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Effect of Deposition Temperature on Titanium Dioxide Thin Films Prepared By Electrostatic Spray Pyrolysis

Ekpekpo Arthur and Ojegu Ogheneruona Ernest

Department of Physics,
Delta State University, Abraka

Abstract

Titanium Dioxide (TiO_2) thin films were deposited on a microscope glass slide using electrostatic spray pyrolysis with a single jet mode at the deposition temperature of 200^0C, 250^0C, 300^0C, 350^0C and 400^0C with a constant deposition time of 15 minutes each. The films were characterized using x-ray diffraction (XRD), UV-VIS spectrometry and profilometry. The X-ray diffraction was used to determine the mineralogy and the crystalline size using Xpert-pro diffractometer system with generator settings 40MA x 45KV and anode material CuKα, (λ1=1.54060Ǻ, λ2 = 1.54443Ǻ), Kα2/Kα1 ration = 0.5. The UV-VIS spectrometer was carried out to investigate the transmittance and optical band gap with a wavelength ranging from 200nm to 800nm. The thickness was also investigated using the profilometry pattern. The X-ray diffraction (XRD) revealed that, the films were amorphous at the deposition temperature of 200^0C. At 250^0C, the films showed only one peak (101) at anatase. At 300^0C, the films were four peaks plane: 101, 103, 004 and 112. As the deposition temperature increases to 350^0C and 400^0C, the peaks appeared to be [101, 103, 004, 112, 200, 105, 211] and [101, 103, 004, 112, 200, 105, 211, 204, 116, 220, 215, 301, 303] respectively. This result indicates that TiO_2 thin films deposited at 300^0C, 350^0C and 400^0C were polycrystalline anatase of titanium dioxide, because the crystalline size increased from 6nm to 15nm. The UV-VIS spectrometer studies shows that, the transmission spectra decreased (98-68%) the optical band gap decreased (3.6eV-3.2eV), and refractive index increased from 2.2 to 2.5 with respect to increased in temperature between 200^0C and 400^0C respectively. The thickness was also affected by deposition temperature.

Keywords: Electrostatic Spray Pyrolysis, Titanium Dioxide

1.0 Introduction

Titanium oxide ($T10_2$) as a wide band-gap semi conductor, its crystals have a high resistivity in order of 10^{15}Rcm. When $T10_2$ is reduced its n-type conductivity increases due to the extent of oxygen loss. Anatase possesses an indirect band gap while rutile has a direct band gap.

In a direct band gap material, if the minimal energy state in the conduction band coincides with the maximal – energy state. In the valence band, electron is return to the valence band. In the indirect band gap material, if the minimal in the conduction band is different from the maximal in the valence band, this enables the excited election to stabilizes at the lower level in the conduction band itself leading to its longer life and greater mobility. In an excitation state, the electron mass of the outer shell electron in the anatase may be lower than the case of the rutile, this explain higher mobility of electron in the anatase. The anatase form have a band gap of 3.2eV with the absorption edge at 386nm which lies in the near uv range. Rutile form has a lower band gap of 3.02ev with the absorption edge in the visible range at 416nm.

It has been reviewed that high concentration of donors can introduce impurity bands in anatase and rutile, and if the concentration of impurity exceeds a critical value, the conduction band impurity become metallic.

The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic material directly. $T10_2$ as a photocatalyst, can carry out hydrolysis, that is break water into hydrogen and oxygen and with hydrogen, can be used as fuel.

Corresponding author: ***Ekpekpo Arthur*** , Tel.: +2348036761367

2.0 Material and Methods

The reagents used in carring out this work are: Analytical grade titanium chloride or titanium (iii) chloride ($TiCl_3$) having titanium concentration of 15% and density 1.2 (nanopol pdh supplier), propanol and glacial acetic acid.
As a precursor, it contained 0.5ml of titanium (iii) chloride ($TiCl_3$) mixed with 14.5ml of propanol and 10ml of glacial acetic acid which was deposited at a temperature of 200^0C, 250^0C, 350^0C and 400^0C with a constant deposition time of 15 minutes. The precursor solution is fed through a nylon tube to a small capillary nozzle which is connected to a voltage of 10,000V. The aerosol is transported to the microscope glass slide on the substrate heater, which was earthed and which the film has to be deposited. The distance from the nozzle tip to the substrate was 9cm and flow rate of 13/14 min, the liquid flowing out from the nozzle, due to the influence of electric field, the liquid form a conical shape and at the apex of the cone, a thin jet emanates which disintegrated into fine and small positively charge droplets.
The size of the electrospray droplets can range from hundreds micrometers down to several tens of nanometers. The droplets generated and the size can be controlled via the flow rate and the voltage of the capillary nozzle.

3.0 Characterization Methods

In the characterization of TiO2 thin films, X-ray diffraction (XRD), UV-Vis spectrometer and profilometry were used.
The X-ray diffraction (XRD) was used to determine the mineralogy and crystallite size of the TiO2 thin films, this pattern was performed using xpert-pro diffractometer system with generator settings 40mA x 45kv and anode material CuKα (λ1=1.54060Ǻ, λ2=1.54443Ǻ), Kα2/Kα1, ratio=0.5 with scan start position (2θ) of 10 and scan end position (2θ) of 100, step size 0.1^0(2θ), scan time per step 249.555, divergence slit = 0.2177mm.
The transmission spectrum in the visible region were determined using the UV-VIS spectrometer. The transmittance of the films were measured and the spectra were recorded in the wavelength ranging from 173-1100nm.
During deposition of TiO_2 thin films, the microscope glass slide on the substrate heater was masked to determine the thickness of TiO_2 thin films.

Researchers [1,2] have reported that brookite phase $T10_2$ may function as a more effective photocatalyst than anatase phase under weak light.

Kumagai et al [3], also reported that the photocatalytic property of $T10_2$ is known to be more effective with anatase phase than rutile phase but brookite in $T10_2$ from as a photocatalyst have been uncommon because it is relatively hard to produce artificially.

Other workers [4,5] have also reported that brookite phase $T10_2$ thin film shows high photoinduced hydrophilicity and high photocatalytic activity compared with rutile and anatase.

4.0 Results and Discussion

The x-ray diffraction (XRD) was carried out to determine the mineralogy and crystallite size. TiO2 thin films were prepared at different deposition temperature of 200^0C, 250^0C, 300^0C, 350^0C and 400^0C with a constant deposition time of 15 minutes. From the XRD analysis, the peak list deposited at different temperature are shown in Table 1.1.

From Fig 1.1 (a,b,c,d,e), the XRD patterns recorded that, the films deposited at 200^0C showed amorphous structure. The films deposited at 250^0C showed (101) peak of anatase. The films deposited at 300^0C showed four peaks of anatase, which includes: 101, 103, 004, and 112.

The films deposited at 350^0C and 400^0C appeared with peak at 101, 103, 004, 112, 200, 105, 211 and 101, 103, 004, 112, 200, 105, 211, 213, 204, 220, 215, 301, 303 respectively. From this result, it is clear that all the peaks are sharp, the films were polycrystalline anatase in nature at deposition temperature of 300^0C, 350^0C and 400^0C and the intensity of this peaks increased as the deposition temperature increases.

The crystalline size was determined using Sherrer's formula [6] as shown in equation (1.1)

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad (1.1)$$

Where D is the crystalline size

K is a constant with a value of 0.9

λ is the wavelength of incident x-ray radiation source (0.154nm for Cukα)

β is the full width at half maximum (FWHM)

θ is the Bragg angle in degrees at the position of the peak maximum

Using Sherrer's formula [6], the sizes obtained at different deposition temperature are given in Table 1.2

From Table 1.2 it is clear that, the crystalline size increases from 6 to 15nm as the deposition temperature increased from 250^0C to 400^0C respectively.
The characterization of titanium dioxide (TiO_2) Thin Film using UV-VIS Spectrometer deposited at different temperature is shown in Fig. 1.2a, Fig. 1.2b, Fig. 1.2c, Fig. 1.2d, Fig. 1.2e and Fig. 1.2f which shows that, the transmittance spectra of TiO_2 films were recorded from the range of 200nm to 800nm. In the visible region of the spectrum, the transmission is very high because no absorption due to excitation of electrons from the valence band to the conduction band leading to optical interference effect. It was observed that as the deposition temperature increases, the transmission spectra decreases from 98% to 68% as shown in Table 1.3.
The optical band gap can be calculated using optical transmittance method which can be determined by the absorption coefficient as shown in equation (1.2)

Where $$\alpha = \ln\left(1/T\right)/t \qquad (1.2)$$

α is the absorption coefficient
T is the transmittance
t is the thickness of the films

Fig 1.2 (b,c,d,e,f) shows graph of optical absorption versus photon energy (hu) at different deposition temperature for the determination of band gap. The result obtained is shown in Table 1.3.
From Table 1.3, shows that, at deposition temperature of 200^0C, 250^0C, 300^0C, 400^0C resulted to band gap of 3.5ev, 3.5ev, 3.4ev, 3.3ev and 3.2ev respectively. This results indicates that as the temperature increases from 200^0C to 400^0C, the energy band gap falls from 3.5ev to 3.2ev, which agrees with previous work on TiO_2 thin films.

The refractive index of the TiO_2 thin films deposited at different temperature was investigated from reflectance data gathered from the UV-VIS spectrometer analysis using the equation (1.3)

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2} \qquad (1.3)$$

Where

n = The refractive index
R = The reflectance
K = The extinction coefficient (Several different measures of the absorption of light in a medium).

Fig. 1.3 shows the graph of wavelength versus refractive index showing the effect of deposition temperature
From Fig. 1.3, the refractive index of TiO_2 thin films deposited at 200^0C, 250^0C, 300^0C, 350^0C and 400^0C yielded 2.2, 2.21, 2.3, 2.4, 2.5 respectively, that is refractive index increases with an increased in temperature. This increase is due annihilation of pores because the film surface gets dense as the deposition temperature increases.
Due to the wide spread of TiO_2 thin films sprayed on the microscope glass slide on the substrate heater, at different deposition temperature, the glass slide was masked to determine the thickness of the films as shown in fig. 1.4
At deposition temperature of 200^0C, 250^0C, 300^0C, 350^0C and 400^0C yielded thickness of 150nm, 300nm, 450nm, 650nm and 800nm respectively. Therefore, an increased in temperature leads to an increased in thickness of TiO_2 thin film.

5.0 Conclusion

From the XRD analysis, at deposition temperature of 200^0C, the films were amorphous while those deposited at 250^0C, 300^0C, 350^0C and 4000C shows that the films were anatase of titanium dioxide. The crystalline size varied with increased in deposition temperature from 6nm to 15nm.

The optical transmittance and the band gap which was investigated using UV-VIS spectrometer, the transmittance decreased from 98% to 68% and the band gap decreased from 3.6ev to 3.2ev as a function of increasing deposition temperature from 200^0C to 400^0C respectively. The thickness of the films were determined using profilometry, the films thickness increased from 150nm to 800nm with increased in deposition temperature [7]

This work has confirmed that electrostatic spray pyrolysis can be effectively used for thin films deposition at the temperature of 200^0C, 250^0C, 300^0C, 350^0C and 400^0C respectively, which indicates that the phase transformation, transmittance, optical band gap, refractive index, crystalline size and the thickness of TiO_2 thin film depends on deposition temperature. This result agrees with the work of [8] who also studied the effect of deposition temperature on TiO_2 thin film using ultrasonic spray pyrolysis.

6.0 Acknowledgements

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Table 1.1 XRD data at different deposition temperature

Temperature ^{0}C	Position [^{0}2θ]	FWHM [02θ]	d-spacing [Å]	Miller indices [hk1]
250^0C	25.3680	0.3966	2.37864	101
300	25.2765	0.3936	3.52356	101
	36.9347	0.2952	2.43790	103
	37.8232	0.2952	2.37864	004
	38.5766	0.2952	2.33390	112
350	25.3765	0.2620	3.34640	101
	236.5032	0.2320	2.45970	103
	37.5875	0.2320	2.98990	004
	38.6015	0.2320	2.37750	112
	48.0323	0.3350	2.98990	200
	53.9400	0.3936	2.69988	105
	55.2045	0.3936	2.66775	211
400	25.3160	0.2373	3.36160	101
	36.9195	0.2373	2.37430	103
	37.0546	0.2373	2.37430	004
	38.8667	0.2373	2.33390	112
	48.1678	0.2373	2.45670	200
	53.2067	0.2373	2.34560	105
	55.0664	0.2373	1.98970	211
	62.7355	0.2952	1.99785	204
	68.8444	0.2952	1.89780	116
	70.2732	0.2952	1.97860	220
	75.0863	0.2952	1.27590	215
	76.0839	0.2952	1.29870	301
	82.7043	0.2952	1.16687	303

Fig. 1.1a, Fig1.1b, Fig.1.1c, Fig. 1.1d and Fig. 1.1e show the XRD of titanium dioxide (TiO_2) Thin Films deposited at different temperature.

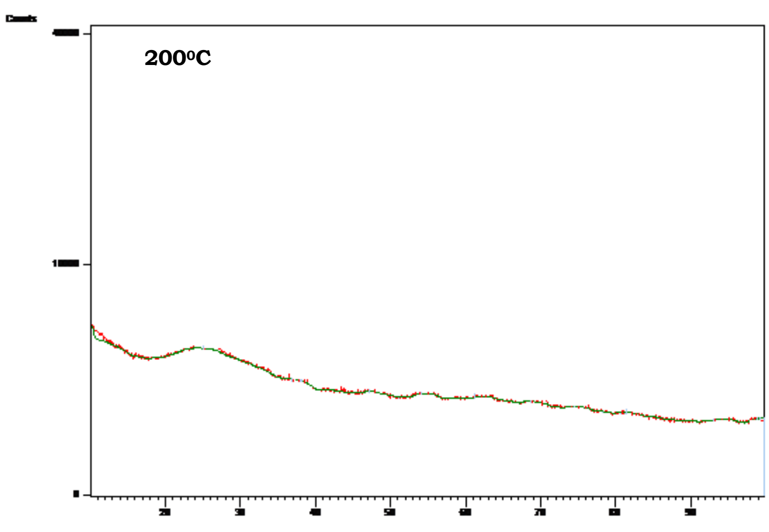

Fig. 1.1(a): XRD of TiO_2 thin films deposited at 200^0C and 15 minutes deposition time

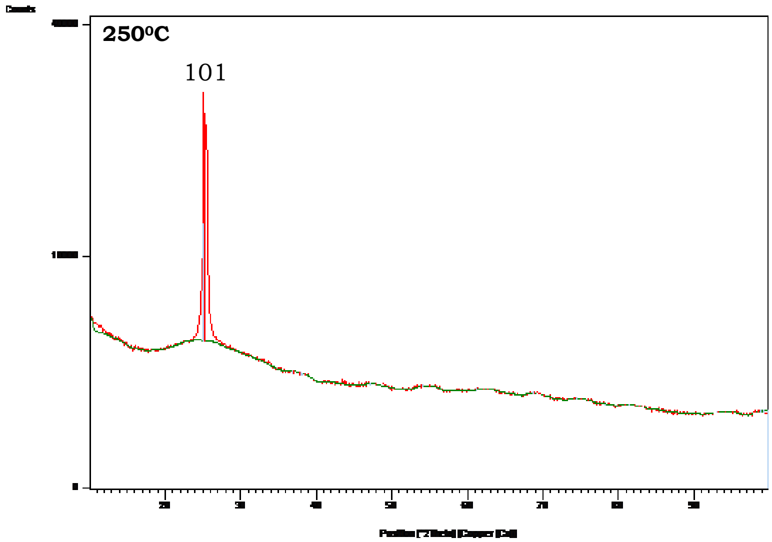

Fig. 1.1(b): XRD of TiO_2 thin films deposited at 250^0C and 15 minutes deposition time

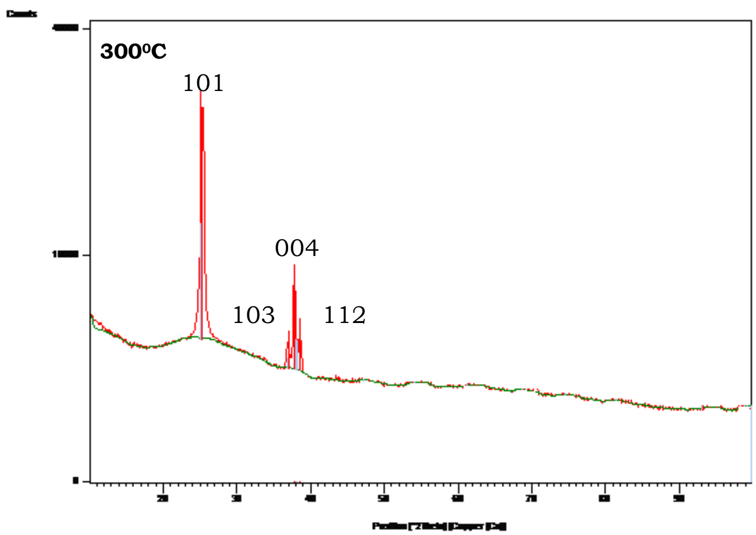

Fig. 1.1(c): XRD of TiO_2 thin films deposited at 300^0C and 15 minutes deposition time

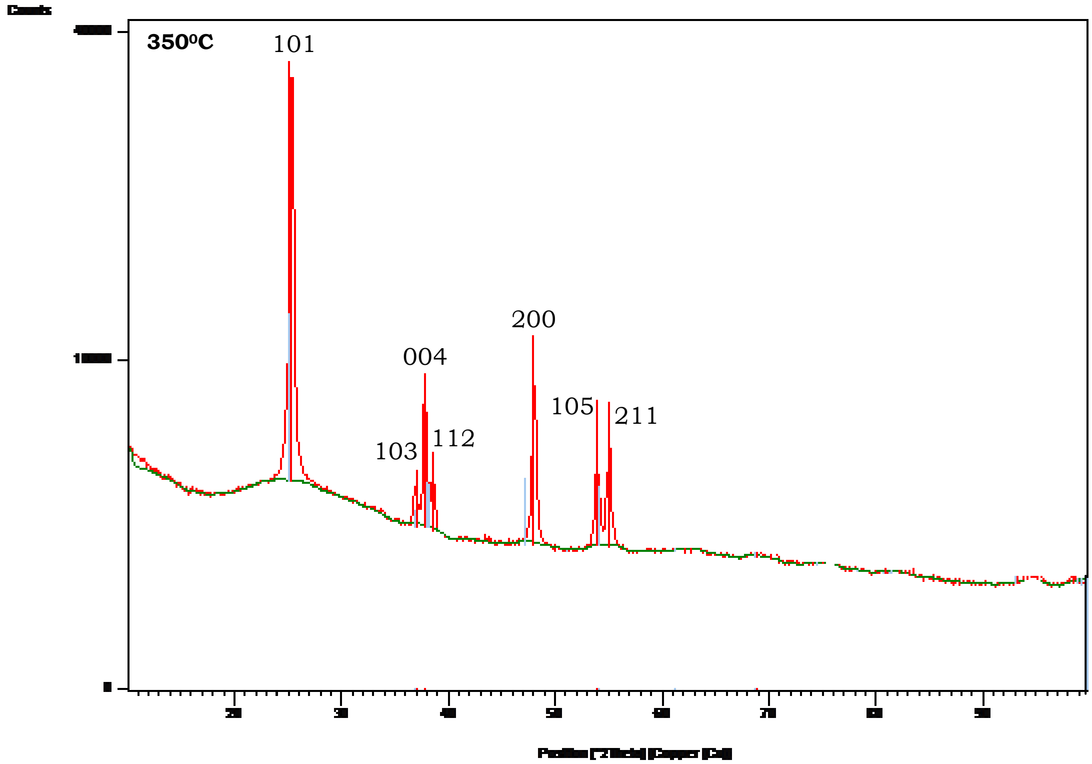

Fig. 1.1(d): XRD of TiO_2 thin films deposited at 350^0C and 15 minutes deposition time

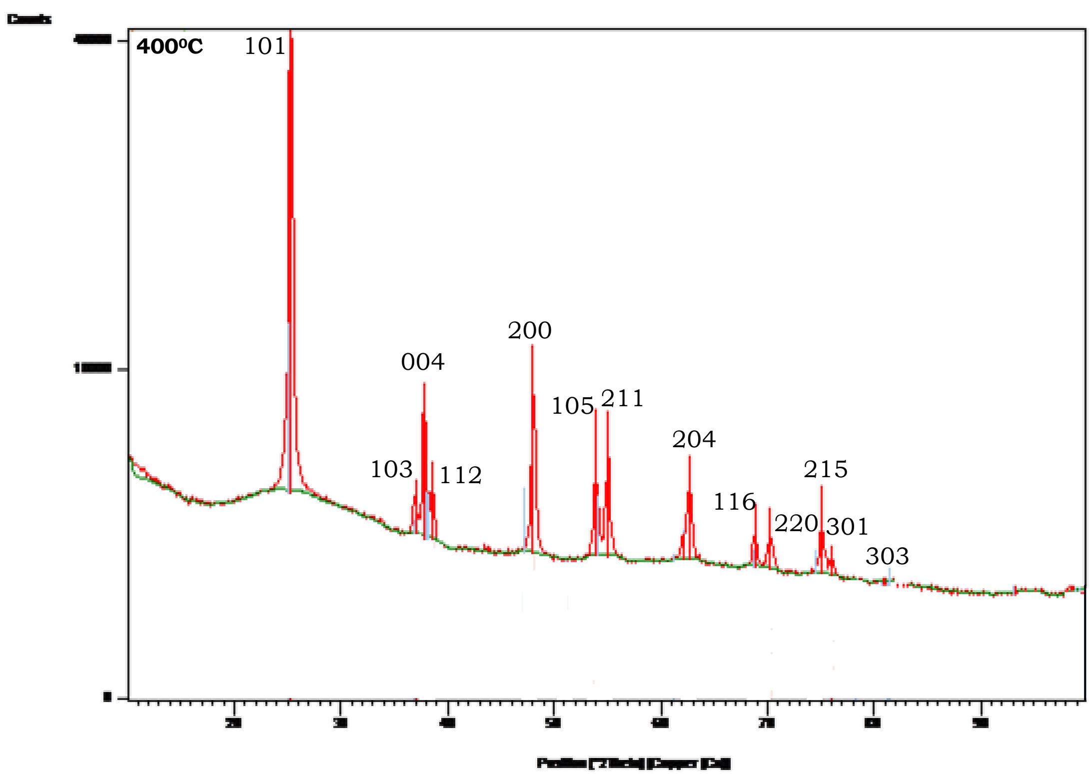

Fig. 1.1(e): XRD of TiO_2 thin films deposited at 400^0C and 15 minutes deposition time

Table 1.2: Crystalline size

Temperature (^{O}C)	Crystalline size (nm)
250	6
300	9
350	12
400	15

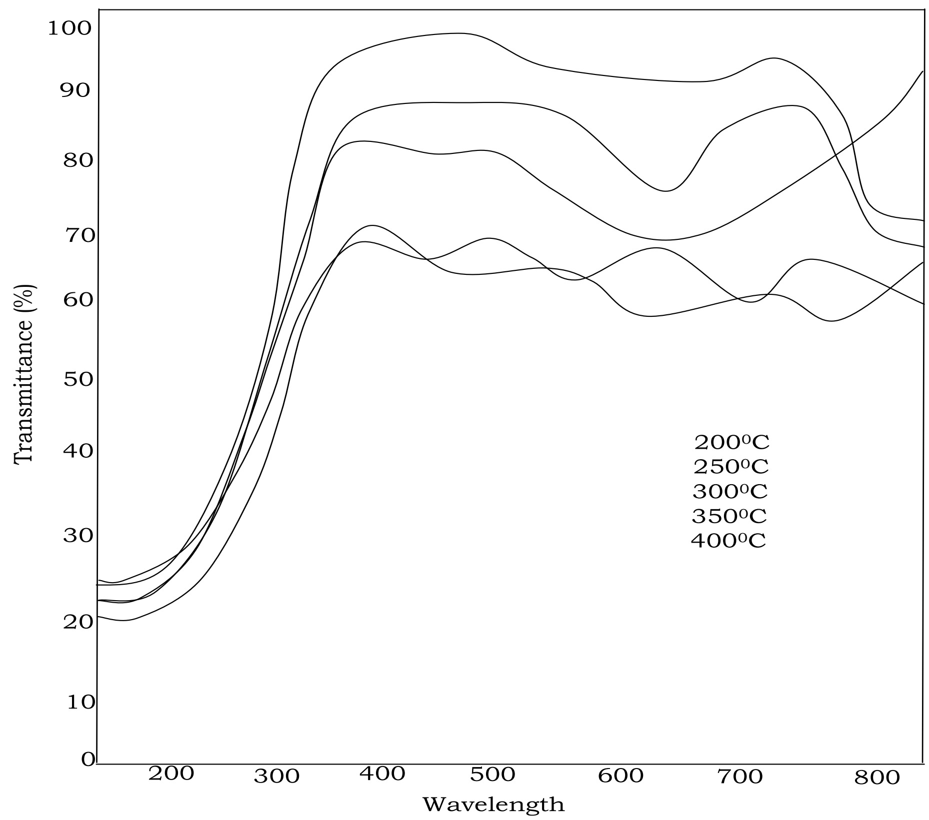

Fig. 1.2(a): UV-VIS light transmission spectra for TiO_2 thin films deposited at different temperature

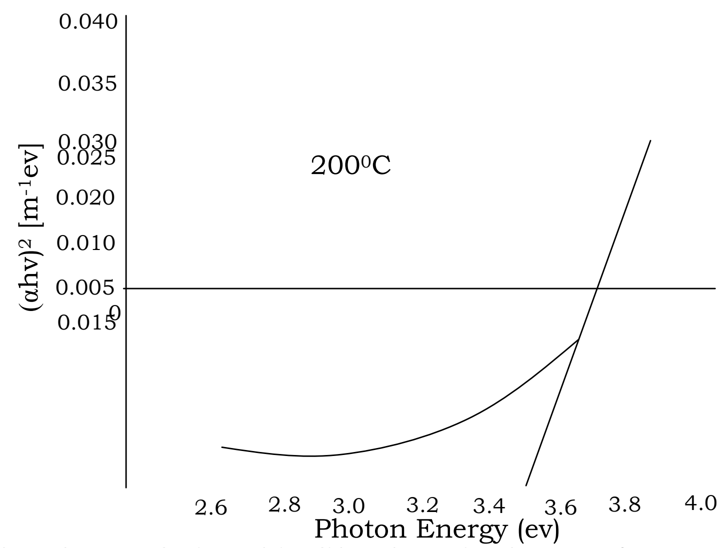

Fig. 1.2(b): Energy band gap of TiO_2 thin film deposited at 200ºC

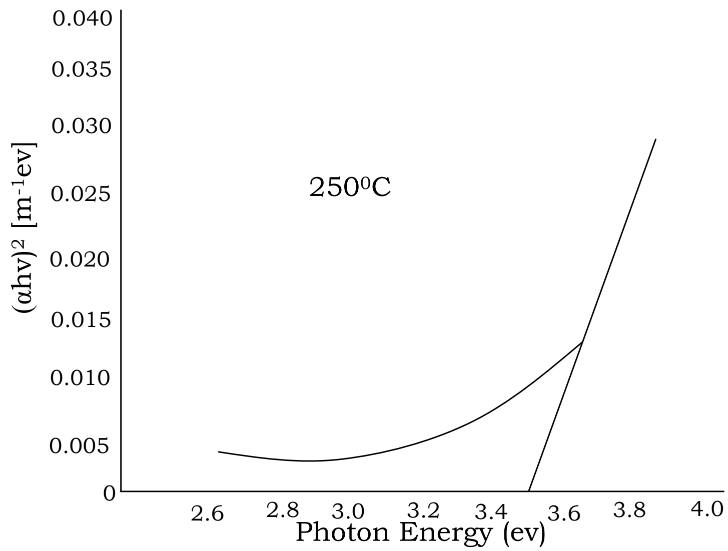

Fig. 1.2(c): Energy band gap of TiO_2 thin film deposited at 250^0C

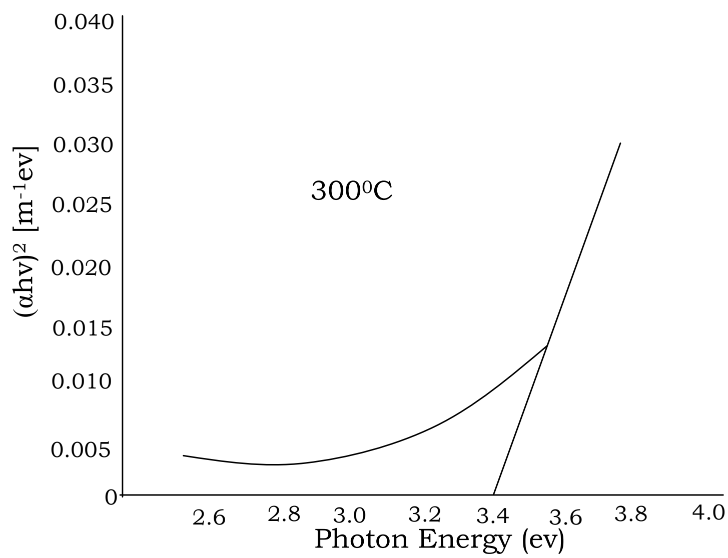

Fig. 1.2(d): Energy band gap of TiO_2 thin film deposited at 300^0C

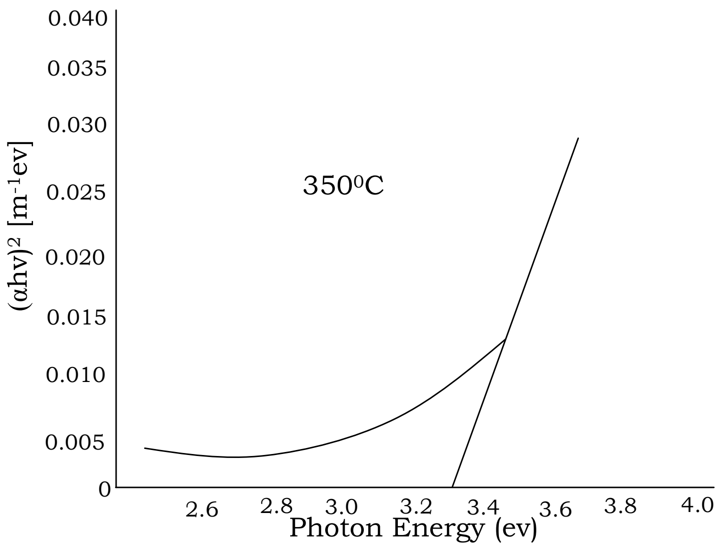

Fig. 1.2(e): Energy band gap of TiO_2 thin film deposited at 350⁰C

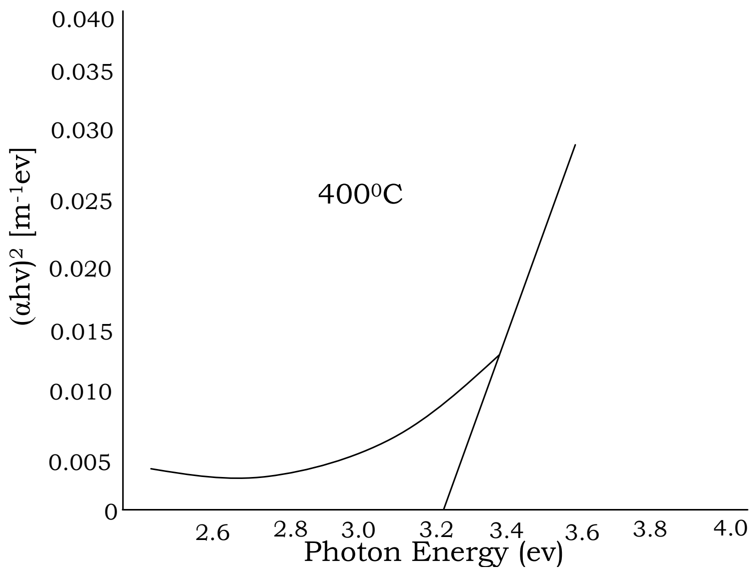

Fig. 1.2(f): Energy band gap of TiO_2 thin film deposited at 400⁰C

Table 1.3: Energy band gap and transmittance at different deposition temperature.

Temperature (^{O}C)	Band gap (ev)	Transmittance %
200	3.5	98%
250	3.5	88%
300	3.4	80%
350	3.3	70%
400	3.2	68%

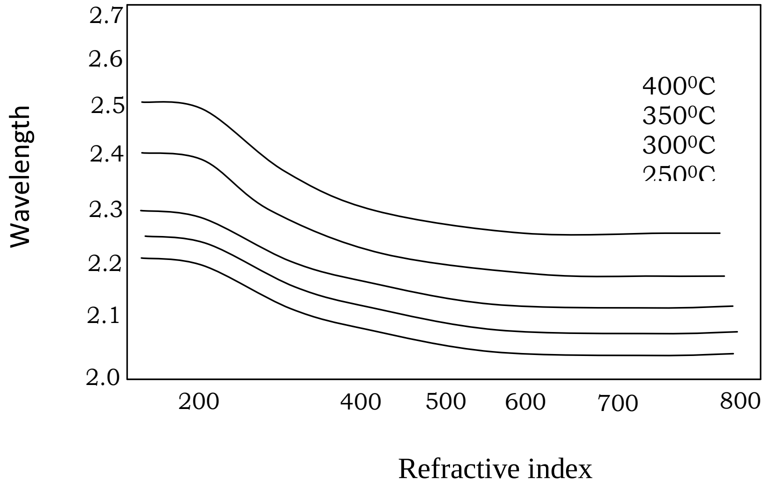

Fig. 1.3: A graph of wavelength versus refractive index showing the effect of deposition temperature

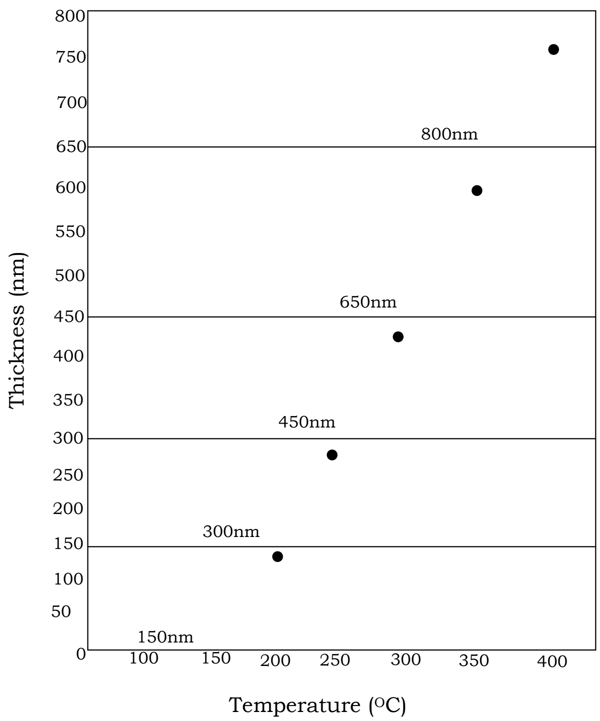

Fig. 1.4: Thickness of TiO_2 thin films deposited at different temperature.

7.0 References

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