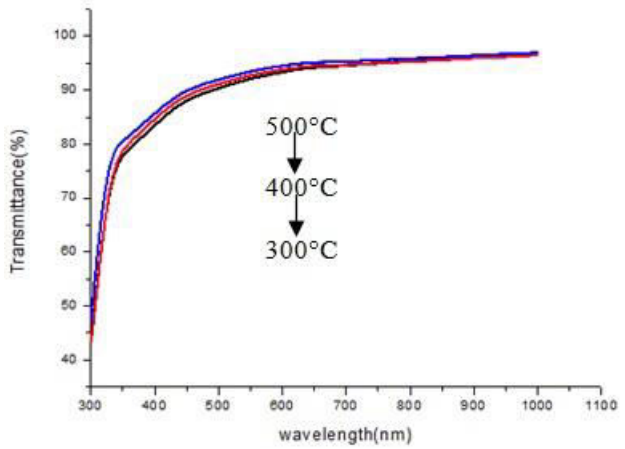


Figure-6. The transmittance spectra of TiO_2 thin films at different annealing temperature (a) 500°C (b) 400°C (c) 300°C.

Figure-6 shows the optical transmittance of the thin films annealed at 300°C, 400°C and 500°C in the spectra region of 300-1000 nm. Glasses were used as substrate in this experiment to prevent the influence of the absorption edge of substrate. Based on the figure, it shows a slight decrease in transmittance with the increasing of annealing temperature. The optimum TiO_2 thin films spectra exhibited high visible transmittance as high as 98% for annealing temperature of 500°C. The energy band gap is evaluated using Tauc's plot based on equations as the following:

$$E = \frac{hc}{\lambda} \quad (2)$$

and

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) \quad (3)$$

While h, c and λ are plank constant (4.136 × 10-15 eV), speed of light (3×108 ms-1) and wavelength, respectively. Where, d and T are the absorption coefficient, film's thickness and transmittance, respectively. Energy band gap normally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in semiconductors. Conversely at the wavelength between 300nm-340nm,the film at 300°C initially shows the lowest transmittance and gradually increases. On the other hand film annealed at 500°C shows the highest transmittance at 1000 nm wavelength. Nevertheless, all samples exhibit more than 90% of transmittance in the visible light region. The transmittance for all annealed samples rises with increasing wavelength.

CONCLUSIONS

This paper presents the results of the optimization process to produce uniform and transparent TiO_2 thin films using sol-gel spin coating. TiO_2 thin films were more uniform using 2ml Titanium (IV) Butoxide. The surface morphology of the TiO_2 thin films were investigated using FESEM measurements. Transparent Titanium dioxide thin films that has been successfully annealed at 500°C. The samples were anatase phases and the particle size was in nanometer scale which is confirmed by XRD pattern analysis. The particle was measured using AFM at annealing temperature of 500°C and the smallest grain size is 49 nm. The surface roughness at 500°C is 1.349 nm. UV-vis spectra showed that the absorption edge of these films were at shorter wavelength. At 500°C the optimum transmittance was obtained which is 98% and sufficient for optoelectronic applications especially for solar cell.

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