Some of Optical Properties of TiO₂ Very Thin Films after Influence of Different Annealing Temperatures

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Abstract: TiO₂ thin films have been prepared firstly by chemical method and then deposited by spin coating technique at 3000 rpm. Films have been annealed at different temperatures (360, 460, 550 and 700°C) for 50 min for each sample. The changes of optical properties with the effect of annealing temperatures such as absorption, transmittance and reflectivity have been recorded by UV-Vis spectrophotometer and characterized while the refractive index and energy gap were calculated by Microsoft Excel program. Curves have been adjusted mathematically by using fourth order polynomial correction for smooth curves. Results and behaviors were found that increased absorption, reflectivity and refractive index with increasing of annealing temperature at the wavelengths confined between ~620~800 nm except at 360°C while the transmittance showed a completely opposite behavior of the absorbance and energy gaps decreasing with increasing of annealing temperature.

Key words: TiO₂ thin films, annealing temperature and energy gap, wavelengths, energy gap, optical properties, refractive index

INTRODUCTION

A thin film is a coating of atoms or molecules which ranging from many nanometer scales at few tens of micrometers in thickness of layer. There are many techniques to deposit thin films including physical and chemical techniques (Knoll and Advincula, 2011), physical deposition techniques are Physical Vapor Deposition (PVD) (Hanlon, 1992), Electron Beam Vapor Deposition (EBPVD) (Harsha, 2006), Molecular Beam Epitaxy (MBE) (Jaeger, 2002), sputtering (Behrisch, 1981), Pulsed Laser Deposition (PLD) (Chrissey and Hubler, 1994), cathodic Arc Deposition (Arc-PVD) (Karpov, 1997) and Electro Hydro Dynamics (EHD) (Wall, 2010) while chemical deposition techniques are including, sol-gel process (Brinker and Scherer, 1990), Langmuir-Blodgett method (Kotov *et al.*, 1994), spin coating (Schubert and Dunkel, 2003), dip-coating (Scriven, 1988), Chemical Vapor Deposition (CVD) (Tavares *et al.*, 2008), Plasma-Enhanced Chemical Vapor Deposition (PECVD) (Ay and Aydinli, 2004) and Atomic Layer Deposition (ALD) (Hans-Jurgen *et al.*, 2013). Thin films have many important applications that have entered the fields of industry and technology; these applications are energy generators such as photo voltaic cells (Pearce *et al.*, 2007) and storage of energy as well as in the manufacturing techniques of the battery (Talin *et al.*, 2016), medical fields specifically in pharmacology in the manufacture of thin films for drug delivery (Dixit and Puthli, 2009). A common

and important application of thin films is electronic and optical applications such as semiconductor devices LED and anti-reflection coatings, respectively as well as (Oh *et al.*, 2003). In recent times, scientists have been interested in the development of thin membranes and deposition techniques because of their technological applications in various fields of technology. One of these materials is titanium dioxide which is one of the important materials that have many applications in many fields which have been used in pigment, renewable energy in solar cells, photo catalysts, super hydrophilic layer and antibiotic surface etc. In present research, we will diagnose the optical properties changes of the titanium dioxide which is prepared by the sol-gel technology and deposit by the spin-cotter technology and its relationship with the annealing temperatures.

MATERIALS AND METHODS

Experimental work: The experimental research includes three sequences parts as follow.

First part: First part is preparation of the chemical solution. The chemical solution was prepared by dissolving 6 mL of Titanium Iso Propoxide (TIP) has purity 97% dropwise to 40 mL ethanol and then add 9 mL glacial acetic acid dropwise. All of the chemical materials mentioned above have high purity and supplied by Sigma-Aldrich. After that put the mixture in closed sealed

Table 1: Sample codes, thicknesses and annealing temperatures at spin speed 3000 rpm

Sample name	T(°C)	Thickness (nm)
T1	360	24.69
T2	460	23.34
T3	550	25.69
T4	700	24.50

flask with size 75 mL on the magnetic stirrer and rotate the mixture for an hour at room temperature in order to obtain a uniform chemical solution.

Second part: Second part is deposition process and thermal annealing. In this part the glass substrates have been cleaned by washing them well with distilled water and then washing by acetone and dried by nitrogen. The glass substrates are carefully putted in ultrasonic bath for 10 min at 40°C to remove the impurities attached on them. Finally, we wash the substrates by propanol and then keep in acetone when needed. Titanium dioxide thin films were prepared by deposit chemical solution on glass substrate by spin coating technique at 3000 rpm. The films have been annealed at different temperatures (360, 460, 550 and 700°C) inside the chamber of furnace for (50 min) for each film.

Third part: Is analysis samples, the thicknesses of the prepared films have been recorded by optical polarization technique by ellipsometry instrument J.A.Woollam M 2000 Ellipsometer and fitted by experimental data fitting (WVASE32®). Software is provided by J.A. Woollam Co., Inc. Show in Table 1.

The last step is the measurement and diagnosis, absorbance, transmittance and reflectivity have been measured by double beam spectrophotometer (UV-Vis). The refractive indices, absorption coefficients and energy gaps have been then calculated by using a hand programmed Microsoft Excel 2010. Fourth order polynomial has been adjusted in order to perform curves by smoothing them and show the regular behavior of the optical properties as functions of the wavelengths.

RESULTS AND DISCUSSION

Optical absorbance: We did not notice a regular behaviors of the optical absorption spectra with the annealing temperature, there were appeared random crossing between the curves at Ultraviolet (UV) region and up to ~620 nm and at regions between (800-900 nm) too, we can speculate this behavior is due to the presence of empty areas or cracks on the films or because of the thinness of films thickness but through careful observation we noticed that in the visible region between the wavelengths (620-800 nm) that absorbance increase

Table 2: Optical absorption with the various annealing temperature at $\lambda = 700$ nm

Sample name	T(°C)	Absorbance
T1	360	0.130
T2	460	0.096
T3	550	0.099
T4	700	0.109

Fig. 1: Optical absorbance as a function of the wavelength at different temperatures

Fig. 2: Optical absorbance with wavelength after polynomial adjustments

with increasing the annealing temperature (460, 550 and 700°C), this behavior can be attributed to the increasing and growing crystalline phases of TiO_2 and then increasing of grain size also this behavior may be because of decreasing of condensation of oxide (oxygen molecular) at this point I specifically agree with the researchers (Fig. 1 and 2). By observing the absorption curves recorded by UV-Vis spectrophotometer, the highest absorption has been recorded at a temperature of 360°C at 620 nm. Table 2 and Fig. 3 refer to the values of optical absorption with the various annealing temperature at a wavelength 700 nm.

Optical transmittance: The optical transmittances have been recorded by using UV-Vis spectrophotometer. We

Fig. 3: Optical absorption with the various annealing temperatures at $\lambda = 700$ nm

Fig. 4: Optical transmittance as a function of the wavelength at different temperatures

observed that the values of the optical transmittance at visible region were normal, especially at the wavelengths between (620-800 nm), the behavior of curves at wavelengths between (620-800 nm) was regular and recognizable, so, it's correct to say in this region that the optical transmittance values decrease with increasing of annealing temperatures (460, 550 and 700°C) due to the growing three crystalline phases titanium dioxide (Anatase, Brookite and Rutile) and also to increase grain size gradually with rising of temperature similar phenomena is reported by Oh *et al.* (2003). At Ultra Violet (UV) region we observed a sharp drop in the values with irregular behavior, so, there are no clear relationships between the behaviors of the curves as a function with both wavelength and annealing temperatures as shown in Fig. 4 and 5.

Transmittance percentage at wavelength 700 nm for example is about 73% at 360°C and at temperature 460°C at same wavelength is 80% and at 550°C was reached to 79.9%. Finally, at 700°C was 78% as shown in Fig. 6 and Table 3. Generally, best optical transmittance has been recorded at visible region is achieved at 550°C, thus, this

Fig. 5: Optical transmittance as a function of wavelength after polynomial adjustments

Fig. 6: Optical transmittance with the various annealing temperatures at $\lambda = 700$ nm

Table 3: Optical transmittance with the various annealing temperature at $\lambda = 700$ nm

Sample name	T(°C)	Transmittance
T1	360	0.730
T2	460	0.800
T3	550	0.799
T4	700	0.780

thin film can be selected in applications of solar cell windows because of their high transmittance at the visible wavelengths and because of their low transmittance at short wavelengths (ultraviolet region).

Reflectance and refractive index: In this part, we will discuss reflectance and refractive index which are considered important optical properties. As we observe in Fig. 7-9 the behavior of the reflectivity spectrum curves have same absorption behavior as the functions of the wavelengths with different annealing temperatures due to the same reasons. The obtained results show that the

Fig. 7: Optical reflectance as a function of wavelength

Fig. 8: Optical reflectance as a function of wavelength after polynomial adjustments

reflectivity values are smaller than transmittance values because of high transparency of prepared films (Eq. 1) proved that:

$$T = 1 - (A + B) \quad (1)$$

Where:

R = Reflectivity

A = Absorbance

T = Transmittance

The refractive indices as the functions of the wavelengths have been calculated mathematically based on the reflectivity and the extinction coefficient as shown in Eq. 2:

$$n = \sqrt{\frac{4R - K^2}{(R-1)^2} - \frac{R+1}{R-1}} \quad (2)$$

Where:

n = Refractive index

R = Reflectance

K = Extinction coefficient

The refractive index increases with increasing wavelength in the ultraviolet region and some part of the

Fig. 9: Optical reflectance with the various annealing temperatures at $\lambda = 700$ nm

Fig. 10: Refractive index as a function of wavelength

Fig. 11: Refractive index as a function of wavelength after polynomial adjustments

visible region until to ~ 630 nm and then decreases in the other part we believe that these results are identical with as noted in Fig. 10 and 11.

While the relationship of the refractive index with annealing temperature, the results showed that there is an

Fig. 12: Refractive index with the various annealing temperatures at $\lambda = 700$ nm

Fig. 13: Energy gap as function of photon energy

abnormal and different behavior in the refractive indices and their relationship with annealing temperature. However, in the region after ~ 630 nm, the results showed that the refractive index increased with an increase in temperature (460, 550 and 700°C). Figure 12 shows the values of the refractive indices with the different annealing temperature at wavelength 700 nm.

Energy gap E_g : The energy gaps were calculated by absorption coefficients and as in Eq. 3 and 4 (20):

$$\alpha = \ln \frac{1}{T} (d)^{-1} \quad (3)$$

$$(\alpha h\nu) = S(h\nu - E_g)^L \quad (4)$$

$$(\alpha h\nu) = \text{cons.} (h\nu - E_g)^2$$

By plotting $(\alpha h\nu)^{1/2}$ note that the values of the energy gaps decrease gradually with the increase in the

Fig. 14: Energy gap with the various annealing temperatures

temperature (450, 450, 700°C) such behavior can be attributed to the mixing of both the crystalline and amorphous phases of the TiO_2 thin film (Fig. 13 and 14).

CONCLUSION

Through careful observation, we noticed that in the visible region between the wavelengths (620-800 nm) that absorbance increase with increasing the annealing temperature (460, 550 and 700°C), this behavior can be attributed to the increasing and growing crystalline phases of TiO_2 and then increasing of grain size also this behavior may be because of decreasing of condensation of oxide (oxygen molecular). Also, we observed that the values of the optical transmittance at visible region were normal, especially at the wavelengths between (620-800 nm), the behavior of curves at wavelengths between (620-800 nm) was regular and recognizable, so, it's correct to say in this region that the optical transmittance values decrease with increasing of annealing temperatures (460, 550 and 700°C) due to the growing three crystalline phases titanium dioxide (Anatase, Brookite and Rutile) and also to increase grain size gradually with rising of temperature. According to the above conclusions, we can suggest that applications such as thin films can be use them as windows of solar cells because of their high transmittance at the visible wavelengths and because of their low transmittance at short wavelengths (ultraviolet region). The obtained results show that the reflectivity values are smaller than transmittance values because of high transparency of prepared films while the relationship of the refractive index with annealing temperature, the results showed that there is an abnormal and different behavior in the refractive

indices and their relationship with annealing temperature. However, in the region after ~630 nm, the results showed that the refractive index increased with an increase in temperature (460, 550 and 700°C). Finally, we note that the values of the energy gaps decrease gradually with the increase in the temperature (450, 450, 700°C) such behavior can be attributed to the mixing of both the crystalline and amorphous phases of the TiO₂ thin film.

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