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Evaluation of Refractive Index Variations of TiO_2:SiO_2:Zr Thin Films by Molar Ratio

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Zr-doped and undoped TiO_2-SiO_2 thin films were fabricated by using sol-gel dip coating. TiO_2:SiO_2:Zr films with different molar ratio were coated on glass substrates. Refractive indexes and the thicknesses of thin films were measured with Metricon 2010 Prism Coupler. The theoretical and measured refractive indexes of thin films were found to be consistently changing with molar ratio. The measured refractive indexes of thin films were lower than the theoretical ones due to the porosity of the structure.

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1. Introduction

Control of the refractive index in thin films is of great importance for a large set of optical devices including antireflection coatings, rugate filters, and other similar applications [1]. Prism coupler is a technique to measure the refractive index and the thickness of the films with high accuracy of over 0.001 for the index of refraction [2, 3].

TiO_2 is most widely used photocatalyst due to its physical, chemical, and optical properties [4–9]. Furthermore, TiO_2 is also applied in other fields such as in dye-sensitized photoelectrochemical cells, photoluminescence, optical coatings, gas sensors, and ultraviolet attenuating agents for sunscreen cosmetic applications [10, 11]. The photocatalytic properties of the TiO_2 depend strongly on the sample preparation conditions, crystal phase, surface area, size distribution, porosity, and the presence of additional components, like metal particles, that are used to enhance the catalytic response [10]. TiO_2-SiO_2 mixed oxide was reported to be more active as a photocatalyst than the pure titania [6, 7]. Furthermore, ZrO_2-TiO_2 composites are also commonly used as a photocatalysts. Zirconium and SiO_2 doping of TiO_2 enhances the photocatalytic activity [7].

TiO_2-SiO_2 thin films are prepared by different techniques such as chemical vapor deposition, chemical spray pyrolysis, electrodeposition, and sol-gel method [12–14]. Sol-gel method is very simple, easy to use, and inexpensive in comparison with the other techniques. Furthermore, it can be used to deposit films on to substrates which have large surface area or complex surfaces [12, 13].

In this work, we report on the synthesis of Zr doped and undoped TiO_2-SiO_2 thin films prepared by sol-gel dip-coating. The refractive index and the thickness of the films were measured by Metricon 2010 Prism coupler and results were compared with the theoretical refractive index.

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2. Materials and methods

2.1 Thin films fabrication

The solution was prepared by using tetraethyl orthosilicate (TEOS, $C_8H_{20}O_4Si$) and tetra-*n*-butylorthotitanate (TBOT, $C_{16}H_{36}O_4Ti$) as SiO_2 and TiO_2 sources, respectively. First, TEOS was mixed with ethanol (C_2H_5OH), acetylacetone ($C_5H_8O_2$) and deionized water (H_2O). The molar ratio of mixture (TEOS: ethanol: acetylacetone: deionized water) was 1:0.5:1:3. Next, hydrochloric acid (HCl) was added dropwise as a catalyst. The measured value of pH was 2.8 at 25 °C. After mixing for one hour, a clear solution was obtained. Then TBOT was added to the solution until the TiO_2:SiO_2 ratios of 10:10 and 15:5 were achieved. The final solution was stirred at 70 °C for 15 minutes. Zirconium (IV) oxynitrate hydrate ($ZrO(NO_3)_2 \cdot xH_2O$) was added to the final solution until TiO_2:SiO_2:Zr molar ratios of 10:10:1 and 15:5:1 were obtained. After aging for 24 hours, the solution was deposited on glass substrates by dip coating with a withdrawal speed of 50 mm/min. Following each coated layer, the films were dried at 400 °C for 10 minutes. The Zr doped and undoped SiO2-TiO2 thin films had sufficient thickness after 12 layers of coating (Fig. 1).

2.2 Prism coupler setup

The films are brought into contact with the base of a prism until there is an air gap in the nanometer level between the film and the prism. An incident laser beam hits the base of the prism and total internal reflection occurs due to the higher refractive index of the prism (n_p) when compared to air. The reflected laser beam strikes a photodetector and the light intensity is measured. At certain angles of incidence, θ, tunneling of photons takes place. The tunneling photons go through the air gap and enter the dielectric film, which causes an instant drop in the intensity of light reaching the detector [3]. For this tunneling to occur properly, the air gap between the prism and the film should be smaller than the wavelength of the incident beam. The angle θ determines the phase velocity of the incident wave in the prism and in the gap, along the surface of the films, $v^{(i)} = (c/n_p)\sin\theta$. The strong coupling of the light only occurs when θ is chosen such that $v^{(i)}$ equals to the phase velocity of one of the characteristic modes. These angles are called mode angles [15, 16] (Fig. 2).

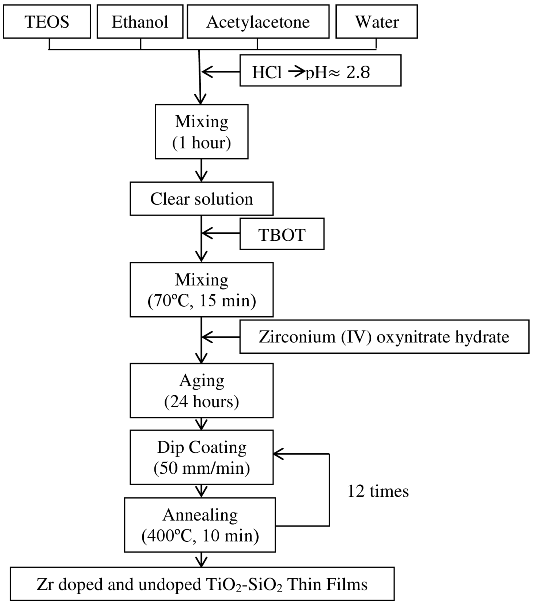

Fig. 1. Flowchart of Zr doped and undoped TiO_2-SiO_2 Thin Films Fabrication.

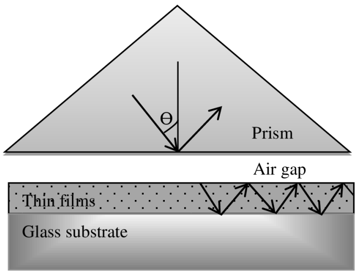

Fig. 2. Prism coupler setup.

3. Results and discussion

The refractive index and the thickness of thin films were measured by using Metricon 2010 Prism Coupler. Figure 3 shows the measured graphs of the films. The refractive indexes and thicknesses of the films with standard deviation are seen in Table. The thickness of the films changed between 789 and 1351 nm after 12 times coating, depending on the molar ratio of constitutes. Higher TiO_2 amounts decreased the thickness while Zr had a more complex effect. Zr had increased the thickness when ratio TiO_2:SiO_2 was equal, while it decreased the thickness in TiO_2 rich films. Similar effect can be seen when the refractive index values are compared. The refractive index of the 10:10 TiO_2:SiO_2 thin films has increased after Zr doping while the refractive index of the 15:5 TiO_2:SiO_2 thin films has decreased after the Zr doping. There was also a significant difference in refractive indexes between the molar ratio of 15:5 and 15:5:1. This difference must have been resulted from higher porosity (41.5%) in the 15:5:1 (TiO_2:SiO_2:Zr) thin films, compared to others (Fig. 4). Figure 3d shows widened peaks compared to others in intensity-step graphs, indicating porosity and supporting the calculated values.

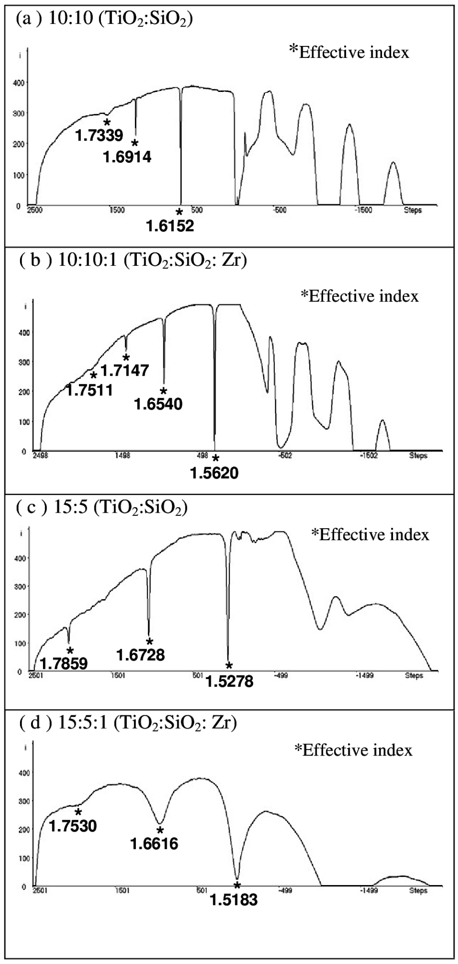

Fig. 3. Intensity (i)-steps (angle) graphs obtained by Metricon 2010 Prism Coupler. Symbol * shows the effective index. Molar ratios of (a) 10:10 (TiO_2:SiO_2), (b) 10:10:1 (TiO_2:SiO_2:Zr), (c) 15:5 (TiO_2:SiO_2), (d) 15:5:1 (TiO_2:SiO_2:Zr).

The theoretical refractive indexes of thin films were calculated by following equation

$$n_{\text{theory}} = \frac{\nu_1 n_1 + \nu_2 n_2 + \nu_3 n_3}{\nu_1 + \nu_2 + \nu_3}, \quad (1)$$

where n_1, n_2, and n_3 are the theoretical refractive indexes of the TiO_2, SiO_2, and Zr, respectively ($n_{TiO_2} = 2.614$, $n_{SiO_2} = 1.544$, and $n_{Zr} = 2.214$), and ν_1, ν_2 and ν_3 are the respective amounts of substance. The calculation results of the theoretical refractive indexes of thin films according to the Eq. 1 are shown in Table. The theoretical and measured refractive index values were found to be consistent. The measured values were lower than the theoretical refractive indexes due to the porosity in the structure (Fig. 4, 5).

TABLE

Theoretical refractive indexes and prism coupler measurements of thin TiO_2:SiO_2:Zr films. n_t – Theoretical refractive index, n_{exp} – experimental refractive index, SD – standard deviation, t – thickness.

molar ratio	n_t	n_{exp}	SD	SD [%]	t [μm]	SD	SD [%]
10:10	2.079	1.7483	0.0003	0.02	1.2288	0.0143	1.17
10:10:1	2.085	1.7632	0.0002	0.01	1.3511	0.0119	0.88
15:5	2.346	1.9260	0.0001	0.00	1.1627	0.0004	0.03
15:5:1	2.340	1.7834	0.0000	0.00	0.7890	0.0004	0.05

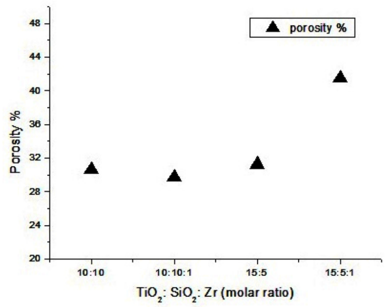

Fig. 4. Graphs of porosity % versus molar ratio of thin films.

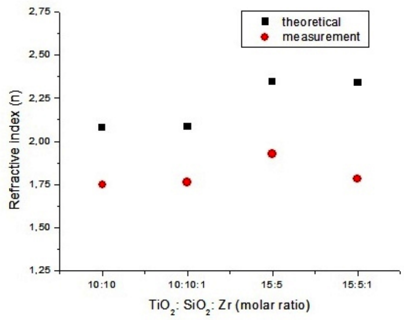

Fig. 5. Graphs of theoretical and measured refractive indexes versus molar ratio of thin films.

Figure 4 shows the porosity % versus molar ratio of films. If the refractive index of the pores was assumed to be 1, the porosity % would be calculated as follows

$$n_{\mathrm{measurement}} = (x + (1 - x)\, n_{\mathrm{theory}}) \times 100. \qquad (2)$$

Here, x is the porosity % of thin films. According to the Eq. 2, the porosity of the thin films with molar ratios of 10:10, 10:10:1, 15:5, 15:5:1 (TiO_2:SiO_2:Zr) was evaluated as 30.6, 29.7, 31.2, and 41.5, respectively (Fig. 4).

4. Conclusions

TiO_2:SiO_2:Zr thin films were fabricated by using sol-gel dip coating. The high accuracy refractive indexes of thin films were measured by Metricon 2010 Prism Coupler. Higher TiO_2 amounts slightly decreased the thickness and significantly increased the refractive index. Zr addition to TiO_2:SiO_2 thin films significantly increased the porosity and decreased the thickness in TiO_2 rich films.

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