Sol-gel deposition of TiO$_2$/PMMA bilayer with the Optical and Antireflection Properties

Gatut Yudoyono, Sudarsono, Nurrisma Puspitasari, Gontjang Prajitno, Hasto Sunarno, Ali Yunus Rohedi, Yono Hadi Pramono, Mochamad Zainuri, and Darminto

Department of Physics, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

E-mail: gyudoyono@physics.its.ac.id

Abstract. Nanomaterials TiO$_2$ have been synthesized by the co-precipitation method using TiCl$_3$ precursor and obtained TiO$_2$ powder with the crystal morphology of nanoparticles and nanorods. TiO$_2$/PMMA bilayer film has been prepared by a spin-coating method, with the first layer used PMMA layer for anti-reflection function and microscope slide glass (MSG) is used as a substrate. The optical properties of TiO$_2$ layers are measured on a single layer with the variation of the spin rate of the spin coater by measuring the absorption as a function of wavelength with used the spectrometers UV-Vis. The TiO$_2$ layer is deposited from a TiO$_2$ solution prepared by mixing TiO$_2$ powder, a binder of ethyl cellulose, and solvent of terpineol with a mass ratio of 1:1:28. The antireflection coating properties of TiO$_2$/PMMA bilayer have been investigated by using transmittance measurement.

1. Introduction

TiO$_2$ thin films are widely used as optical devices, such as high reflectance layers, anti-reflection coating (ARC) [1]. TiO$_2$ films have been prepared by different methods, such as chemical vapor deposition [2], electron beam evaporation [3], sol-gel method [4]. The sol-gel method has many advantages over other techniques such as purity, homogeneity, flexibility, control over composition, ease of processing, stoichiometric control, and the ability to coat large areas. [5]. The films of TiO$_2$ can increase reflectance on the substrate due to its high index refractive, but used of a combination with materials of low index refractive (interference-type multiple layers) will provide reflectance lower. The SiO$_2$ material is generally used as a low index refractive material in multilayers structures with a combination of TiO$_2$ material used in antireflection devices. In this paper reported the characteristics of bilayers anti-reflection coating using TiO$_2$ layers with different of crystal structure, i.e. nanoparticles and nanorods. The deposition of layers was performed using the sol-gel technique of spin-coating. The layer of poly-(methyl methacrylate) (PMMA) was used as the first layer to provide anti-reflection function, because it has lower a index refractive then TiO$_2$ material.

2. Experimental Method

Titanium (III) chloride (TiCl$_3$) as its precursor have been used to synthesized of TiO$_2$ nanomaterials using coprecipitation method, to obtained TiO$_2$ powder with the crystal morphology of nanoparticles and nanorods. TiO$_2$ nanoparticles formed by TiCl$_3$ were mixed with distilled water with ratio 1:5 (v/v), and the mixed solution was stirred for 30 minutes. Because the pH value of the TiCl$_3$ solution is very low so that no precipitation occurs, and precipitation can be accelerated by increasing the pH
value. The increase in pH value was carried out by adding a precipitation agent (NH₄OH aqueous solution, JT Baker, 28-30%) into the TiCl₃ water mixture. In this research, the pH of the solution was adjusted at values 9 and 3 to obtain anatase and rutile phases [6,7]. The solution continues to be stirred, and later will form a precipitate of white titanium hydroxide. The solutions were precipitated for overnight, and then were dried at 100°C, and the precipitates were subjected to heat treatment with calcination at 400°C for 3 h, because based on previous studies [6] that the TiO₂ crystals have been formed at a temperature of 372°C, and below of the temperature of the residual of NH₄Cl have decomposed.

TiO₂ nanorods were synthesized by mixing 100 mL titanium tri-chloride (15% TiCl₃, Merck) with 200 mL of NaCl solution (1M and 5M). The mixture is stirred for 30 minutes then put in an oven for 7 hours at 200°C. The pH value of the solution is set at a value of around 9-10 with added the NH₄OH solution (J.T. Baker, 28-30%). The mixture is stirred for 30 minutes, and then left overnight, then washed with distilled water and filtered. The precipitate was calcined for 3 hours at 300°C [8,9].

The synthesized TiO₂ were used to prepare a film on the microscope slide glass (MSG) substrate with sol-gel deposition method by spin coating technique. TiO₂ solutions for spin coating is prepared by homogenization process as the mixture of TiO₂ nanopowder, terpineol (solvent), and ethyl cellulose, with the composition of a ratio of weight 2:2:56. There are four kinds of TiO₂ solution was created, namely TiO₂ nanoparticles of anatase and rutile, TiO₂ nanorods of anatase and rutile, each samples were made a single layer on a substrate MSG with a spin coating speed of which varied from 1000 rpm to 5000 rpm for 20 seconds in temperature room, and then the film is dried at 250°C for 20 minutes so the solvent disappears.

Bilayers were made by adding an outer layer, the PMMA (Merck) layer above a single layer. The PMMA layer was deposited on the TiO₂ layer with a rotation speed of 2000 rpm for 20 seconds and then the film is dried at 100°C for 10 minutes. The outer layer used by PMMA layer because PMMA is a transparent material in the region of 400-1100 nm, although PMMA has absorption bands in the infra-red range (1100-3100 nm) [10].

The crystallization of powder and the films of the TiO₂ were examined by X-ray diffraction (XRD) with Cu Kα radiation over a range 2θ < 2θ < 70°. Lambda 950 spectrometer used to measurement of the transmission spectra of the TiO₂ single layer, the TiO₂/PMMA bilayered and the absorbance spectra of the TiO₂ single layer under normally incident light.

3. Results and Discussion

Based on the diffraction pattern of the powder of TiO₂ nanomaterials result of the synthesis, it was found that the anatase TiO₂ nanoparticles were obtained when the pH of the solution was adjusted to a value of 9, while the rutile phase when the pH of the solution was 3. Nanorod TiO₂ synthesis obtained an anatase phase when the molarity of NaCl is 1M, and for the rutile phase when molarity NaCl 5M. The diffraction pattern of TiO₂ powder of nanorods rutile (Rr), and nanoparticles rutile (Pr) is shown in Figure 1. Shown in the figure that rutile phase TiO₂ is formed, which is indicated by the presence of the main peak, 2θ = 27.5°, 36.1°, and 54.4° (JCPDS Card No. 21-1276). At peak intensities TiO₂ nanorods (101), (211) and (002) with diffraction angles of 2θ = 36.1°, 54.4°, and 62.8° are relatively high compared to the peak intensity for TiO₂ nanoparticles. This shows the characteristics of the nanorod structure as reported by Zhang et al. [11]. The peak relative intensity (002) shows the growth parameters and shows the relative length of the nanorods formed [12].
Figure 1. XRD spectra of TiO2 powder of phase rutile of nanoparticles and nanorods

Figure 2. Absorption spectral of sample single layer TiO₂ phase rutile of nanoparticles and nanorods
Figure 2 shows the spectral absorption of a single layer sample of nanoparticles and nanorods of rutile phase with variations of spin rate (1000-5000 rpm). It is shown in Figure 2 that the sample absorption spectrum with a spin-coater speed of 5000 rpm has the smallest absorbance for short wavelength spectra (<300 nm). When viewed from the dependence of the magnitude of the absorbance on the thickness of the layer, it appears that the thickness of the deposition layer with the spin coating method is not much different.

Based on the absorption spectra of TiO$_2$ single-layer can be calculated the amount of gap energy using Tauc model and Urbach energy using Urbach’s equation, as shown in Table 1. The absorption spectra of all samples are very small for the range of wavelength > 350 nm which this is the spectrum range of the visible light, and the value is large enough for the spectrum range of the UV (<350 nm). Based on this spectrum we get the range of the band gap from the layer. The value of band gap of all layers with all variations of spin rate is greater than the band gap of TiO$_2$ in the form of powder (E$_g$ = 3.0-3.2 eV). The gap energy of layer is greater because in the layer still has a binder (ethyl cellulose) so it can enlarge the energy gap.

**Table 1.** Optical Band gap and Urbach energy for TiO$_2$ single layer

| Material TiO$_2$ | Sample | Spin rate(rpm) | Band gap (E$_g$, eV) | Urbach energy (E$_u$, meV) |
|------------------|--------|----------------|----------------------|---------------------------|
| nanoparticle rutile | Pr2    | 2000           | 3.68                 | 254                       |
|                  | Pr3    | 3000           | 3.67                 | 262                       |
|                  | Pr4    | 4000           | 3.70                 | 228                       |
|                  | Pr5    | 5000           | 3.67                 | 262                       |
| nanorods rutile  | Rr1    | 1000           | 3.65                 | 255                       |
|                  | Rr2    | 2000           | 3.68                 | 255                       |
|                  | Rr3    | 3000           | 3.68                 | 255                       |
|                  | Rr4    | 4000           | 3.66                 | 204                       |
|                  | Rr5    | 5000           | 3.70                 | 221                       |

**Figure 3.** Transmittance spectra of TiO$_2$/PMMA bilayer.
Figure 3 shows the transmittance for TiO$_2$/PMMA bilayer, with the structures is (g/T/M/A); g = glass; T = TiO$_2$; M = PMMA; a = air; Pa = nanoparticle anatase; Pr = nano-particle rutile; Ra = nanorods anatase; Rr = nanorods rutile. It is shown in the figure that all bilayer samples have a higher transmittance than substrate transmittance, as well as that the TiO$_2$ nanorods layer has a higher transmittance than the structure of TiO$_2$ nanoparticles. Transmittance bilayer with nanorod TiO$_2$, rutile phase is higher than anatase phase, but with reversed TiO$_2$ nanoparticles. The PMMA layer with a index refractive smaller than the index refractive of TiO$_2$ can be increased the transmittance of the TiO$_2$ layer, so it is likely that the bilayer TiO$_2$/PMMA structure can be used as a bilayer coating acting as the antireflection layer.

4. Conclusion
Nanomaterial TiO$_2$ has been successfully fabricated using TiCl$_3$ as a precursor with the morphology of nanoparticle and nanorods with anatase and rutile phases. Based on the peak ratios of the diffraction pattern, we can see the formation of nanorod TiO$_2$ morphology. Optical properties of single layers such as optical band gap and Urbach energy can be calculated from spectral of absorption. The bilayer TiO$_2$/PMMA structure can be used as a bilayer coating acting as the antireflection layer.

5. Acknowledgements
This work was financially supported by Lembaga Penelitian dan Pengabdian Kepada Masyarakat-Institut Teknologi Sepuluh Nopember (LPPM-ITS) with no. 1187/PKS/ITS/29018. The authors thank Prof. Jyh-Ming Ting and the Mina laboratory, Department of Materials Science and Engineering, National Cheng Kung University, Taiwan for measurements of spectrometer.

6. Reference
[1] J.-A. Jeong, H.-K. Kim, Thickness effect of RF sputtered TiO2 passivating layer on the performance of dye-sensitized solar cells, Sol. Energy Mater. Sol. Cells. 95 (2011) 344–348. doi:10.1016/j.solmat.2010.02.008.
[2] D. Byun, Y. Jin, B. Kim, J.K. Lee, D. Park, Photocatalytic TiO 2 deposition by chemical vapor deposition, J. Hazard. Mater. 73 (2000) 199–206.
[3] C. Yang, H. Fan, Y. Xi, J. Chen, Z. Li, Effects of depositing temperatures on structure and optical properties of TiO 2 film deposited by ion beam assisted electron beam evaporation, Appl. Surf. Sci. 254 (2008) 2685–2689.
[4] M. Jokinen, M. Pääti, H. Rahiala, T. Peltola, M. Ritala, J.B. Rosenholm, Influence of sol and surface properties on in vitro bioactivity of sol-gel-derived TiO2 and TiO2-SiO2 films deposited by dip-coating method, J. Biomed. Mater. Res. 42 (1998) 295–302.
[5] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, Prog. Solid State Chem. 32 (2004) 33–177. doi:10.1016/j.progsolidstchem.2004.08.001.
[6] G. Yudoyono, N. Ichzan, V. Zharvan, R. Daniyati, H. Santos, B. Indarto, Y.H. Pramono, M. Zainuri, Darminto, Effect of calcination temperature on the photocatalytic activity of TiO2 powders prepared by co-precipitation of TiCl3, in: AIP Conf. Proc. 1725, AIP Publishing, Semarang, Indonesia, 2016: p. 020099. doi:10.1063/1.4945553.
[7] G. Yudoyono, V. Zharvan, N. Ichzan, R. Daniyati, B. Indarto, Y.H. Pramono, M. Zainuri, Darminto, Influence of pH on the formulation of TiO2 powder prepared by co-precipitation of TiCl3 and photocatalytic activity, in: AIP Conf. Proc. 1710, AIP Publishing, Solo, Indonesia, 2016: p. 030011. doi:10.1063/1.4941477.
[8] G. Yudoyono, Y.H. Pramono, M. Zainuri, Darmindo, Optical properties of TiO2 nanorod/PMMA bilayered film and the application for anti-reflection, Micro Nano Lett. 12 (2017) 787–792. doi:10.1049/mnl.2017.0211.

[9] H.N. Widaryanti, Fabrication and Characterization Nanoparticles and Films of TiO2, Thesis, Institut Teknologi Sepuluh Nopember, 2013.

[10] M.E. Nicho, M. Trejo, A. Garcia-Valenzuela, J.M. Saniger, J. Palacios, H. Hu, Polyaniline composite coating interrogated by a nulling optical-transmittance bridge for sensing low concentrations of ammonia gas, Sens. Actuators B. 76 (2001) 18–24.

[11] Z. Zhang, X. Zhong, S. Liu, D. Li, M. Han, Aminolysis Route to Monodisperse Titania Nanorods with Tunable Aspect Ratio, Angew. Chem. Int. Ed. 44 (2005) 3466–3470. doi:10.1002/anie.200500410.

[12] M. Rajabi, S. Shogh, A. Iraji zad, Defect study of TiO2 nanorods grown by a hydrothermal method through photoluminescence spectroscopy, J. Lumin. 157 (2015) 235–242. doi:10.1016/j.jlumin.2014.08.035.