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DEPOSITED TIO_2 THIN FILMS BY ATOMIC LAYER DEPOSITION (ALD) FOR OPTICAL PROPERTIES

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ABSTRACT

The thin films ceramic oxide can be fabricated by ALD because this technique promises to control the deposition on an atomic scale by sequentially dosing the surface with appropriate chemical precursors, and by promoting surface chemical reactions that are inherently self-limiting. TiO_2 has been widely used in photocatalysts, due to its photosensitivity and thermal stability. TiO_2 also has strong absorption in the UV range, at around 3.3 eV. ALD deposition cycle and temperature would determine the surface morphology of TiO_2 thin films from a very smooth surface to a rough surface, which is important for their functional applications. The combined results of XRD and AFM show that the deposition temperature played an important role in the growth of TiO_2 thin films and the phase transition from amorphous to anatase. These results demonstrated a self-limiting of 0.017 - 0.024 nm/cycle growth of the TiO_2 thin films using TTIP and H_2O, at deposition temperatures ranging from 100˚C to 300˚C. The optical properties of TiO_2 thin films were also influenced by the deposition temperature. In addition, UV luminescence (at 353 nm) was present in the TiO_2 thin films deposited at 200˚C whereas there was no UV luminescence for pure bulk TiO_2.

Keywords: atomic layer deposition, TiO_2, thin films, deposition, optical properties.

INTRODUCTION

ALD (Atomic Layer Deposition) is an ideal technique for the deposition of nanostructured scale thin films in single layer (Hussin *et al.*, 2012) and multilayer (Hussin *et al.*, 2014). The application of thin films depends on its properties. The optical property of thin films depends on the interaction of light with electrons. The optical properties of thin films will measure their response to electromagnetic waves, mainly in the wavelength spectrum of visible light, from 400 to 700 nm. When light interacts with solids, liquids, and gases, one can be satisfied with the phenomena of reflection, refraction, scattering, absorption with or without altering the frequency of light and polarization. Luminescence indicates the impulsive emission of light by excited atoms in the material.

TiO_2 in its anatase structure has a lower resistance and a higher response to gas adsorbents than in its rutile structure, which is stable at higher temperatures (Wisitsoraat *et al.*, 2006). The most attractive aspects of TiO_2 are that the types of photochemistry responsible for photocatalysis and hydrophilicity are completely different even though both can occur simultaneously on the same surface (Fujishima *et al.*, 2000). TiO_2 has been widely used in photocatalysts, due to its photosensitivity and thermal stability and also optical properties (Dang *et al.*, 2014). TiO_2 also has strong absorption in the UV range, at around 3.3.

EXPERIMENTAL PROCEDURE

TiO_2 thin films were deposited on silicon (100) and microscope glass substrate by Atomic layer deposition (ALD) with Titanium (IV) isopropoxide (TTIP) in 25 g packages in a stainless steel cylinder. H_2O (Deionized water) was used as the second precursor in a stainless steel cylinder as well. The substrates were ultrasonically cleaned using acetone. The pressure of the ALD chamber was maintained at 50 kPa, and the N_2 carrier gas was set at 20 sscm. The TTIP was heated to 75°C and the water was kept at room temperature in order to provide sufficient vapour for the TiO_2 ALD process. The precursors pulse rates for TTIP and H_2O were set at 0.20 s and 0.15 s, respectively. The ALD cycles sequence H_2O/ N_2/TTIP/ N_2 on the substrates.

The deposition temperatures used in ranged from 100°C to 300°C. The phase and crystal structure of TiO_2 thin films were characterized by X-ray diffractometer XRD, (Siemens Kristalloflex - D500 Cu Kα radiation with wavelength of 1.5406A°). The surface morphology and roughness of the films was evaluated by Atomic force microscope (AFM, Veeco CPII-Research Scanning Probe Microscope).The photoluminescence of the multilayer thin films were measured by Hitachi F-2500 fluorescence spectrometer. The optical transmittance spectra were measured by Biochrom Libra S33 UV/Vis-spectrometer.

RESULTS AND DISCUSSIONS

Figure-1 shows the XRD patterns indicating the change of crystallinity with an increasing deposition temperature. The XRD measurement revealed that crystalline TiO_2 thin films with an anatase (JCPDA 00-021-1272) structure were obtained at deposition temperatures of 200 ˚C, 250 ˚C, and 300 ˚C, for 3,000 deposition cycles. The main peak for anatase (101) (2θ=25.3°) was observed at 200 ˚C, 250 ˚C, and 300 ˚C. No crystalline phase was detected in the films grown at

100 ˚C. No peaks were identified with the sample at 100 °C, suggesting that the TiO_2 was amorphous. Obviously, there existed a phase transition in the growth of TiO_2 thin films with temperature.

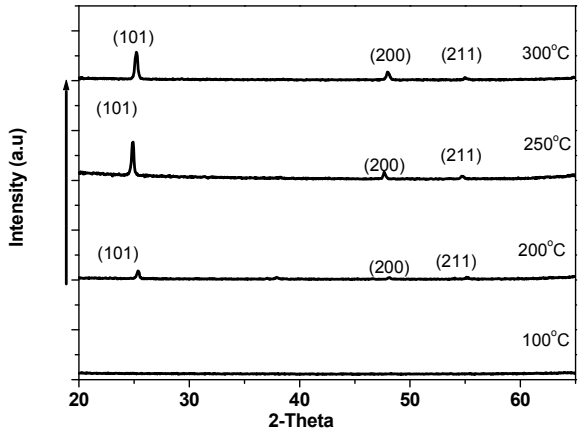

Figure-1. XRD patterns of TiO_2 thin films.

As shown in Figure-1, the intensity at (101) increased with the increasing deposition temperature. Aarik *et al*. (2001) found a similar result at deposition temperatures below 200 ˚C, with titanium ethoxide and water as precursors. Crystal growth was reflected by the intensity of the XRD peaks at (101), which were generally increased by the deposition temperatures. Moreover, Ritala *et al*. (Ritala *et al.*, 1994) observed that the intensity of the XRD peaks increased 3-fold when the temperature increased from 250 ˚C to 325 ˚C. They found only the (101) orientation in all the films but after increasing the cycles to 6000-8000, they observed (101), (200), and (211). However, in our study, the orientation (101), (200), and (211) were found above 200 °C at 3000 cycles. ALD is a promising technique for the growth of TiO_2 films with an anatase structure at lower temperatures (i.e. 200 °C) as compared with other techniques which would require annealing of up to 400 °C (Ohara *et al*., 2008; Porkodi and Arokiamary, 2007;Edusi *et al*., 2012).

Morphology analysis of TiO_2 thin film with different process parameters

The AFM images and RMS of the TiO_2 thin films deposited at different temperatures are shown in Figure-2 and 3, respectively. According to the AFM measurement, the highest roughness of the films was formed at 200 ˚C and the film surface became smooth after 250 ˚C. Figure-2(a) shows the amorphous films at 100 ˚C. As seen in Figure-2(d) the films consisted of well grown particles after the deposition temperature increased to 300 ˚C. The increased deposition temperature results in a more regular appearance of the particles, which can be observed from the AFM images. The surface roughness also increased from 1.6 nm to 9.7 nm at deposition temperatures of 100 ˚C to 200 ˚C, respectively. However, the surface became smooth and RMS reduced when the deposition temperature continued to increase from 8.52 nm to 6.31 nm for 250 ˚C to 300 ˚C, respectively.

Kim *et al*. (2011) found the RMS of TiO_2 deposited by TTIP and H_2O at 250 °C were greater than 260 °C. They suggested that this was related to the thermally activated nucleation process, which results in a larger number of smaller grains at higher deposition temperatures. Similar surface roughness behaviour is seen in this work, but Kim *et al.* (2011) only studied two different temperatures. In contrast, Lee *et al*. (2004) obtained that the RMS of TiO_2 films deposited using $Ti(OPr^i)_2(dmae)_2$ increased with deposition temperature. The results revealed that during the early stages of the film growth, clusters or agglomerates were formed [Figure-2(b)], and as the growth proceeded, these agglomerates grew both horizontally and vertically, and finally they coalesced to form spherical particles [Figure-2(d)]. It is suggested that the agglomerates were driven by the interface energy between the TiO_2 film and the substrate. The possible mechanism for the migration needed for the agglomerates included the gas-phase migration of volatile intermediates, and surface migration of the hydroxyl group during the ALD process (Ritala *et al.*, 1994).

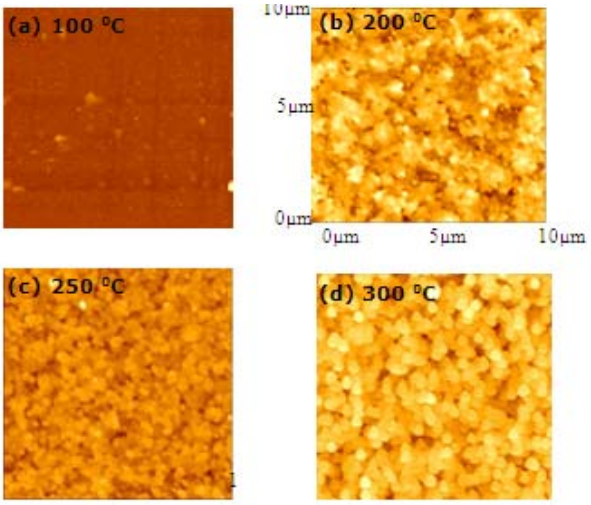

Figure-2. AFM morphology TiO_2 thin films deposited at different deposition temperatures (a) 100 °C (b) 200 °C (c) 250 °C and (d) 300 °C [Substrates: Silicon wafer (100)].

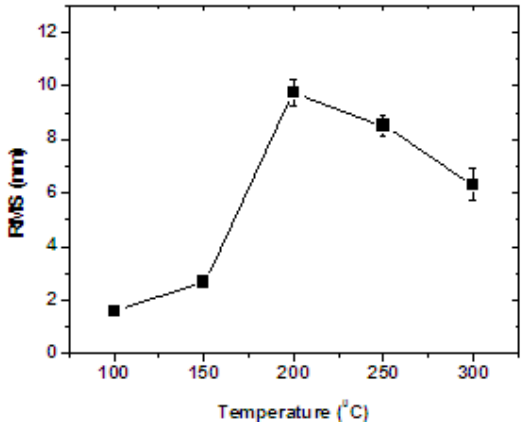

Figure-3. RMS of TiO_2 thin films deposited at different deposition temperatures [Substrates: Silicon wafer (100)].

PL analysis of TiO_2 thin film with different process parameters

Figure-4 displays the room temperature PL spectra of TiO_2 thin films deposited at different temperatures. Interestingly, the spectra exhibit peaks in the UV region with deposition temperatures of above 200˚C.

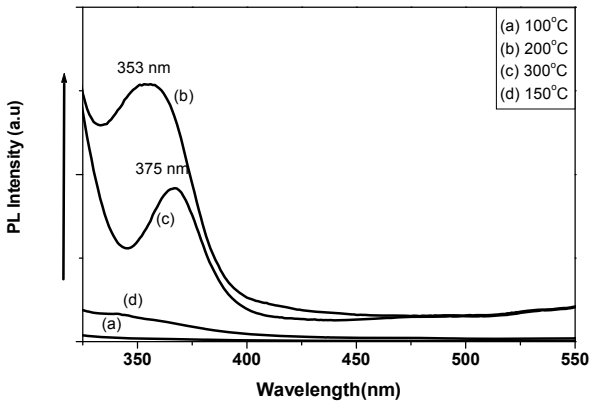

Figure-4. PL intensity of TiO_2 thin films deposited at different temperatures.

Figure-4 show the deposition temperature affected the PL response of TiO_2 thin films deposited at 100 ˚C and 150 ˚C which did not demonstrate any PL peak. The UV luminescence energy shifted to a higher energy direction with a decrease of deposition temperature. The UV luminescence peaks are located at 375 nm (3.32 eV) and 353 nm (3.5 eV) for TiO_2 thin films of 300 ˚C and 200 ˚C, respectively. Both samples have strong bands appearing at 320 nm to 380 nm, which are assigned to the characteristic emission of free excitations of anatase TiO_2 thin films (Yuwono *et al*., 2006). The photo-luminescent spectra of anatase-TiO_2 can generally be attributed to three origins, namely surface states, self-trapped, and oxygen vacancies (Yuwono *et al*., 2006). The surface state acts as donor and acceptor sites and hence photo-generated charge carriers tend to be trapped at the surface of the semiconductor. The electrons in TiO_2 are derived from local defects due to oxygen deficiencies and adsorbed species on the surface (De La Garza *et al*., 2005). The band at 420 nm is normally assigned to self-trapped excitons localized on TiO_2, and the band at 460 nm is attributed to oxygen vacancies which can easily capture photo-induced electrons to form excitons and finally, the band at 510 nm is attributed to surface defects. The defects are correlated to the degree of crystallinity (Niedermeier *et al*., 2012; Yamamoto and Ohno, 2012). As shown in Figure-3 no peak appears at 510 nm, which again indicates good crystallinity. Anatase-TiO_2 is an indirect band gap semiconductor (Diebold, 2003). The electron between the valance band and the conduction band is of low efficiency, owing to the participation of photons during the transition process, which leads to the poor emission behaviour. However, bulk TiO_2 and TiO_2 nanostructures generally have no UV luminescence under normal conditions (Ming *et al*., 2009;Yuwono *et al*., 2006). The observation of UV luminescence demonstrates a more efficient electron transition in the TiO_2 thin film, which is the variation of oscillator strength of the allowed direct transition (Ming *et al*., 2009).

Optical transmittance of TiO_2 thin films with different deposition processes

In this study, the optical transmittance spectra of TiO_2 thin films with different cycles, in a wavelength range of 300 to 800 nm, are shown in Figure-5. The transmittance is dependent on the deposition temperature and cycles.

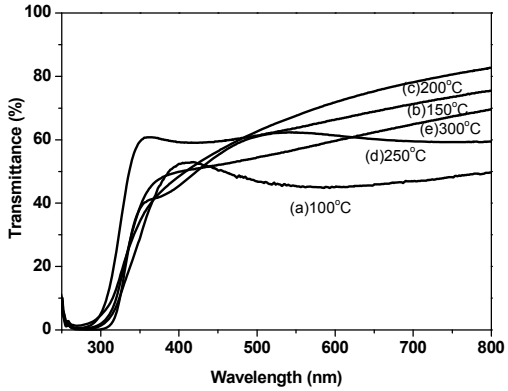

Figure-5. The transmittance of TiO_2 thin film deposited at different deposition temperatures.

As we know, the films containing large amounts of rutile were clearly more transparent (Nussbaumer *et al*., 2002). The film with an amorphous structure has shown a transmittance of between 40-60%. Only a few studies have reported regarding the transmittance of TiO_2 thin film using ALD (Kasikov *et al*., 2006;Kim *et al*., 2008). Kim (Kim *et al*., 2008) deposited amorphous films using TTIP and observed a transmittance of 35%. From the

absorbance results and the absorbance spectra data, the band gap (E) was calculated. Figure-5 shows that the band gap of the TiO_2 thin films was obtained by plotting $(\alpha hv)^{0.5}$ versus (hv). The band gap values, obtained from the plots for 100 ˚C, 150 ˚C, 200 ˚C, 250 ˚C and 300 ˚C were 3.04 eV, 3.36 eV, 3.18 eV, 3.20 eV and 3.21 eV respectively. As the band gap for anatase was ~3.2 eV (Pierson and H.O., 1999;Mo and Ching, 1995;Diebold, 2003), it confirms that the TiO_2 thin film deposited at 200 ˚C and above have an anatase structure.

CONCLUSIONS

ALD technique was used to deposit TiO_2 thin films. The ALD deposition cycle and temperature would determine the surface morphology of TiO_2 thin films from a very smooth surface to a rough surface, which is important for their functional applications. The optical properties of TiO_2 thin films were also influenced by the deposition temperature. In addition, UV luminescence (at 353 nm) was present in the TiO_2 thin films deposited at 200 ˚C whereas there was no UV luminescence for pure bulk TiO_2. The XRD measurement revealed that crystalline TiO_2 thin films with an anatase. The XRD patterns indicate the change of crystallinity with an increasing deposition temperature.

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REFERENCES

Aarik, J., Karlis, J., Mandar, H., Uustare, T. &Sammelselg, V. 2001. Influence of structure development on atomic layer deposition of TiO_2 thin films. Applied Surface Science, 181, 339-348.

Dang, V.-S., Parala, H., Kim, J. H., Xu, K., Srinivasan, N. B., Edengeiser, E., Havenith, M., Wieck, A. D., De Los Arcos, T., Fischer, R. A. and Devi, A. 2014. Electrical and optical properties of TiO_2 thin films prepared by plasma-enhanced atomic layer deposition. physica status solidi (a), 211, 416-424.

De La Garza, L., Saponjic, Z. V., Dimitrijevic, N. M., Thurnauer, M. C. and Rajh, T. 2005. Surface States of Titanium Dioxide Nanoparticles Modified with Enediol Ligands. The Journal of Physical Chemistry B, 110, 680-686.

Diebold, U. 2003. The surface science of titanium dioxide. Surface Science Reports, 48, 53-229.

Edusi, C., Sankar, G. and Parkin, I. P. 2012. The Effect of Solvent on the Phase of Titanium Dioxide Deposited by Aerosol-assisted CVD. Chemical Vapor Deposition, 18, 126-132.

Fujishima, A., Rao, T. N. and Tryk, D. A. 2000. Titanium dioxide photocatalysis. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1, 1-21.

Hussin, R., Choy, K. L. and Hou, X. H. 2014. Fabrication of Multilayer ZnO/TiO_2/ZnO Thin Films with Enhancement of Optical Properties by Atomic Layer Deposition (ALD). Applied Mechanics and Materials, 465, 916-921.

Hussin, R., Hou, X. H. and Choy, K. L. Growth of ZnO Thin Films on Silicon Substrates by Atomic Layer Deposition. Defect and Diffusion Forum, 2012. Trans Tech Publ, 159-164.

Kasikov, A., Aarik, J., Mandar, H., Moppel, M., Pars, M. and Uustare, T. 2006. Refractive index gradients in TiO2 thin films grown by atomic layer deposition. Journal of Physics D-Applied Physics, 39, 54-60.

Kim, G. M., Lee, S. M., Michler, G. H., Roggendorf, H., Goiˆ Sele, U. and Knez, M. 2008. Nanostructured Pure Anatase Titania Tubes Replicated from Electrospun Polymer Fiber Templates by Atomic Layer Deposition. Chemistry of Materials, 20, 3085-3091.

Kim, S. K., Hoffmann-Eifert, S., Reiners, M. and Waser, R. 2011. Relation between Enhancement in Growth and Thickness-Dependent Crystallization in ALD TiO_2 Thin Films. Journal of the Electrochemical Society, 158, D6-D9.

Lee, J. P., Park, M. H., Chung, T.-M., Kim, Y. & Sung, M. M. 2004. Atomic Layer Deposition of TiO_2 Thin Films from Ti(OiPr)2(dmae)2 and H_2O. Bull. Korean Chemical. Society, 25, 475-479.

Ming, L., Kui, C., Wenjian, W., Chenlu, S., Piyi, D., Ge, S., Gang, X. and Gaorong, H. 2009. Size-dependent ultraviolet luminescence and low-field electron emission of TiO_2 nanodots formed by phase-separation-induced self-assembly. Journal of Physics D: Applied Physics, 42, 105414.

Mo, S.-D. and Ching, W. Y. 1995. Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. Physical Review B, 51, 13023.

Niedermeier, M. A., Magerl, D., Zhong, Q., Nathan, A., Korstgens, V., Perlich, J., Roth, S. V. and Muller-Buschbaum, P. 2012. Combining mixed Titania morphologies into a complex assembly thin film by iterative block-copolymer-based sol-gel templating. Nanotechnology, 23, 145602.

Nussbaumer, R. J., Caseri, W., Tervoort, T. and Smith, P. 2002. Synthesis and Characterization of Surface-modified Rutile Nanoparticles and Transparent Polymer Composites Thereof. Journal of Nanoparticle Research, 4, 319-323.

Ohara, C., Hongo, T., Yamazaki, A. and Nagoya, T. 2008. Synthesis and characterization of brookite/anatase complex thin film. Applied Surface Science, 254, 6619-6622.

Pierson & H.O. (eds.) 1999. Handbook of Chemical Vapor Deposition (CVD) - Principles, Technology and Applications William Andrew Publishing/Noyes.

Porkodi, K. and Arokiamary, S. D. 2007. Synthesis and spectroscopic characterization of nanostructured anatase Titania: A photocatalyst. Materials Characterization, 58, 495-503.

Ritala, M., Leskela, M. and Rauhala, E. 1994. Atomic Layer Exitaxy Growth of Titanium Dioxide Thin Films from Titanium Ethoxide. Chemistry of Materials, 6, 556-561.

Wisitsoraat, A., Tuantranont, A., Comini, E., Sberveglieri, G. and Wlodarski, W. 2006. Gas-sensing characterization of TiO_2-ZnO based thin film. 2006 IEEE Sensors, Vols 1-3, 964-967.

Yamamoto, T. and Ohno, T. 2012. A hybrid density functional study on the electron and hole trap states in anatase titanium dioxide. Physical Chemistry Chemical Physics, 14, 589-598.

Yuwono, A. H., Zhang, Y., Wang, J., Zhang, X. H., Fan, H. and Ji, W. 2006. Diblock Copolymer Templated Nanohybrid Thin Films of Highly Ordered TiO_2 Nanoparticle Arrays in PMMA Matrix. Chemistry of Materials, 18, 5876-5889.