Optical properties of the anatase phase of titanium dioxide thin films prepared by electrostatic spray deposition

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Titanium Dioxide (TiO_2) thin films were prepared by electrostatic spray deposition using 12.5ml of propanol, 10 ml of glacial acetic acid and 1.4ml of titanium (iii) chloride ($TiCl_3$) as precursor. These mixtures were deposited on microscope glass slide on a heated substrate at a temperature of 370 and 420°C with constant time of 10 min. The films were characterized using UV- visible spectrometer (UV –vis), with an integration time of 21 and 150 min for transmittance and reflectance respectively. From the results obtained from the transmittance spectra it was observed that TiO_2 thin film gives a visible transmittance of 86 and 79% at deposition temperature of 370 and 420°C, the films also displayed a high absorbance at 420°C and decreases at 370°C. This shows that high absorbance gives rise to a low transmittance. The optical band gap values gotten from the extrapolation of the linear part were 3.88 eV and 3.81 eV, which is in line with other Anatase that is 3.8 eV and the refractive index was also evaluated.

Key words: TiO_2, thin films, spray deposition, band gap.

INTRODUCTION

Titanium dioxide (TiO_2) occurs as a white oxide, which appear in the form of anatase, rutile and brookite, the anatase and rutile are tetragonally in crystal form, while brookite is structured in orthorhombic form (Shelke et al., 2012). Anatase is metastable in nature, it can easily be reverted into rutile at a high temperature of about 600°C and above (Satoh et al., 2013). The rutile form is the most stable phase of titanium dioxide (Hanaor et al., 2011), TiO_2 can be deposited as a powder form or thin film, when deposited in powder form it serve as a pigment that is applicable to products such as plastics, papers, paints and coatings (El.- Sherbiny et al., 2014). On the other hand, when deposited as a thin film, it is well known to be exceptionally good for several applications, which includes photocatalyst, solar cell (Garzella et al., 2000), anti-fogging and self cleaning materials which could be applicable in building and automotive glasses (Sun et al., 2007). TiO_2 is a semiconductor with a band gap ranging from 3.2 to 3.8 eV (Nandani et al., 2018). Different methods have been used for the preparation of TiO_2 thin film. These methods includes, ultrasonic spray pyrolysis (Nakaruk et al., 2010), sputtering (Dakka et al., 1999), thermal evaporation (Bedikyan et al., 2013) and sol gel method (Essalhi et al., 2016). In this work, electrostatic spray deposition has been employed to study the optical properties of TiO_2 thin film due to its advantages, such as simple apparatus, low cost, capacity for mass production, large surface area coverage and rapid film growth rates. Electrostatic spray deposition is a process of liquid atomization by means of electrical forces, in which a thin film is deposited by spraying a solution on a heated surface where the constituent react to form a chemical component. It is a method that consists of precursor solution, substrate heater, temperature controller and atomizer.

MATERIALS AND METHODS

TiO_2 thin films were prepared by electrostatic spray deposition, using 12.5 ml of propanol, 10ml of glacial acetic acid and 1.4 ml of titanium (iii) chloride ($TiCl_3$) as a precursor. This mixture was deposited on a microscope glass slide placed on a heated substrate at a temperature of 370 and 420°C with a constant deposition time of 10 min. The deposited TiO_2 thin films were characterized by Ultraviolet – visible spectrometer to study the optical properties of TiO_2 thin film, and the absorbance, transmittance and reflectance measurement where recorded with an integration time of 21 and 150 min respectively, in the range of 300 to 800nm for the film deposited at 370 and 420°C.

The absorbance measurement was obtained by converting the transmittance data to absorbance using (Snoeyink and Jenkins, 1980):

$$A = 2 - \log(\%\, T) \qquad (1)$$

Where, A is the absorbance and T is the transmittance.

The band gap was obtained using Tauc plot method (Equation 2) (Essalhi et al., 2016)

$$\alpha hv = B(hv - Eg)^2 \qquad (2)$$

where α = absorption coefficient, B = constant that does not depend on hv, h = Plank's constant,

v = photon energy and Eg = energy band gap

The absorption coefficient α of the TiO_2 thin film were calculated using (Mohammed et al., 2018)

$$\alpha = 2.303\ A/t \qquad (3)$$

where A is the absorbance and t is the thickness of the film.

Refractive index *n* of TiO_2 thin film was determined using (Chabou et al., 2019)

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

where, n is refractive index, R is the reflectance and K is the extinction coefficient which can be calculated by Equation 5 (Chabou et al., 2019)

$$K = \frac{\alpha\lambda}{4\pi} \qquad (5)$$

RESULTS AND DISCUSSION

The results obtained in this research are discussed using the graphs plotted as shown in Figure 1 to 5, showing the graphical presentation of transmittance T, on the wavelength λ, within the spectra range of 300 to 800 nm of the deposited thin film at a temperature of 420 and 370°C respectively. The film deposited at 370°C gives a high visible transmittance of (0.86 = 86%). With increase in temperature at 420°C, the film exhibits a visible transmittance of (0.79 =79%). This high transmittance shows that TiO_2 thin films are transparent in the visible region. In the transmittance spectra, the absence of interference fringes were notice; which occurs as a result of the film roughness.

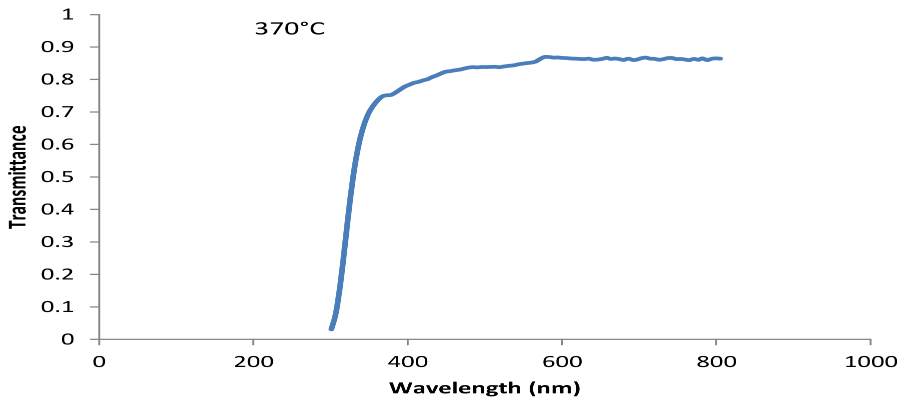

Figure 1. Transmittance spectra of TiO_2 films deposited at 370°C.

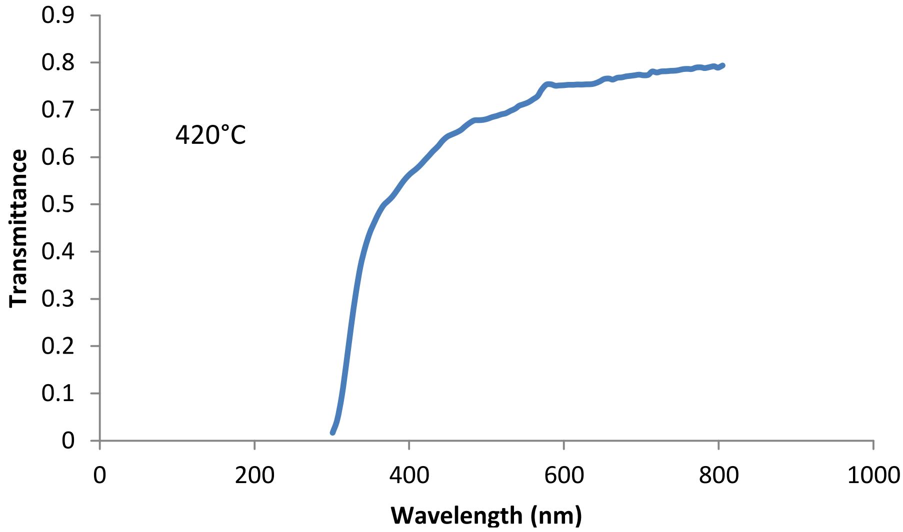

Figure 2. Transmittance spectra of TiO_2 films deposited at 420°C.

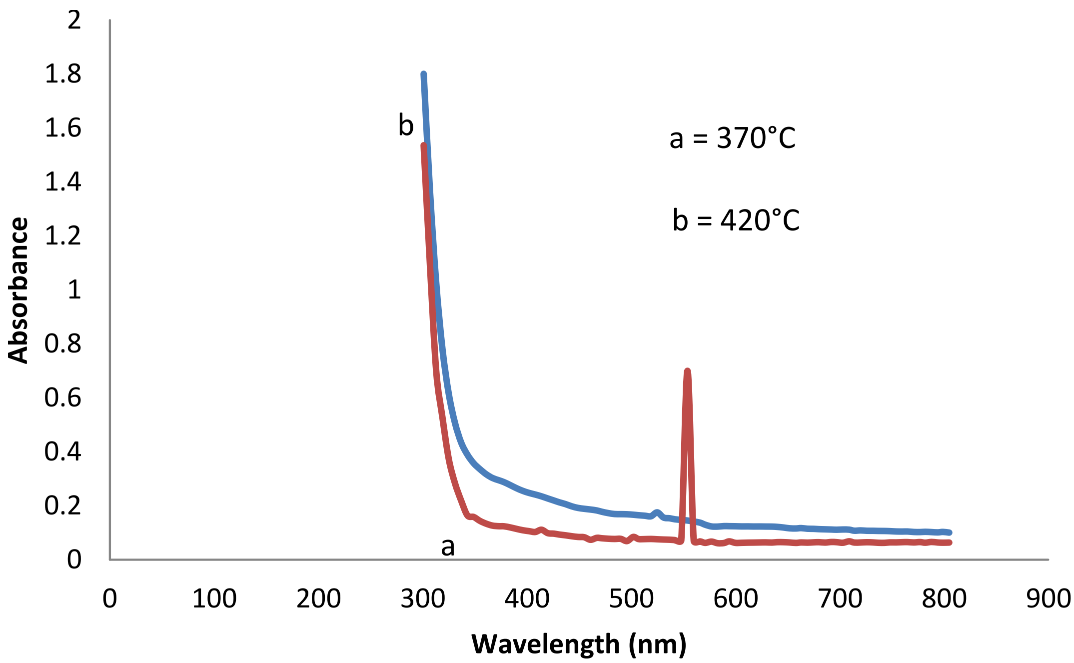

Figure 3. Absorbance spectra for TiO_2 thin film at 370 and 420°C.

The absorbance of TiO_2 film is shown in Figure 3 and it elucidates the experimental behavior of TiO_2 thin film when deposited at 420°C, these deposits displayed a high absorbance and decreases at a temperature of 370°C. Figures 4 and 5 shows the band gap deposited at temperatures of 370°C and 420°C respectively. These band gaps were obtained using Tauc plot method as shown in equation (2) while the absorption coefficient α of the TiO_2 thin film was calculated using equation (3).

From Figures 4 and 5, the value of optical band gap were calculated by plotting $(\alpha h\nu)^2$ against photon energy. The extrapolation of the linear part gives a direct band gap, the band gap value of the film deposited at 370°C is 3.88 eV, while the film deposited at 420°C lead to a band gap of 3.81 eV. The results obtained here also confirmed the results of Nandani et al. (2018) who studied the effect of deposition temperature on the optical properties of TiO_2 thin film. Nandani et al. (2018) reported a temperature of 200°C with a band gap of 3.52 eV, and at a high temperature of 550°C,

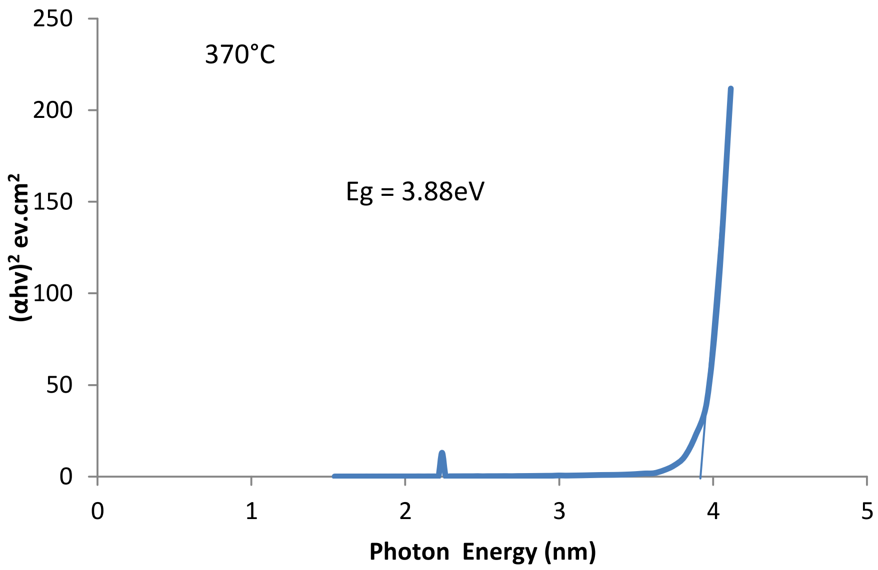

Figure 4. Band gap of TiO_2 film deposited at 370^{o}C using Tauc Plot method.

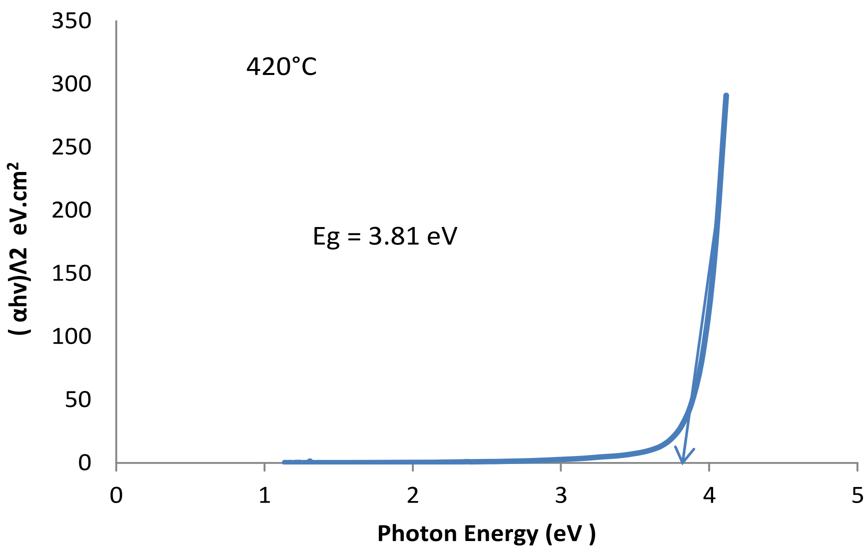

Figure 5. Band gap of TiO_2 film deposited at 420^{o}C using Tauc Plot method.

they obtained a band gap of 3.27 eV. This indicates that temperature as a deposition parameter affects the band gap of TiO_2 thin film. The refractive index of TiO_2 thin film calculated from equation 4 shows the refractive index with a mean value of 2.4 and 2.5 for the film deposited at 370 and 420°C varies with temperature.

CONCLUSIONS AND RECOMMENDATION

The optical transmittance of TiO_2 thin film determined by UV-VIS spectrometer prepared by spray deposition has been studied extensively in this research. The results show that the transmittance decreases from 86% to 79% due to increase in temperature. This value falls within the region of high transparency which makes TiO_2 an excellent interest for thin films. The extrapolated plot was linear; hence TiO_2 has a direct energy band gap. We recommend that other techniques and methods like, spin coating, electron beam evaporator be employed to study TiO_2 thin film. We also suggest that the time frame should be extended as this research was limited to a maximum of 10 min.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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