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The Effect of pH Value and Ageing Time of Solution on the Physical Properties of TiO_2 Film

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Abstract **–**TiO_2 films have been deposited by sol gel spin coating technique onto glass and p-Si substrates. TiO_2 films were prepared using two different sols. The physical properties of the TiO_2 films were examined based on two different parameters. In the first study, the pH value of the solution was changed, in the second study, the ageing time of the solution were changed. X-ray diffraction (XRD) study showed that TiO_2 films have tetragonal (anatase phase) crystal structure. The best crystallization was observed in TiO_2 films deposited using 144 hours of aging solution for both substrates (glass and p-Si). The surface morphology of the deposited film was characterized by field emission scanning electron microscope (FESEM). FESEM images showed that the surfaces of the TiO_2 films were highly porous. The optical band gap (E_g) of the films were determined by Tauc's method. It was found that the optical band gap increased with the increasing ageing time but the change in ph value did not cause a regular change in the optical band gap.

Keywords – *TiO_2, sol gel spin coating, pH value, ageing time, physical properties.*

I. Introduction

In recent years, TiO_2 has been used in many researches due to its different chemical, electrical and optical properties. It also has interesting structural properties, for example TiO_2 has three different crystal phases which are anatase, rutile and brookite [1]. Anatase is irreversibly transforms to a stable rutile phase at a given temperature. Also, it has wide band gap, high refractive index and high transmittance in the visible region [2]. Due to these properties, it is used in reflective coatings, protective coatings and gas sensors in solar cells and optical circuits [3]. The physical properties of TiO_2, such as crystal structure, crystallite size and porosity are studied to support such applications. TiO_2 films can be prepared by different methods such as spray pyrolysis [4], chemical vapor deposition [5] and sol-gel method [6]. However, these methods have limitations in the depositing of films with high quality crystal structure. Among these methods, the sol-gel method has many superior properties, such as controlling the film coating process, low operating temperature, easy coating of large areas, low hardware costs and obtaining homogeneous films.

In this study, TiO_2 films were produced using the sol gel spin coating technique. Since the physical properties of the TiO2 films depend on the manufacturing parameters, the effects of both the pH value and the ageing time of the solution on the physical properties of the TiO_2 film were investigated.

II. EXPERIMENTAL DETAILS

A. *Preparation of the TiO_2 films*

In this study, tetrabutyl orthotitanate ($Ti(OC_4H_9)_4$) was used as a liquid source of titanium. Six different solutions with pH ranging from 3.40 to 10.01 were prepared (Table 1). TiO_2 films were obtained by using sol gel spin coating technique on glass and p-Si substrates with a spin speed of 3000 rpm. After each coating, TiO_2 films were placed in an oven for 10 min at 300ºC. After five coatings, TiO_2 films were oven-dried for 1 h at 400ºC. Table 1 shows the sample codes of deposited films and the amount of the components in solution. Structural and morphological characterizations of the films were studied. As a continuation of this work, TiO_2 films were obtained using solutions of different ageing. The effect of the ageing time of the solution on the quality of the film was investigated by using the solution prepared without addition of acetic acid (AcAc) (without changing the pH value). To investigate the effect of the ageing time of the solution on the film quality, the solutions were kept in dark for 24 (1 day), 48 (2 days) and 144 hours (six days). After than, TiO_2 films were produced on glass and p-Si substrates using these solutions (Table 2). The thickness of the films produced on glass substrate was determined and given in Table1-2.

B. *Characterization of the TiO_2 films*

The thicknesses of the films were determined with Mettler Toledo MX5 microbalance by using weighing method. The crystalline structure of TiO_2 films were investigated by Bruker D8 Advance X-ray automatic diffraction (XRD) with CuKα radiation (λ=1.54056 nm) at 40 kV and 40 mA. The scanning speed was determined as 0.02 degrees/s in phase analysis. Surface morphology of TiO_2 films was studied by field emission scanning electron microscope (FESEM, ZEISS Ultraplus). The optical transmittance measurements were recorded with a double beam Shimadzu UV-2450 spectrophotometer.

Table 1. Growth parameters of TiO_2 films and thicknesses of TiO_2 films at different pH values

Sample	Substrate	$Ti(OC_4H_9)_4$ (ml)	Ethanol (ml)	Water (ml)	AcAc (ml)	pH	Thickness (nm)
T-C-0	glass	0.8	8	0.2	0	10.01	**273**
T-S-0	p-Si						-
T-C-0.4	glass	0.8	8	0.2	0.4	4.84	**84**
T-S-0.4	p-Si						-
T-C-0.5	glass	0.8	8	0.2	0.5	5.24	**126**
T-S-0.5	p-Si						-
T-C-1	glass	0.8	8	0.2	1	4.98	**396**
T-S-1	p-Si						-
T-C-2	glass	0.8	8	0.2	2	4.23	**424**
T-S-2	p-Si						-
T-C-4	glass	0.8	8	0.2	4	3.40	**317**
T-S-4	p-Si						-

Table 2. Growth parameters of TiO_2 films and thicknesses of TiO_2 films at different ageing times

Sample	Substrate	Solution Ageing Time	Explanation	Thickness (nm)
T-C-24h	glass	24 hours (1 day)	Two different films were obtained on 2 different substrates (glass and p-Si) using the AcAc-free and 24-hour solution	**189**
T-S-24h	p-Si			-
T-C-48h	glass	48 hours (2 days)	Two different films were obtained on 2 different substrates (glass and p-Si) using the AcAc-free and 48-hour solution	**202**
T-S-48h	p-Si			-
T-C-144h	glass	144 hours (6 days)	Two different films were obtained on 2 different substrates (glass and p-Si) using the AcAc-free and 144-hour solution	**1410**
T-S-144h	p-Si			-

Table 3. Average crystallite size values of TiO_2 films deposited on glass and p-Si substrates using solutions prepared at different pH values

	T-C-0	T-C-04	T-C-05	T-C-1	T-C-2	T-C-4
Average Crystallite Size (nm)	31.74	-	-	42.75	31.74	-
	T-S-0	**T-S-04**	**T-S-05**	**T-S-1**	**T-S-2**	**T-S-2**
	39.39	24.95	21.16	23.77	19.60	21.22

Table 4. Average crystallite size values of TiO_2 films deposited on glass and p-Si substrates using solutions of different ageing times

	T-C-0	T-C-24h	T-C-48h	T-C-144h
Average Crystallite Size (nm)	31.74	32.10	46.24	83.41
	T-S-0	**T-S-24h**	**T-S-48h**	**T-S-144h**
	39.39	35.16	46.75	55.61

III. RESULTS

Thickness calculations were made only for glass substrates and were given in Table 1 and Table 2. The film thicknesses were estimated by weighing method. While the thickness of the films did not show a regular change with the change in the pH of the solution, it increased with the ageing time of the solution.

Fig.1-4 show the XRD spectra of films. The average crystallite size of the films was calculated using Scherrer equation and given in Table 3-4.

Figs. 5 and 6 are FESEM images of the TiO_2 films.

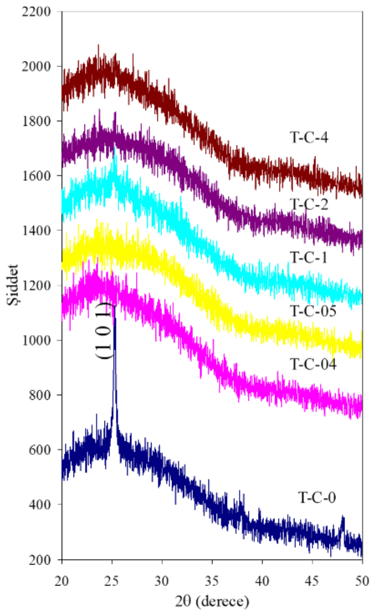

Fig. 1. XRD patterns of TiO_2 films deposited on glass substrates using solutions prepared at different pH values

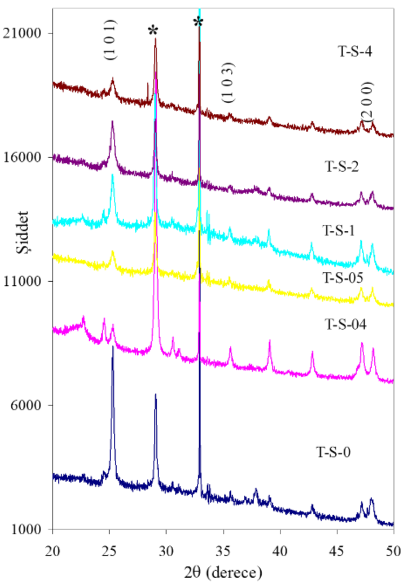

Fig. 2. XRD patterns of TiO_2 films deposited on p-Si substrates using solutions prepared at different pH values (*:p-Si substrate)

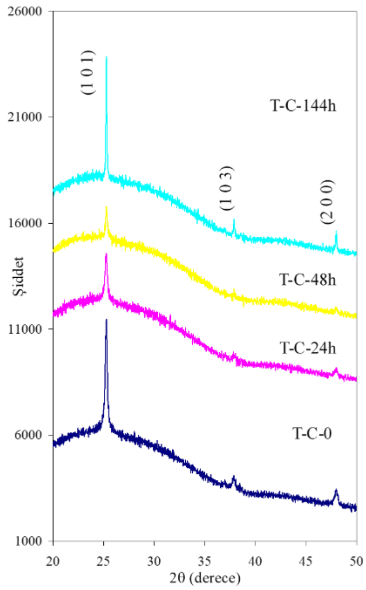

Fig. 3. XRD patterns of TiO_2 films obtained on glass substrates by using solutions in different ageing times

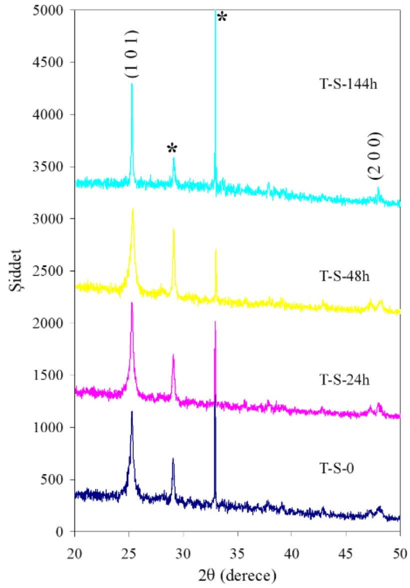

Fig. 4. XRD patterns of TiO2 films obtained on p-Si substrates by using solutions in different ageing times (*: p-Si substrate)

Optical band gap E_g for TiO_2 films can be calculated by Equation (1) called the Tauc law [7].

$$\alpha h\nu \approx \left(h\nu - E_g\right)^n \quad (1)$$

where, α is the absorption coefficient, $h\nu$ is the photon energy and E_g is the optical band gap, n is a constant that can take 0.5 (allowed direct transition) or 2 (allowed indirect transition). Using the absorption spectra measured at room temperature, the $h\nu - (\alpha h\nu)^2$ graphs of the TiO_2 films were plotted using Equation (1). Fig. 2 and Fig. 3 show graphs of $(\alpha h\nu)^2$ versus $h\nu$ for the TiO_2 films. The band gap values were given in Table 5 and Table 6.

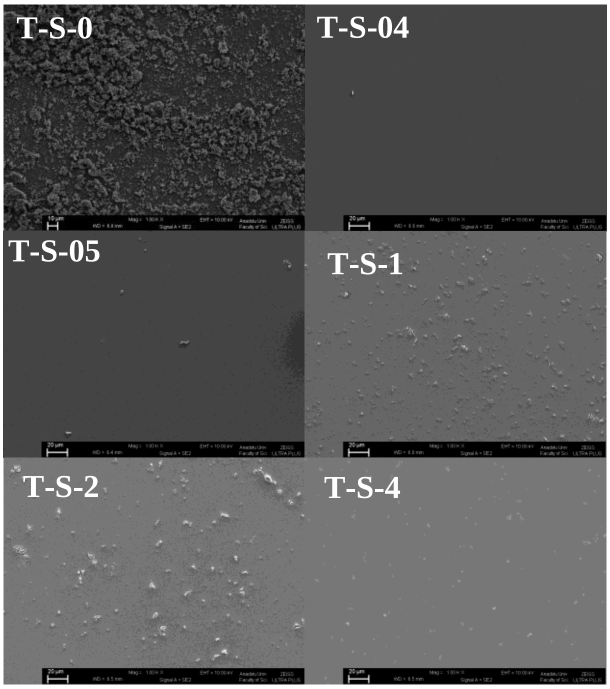

Fig. 5. FESEM images of TiO_2 films deposited on p-Si substrates using solutions prepared at different pH values

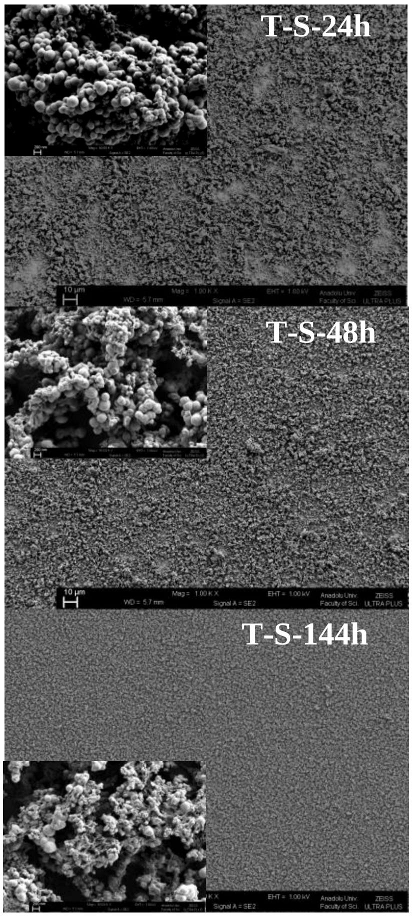

Fig. 6. FESEM images of TiO_2 films deposited using different ageing solutions

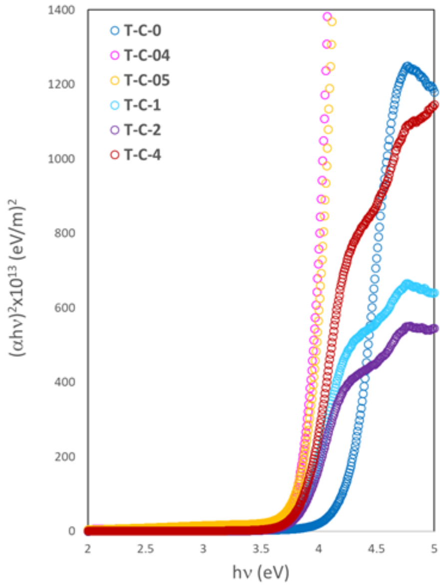

Fig. 7. $(\alpha h\nu)^2$- hν curves for TiO_2 films deposited on glass substrate

Table 5. Band gap values of TiO_2 films deposited on glass substrates using solutions prepared at different pH values

Sample	Band gap (eV)
T-C-0	3.95
T-C-04	3.64
T-C-05	3.55
T-C-1	3.65
T-C-2	3.70
T-C-4	3.68

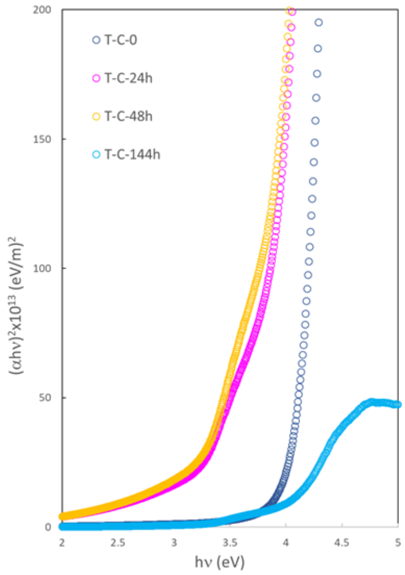

Fig.8. $(\alpha h\nu)^2$ - hν curves for TiO_2 films deposited on glass substrate using solutions prepared at different ageing time

Table 6. Band gap values of TiO_2 films deposited on glass substrates using solutions prepared at different ageing time

Sample	Band gap(eV)
T-C-24h	3.06
T-C-48h	3.14
T-C-144h	3.20

IV. DISCUSSION

The diffraction peaks in Fig. 2 and 3 match well with the crystal structure of the anatase TiO_2 phase (tetragonal, JCPDS 21-1272). The preferential growth orientation was determined using a texture coefficient TC(hkl). It has been observed that all films have (101) orientation. As shown in Fig. 1 and 2, AcAc addition caused structural deterioration in the films. When the films deposited on the p-Si substrate are examined, the quality of the TiO_2 films is better than the films deposited on the glass substrate. When XRD patterns of TiO_2 films obtained on both glass substrate (Fig.3) and p-Si substrate (Fig.4) were analyzed using solutions at different ageing times, the best crystallization was observed in the TiO_2 film deposited using 144 hours of ageing solution. While the average crystallite size increased with increasing ageing time, the correlation was not observed between pH value and crystal size. Fig.3 - 4 show that the peaks in the XRD pattern is sharper at the time aging of 6 days, indicating a higher level of crystallinity. This aging time is related to the process of change in the physical properties of the solution during the polymerization and transformation phase [8].

FESEM images of the films obtained using the AcAc added solution are given in Figure 5. FESEM images showed that there were deteriorations in the structure of the films obtained by using low pH solutions (by the addition of acetic acid, AcAc). As shown in Fig. 6, the surfaces of the TiO_2 films are highly porous and TiO_2 films consist of spherical structures with a diameter of about 200 nm. Figure 6 shows that TiO_2 films deposited using aged solutions are better coated than TiO_2 films deposited using low pH solutions. In particular, the TiO_2 film coated using 144 hours of ageing solution almost covered the substrate.

The optical band gap of the TiO_2 films did not show a regular change with the change in the pH value. The optical analyses showed that the optical band gap of TiO_2 films increased with increasing ageing time.

V. CONCLUSION

TiO_2 films have been deposited by sol gel spin coating technique. The deposition was performed on glass and p-Si substrates. The film thickness can be controlled by the ageing time of solution. The best XRD spectra were observed in the TiO_2 film obtained using 144 hours (6 days) of ageing solution. The results indicate that an increase in the ageing time led to the increase in the particle size of TiO_2 films. FESEM analysis indicates that the decrease in pH value prevents film formation. The optical analyses show that the optical band gap of TiO_2 increased with increasing ageing time. In this study, the increase of the band gap can be related to the increase in the thickness of the films.

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