Tailored Physical and Optical Traits of TiO Thin Film formed Via Spray Pyrolysis Strategy: Influence of Annealing Temperature Change

M.L. Hussein[1], Ghada A. Kadhim[2], Ali Aqeel Salim[3*]

Abstract

Based on the worldwide technological interest, titanium oxide (TiO) thin film with its adapted form is well-known in the solar batteries and optoelectronic devices. Hence, we prepared a thin film upon a glass substrate using a chemical spray pyrolysis approach. Varied annealing temperatures (303, 323, 373, 423, 473 and 523 K) were used to establish the physicochemical properties of TiO thin film. The transmittance spectra values were observed between 50% and 70% with extinction coefficient value ~ 0.28 cm−1. Consequently, the bandgap of the TiO were steadily decreased with enlarging the annealing temperature from 3.5 eV up to 2.8 eV.

Key Words: Spray Pyrolysis, TiO T9hin Film, Annealing Temperature, Optical Properties, Structure.

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Introduction

Transition metal oxides (TMO) are compounds which combined of oxygen (O) atoms bound to transition metals such as Fe, Cu, Ni, Mn, Cu, and Ti. TMO with various oxidation states is being known as promising materials for super capacitors (Pareek *et al*, 2019; Yang *et al*, 2019). In the last few years, a typical transition metal oxide, manganese oxide (MnO_2), ruthenium oxide (RuO_2), vanadium pentoxide (V_2O_5), cerium oxide (CeO_2), cobalt oxide (Co_2O_3), nickel oxide (NiO) and titanium monoxide (TiO) have been involved to improve the optical characteristic efficiency toward the photonic applications (Kuan *et al*, 2018; Wang *et al*, 2017). Moreover, TMO reveal highly efficient properties that are useful to catalytic applications, including mechanical and thermal stability (Yang *et al*, 2019). Titanium oxide (TiO) is defined as titanium (Ti) and an oxygen (O) inorganic chemical compounds that possibly can be prepared from titanium metal at nearly 1500°C and titanium dioxide (TiO_2) (Kularatna, 2014; Solano *et al*, 2019). The titanium oxide cubic metallic is one of the most important material due to its extremely wide homogeneity range with oxygen content adjustable from 0.80 to 1.304 X 10^{-7}, magnetic, optical, structural low electrical resistivity (~400 μΩ cm), and electrical. Also, it has high efficiency as a diffusion barrier against the interdiffusion of Si and Al properties from bulk TiO material have been commonly reported (Yang *et al*, 2019; Wang *et al*, 2017). TiO has four diverse phases: cubic, β- TiO with a superstructure of rock-salt TiO, monoclinic α-TiO and hexagonal ε-TiO (Solano *et al*, 2019; Han *et al*, 2018), these composites have a wide range of homogeneity with high interest for industrial applications.

Corresponding author: Ali Aqeel Salim
Address: [1]Department of Physics, College of Science, University of Kerbala, Kerbala, Iraq; [2]Department of Physics, College of Science, University of Wasit, Wasit, Iraq; [3*]Laser Center & Physics Department, Faculty of Science, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia.
[3*]E-mail: asali@utm.my

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Moreover, the refraction index of these materials is considered to be used as design parameter and optical device systems including gas sensors, filters, switches, modulators, optical waveguides, anti-reflective coating, and both air and water purifiers (Swaminathan *et al*, 2018; Kadhim *et al*, 2021).

Chemical spraying pyrolysis approach is well-known as a promising thin-film preparation method due to its effortless preparation, economical and capable to control film parameters such as thickness, the temperature of bases and potential for use in many important thin-film applications (Mardare *et al*, 2010). The chemical spray deposition method, according to the kind of reaction, can be divided into three sets (Filipovic *et al*, 2014). In the first set, the droplets of the solution reside on the heated substrate as the solvent evaporates and ingredients may react in the dry state. The second set denotes a process in which the solvent evaporates before the drops reach the heated substrate and the dry solid impacts on the surface via decomposition. In the third set, there are processes where the solvent evaporates such as the droplets approach the surface with the subsequent heterogeneous reaction of the components of the solution (Veena *et al*, 2018). The important parameters of this controlled process are the substrate temperature, nozzle-to-substrate distance, solution content and concentration and the carrier gas flow rate. Among these parameters, the substrate temperature has been considered as the utmost important factor in producing thin film from spray pyrolysis processing; this is because the droplets drying, decomposition, crystallization, and grain growth depend strongly on this factor (Arunachalam *et al*, 2015).

Furthermore, the conducting heat treatment process of the prepared thin film through control annealing temperature, where, the samples may be exposed to specific temperatures and for a certain period in the air or vacuum with the presence of a specific gas as required. Herewith the annealing may cause reduction in the structural defects that transfer its the kinetic energy of the atom's material obtaining in the two cases. First, a configure with remove secondary levels within the energy gap leads to reduce or increase the film's resistance, and second that involves re-arrangement of atoms within the crystal structure of the material (Aziz *et al*, 2019). The TiO thin film prepared by chemical spraying pyrolysis method at varied annealing temperatures. The physiochemical properties were determined and characterized using UV-Vis, PL and FTIR spectrophotometers.

Experimental

Material Used

Titanium oxide (TiO) thin film were prepared using thermal chemical spraying on thin glass bases heated to a temperature of 350 ± 10°C. The spray solution was made using titanium chloride ($TiCl_3$), a liquid of purple color with a molecular weight (154.225 g/ml) of purity (99.9%), 7.317 gm of titanium chloride (TiCl3) were added at a concentration of 0.5 mol/L into 100 ml distilled water. The mixture is rotated using a magnetic stirrer to obtain the spray solution. Thereafter, the spray solution poured into the spray tank with forming a spray distance of 30 cm between glass bases and nozel, where the glass bases were placed upon the electric heater till reaching the desired temperature 350 ± 10 ° C. Afterward, the spraying process was take approximately 5 sec, followed by a cutoff in the nearly second 3 and evaporate the gases through heating process to form a titanium oxide (TiO) membrane on the glass base. This process has been repeated several times for customizing the required thickness. Thin films were annealed at five temperatures (323, 373, 423, 473 and 523 K), to evaluate the efficiency of physiochemical properties.

Characterization of TiO Thin Film

The atomic bonds of TiO thin film were analyzed through the Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu IR Affinity-1 system) using solid KBr discs technique. The absorption spectra of the TiO was measured using UV-visible spectrophotometer (Union space international Uv1601) in the wavelength range of 300-1200 nm. The photoluminescence (PL) measurement was carried out under Spectro Fluorometer SL 174, Elico, India, in the range of 300 upto 900 nm. All characterizations have been performed at room temperature.

Theoretical

Optical transmission (T) is defined that it is the ratio of the transmitted rays (I) to the incident rays (I_o) intensity on the substance as shown in the following equation: (Lee, 2019)

$$T = I/I_0 \qquad (1)$$

Absorption (A) is calculated by the following equation: (Calnan, 2014)

$$A = -\log(T) \qquad (2)$$

Result and Discussion

Figure 1 exemplifies the FTIR spectra of the TiO thin film (ranged of 400-4000 cm^{-1}) dependent various annealing temperatures. The appearance of absorption peaks of TiO thin film revealed a minor blue shift and broad with a change in the intensities. Where, the absorption band which located at 3439 cm^{-1} was assigned to strong stretching vibration of hydroxyl groups (O-H) of phenols and water (Simionescu *et al*, 2019). The symmetric band at 2924 cm^{-1} was corresponded to the carbonyl hydroxyl (C-H) of alkanes (Spiridonova *et al*, 2019). The presence of carbony1 (C=O groups) of alkenes structure in the absorption band positioned at 1642 cm^{-1} with slight shifting into lower wavenumber was due to the Ti–O interaction and deformation vibration of Ti-OH stretching mode which supported by the detected expansion and blue shift in the transmittance peak of UV-Vis (Figure 2 a) (Nam *et al*, 2012). The occurrence of tiny peak at 1437 cm^{-1} was contributed to strong stretching of Ti-OH amines groups that verified the influence of annealing temperature on the TiO thin film coating. The peak placed at 1060 cm^{-1} was consigned to the C-H bend with a decrease intensity which indicates to the elimination of moisture that caused improvement the characteristics of the thin film (Veena *et al*, 2018).

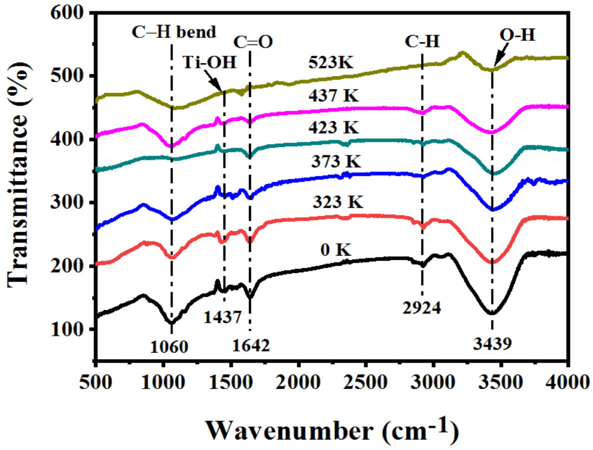

Fig. 1. FTIR spectra of TiO thin films prepared via chemical spray pyrolysis at various annealing temperatures.

Fig. 2 (a) displays the transmittance spectra of TiO thin films prepared on glass substrates at various annealing temperatures. These spectra were measured in the wavelength range of 300-1100 nm and observed in the transmittance values between 50% and 70%. It is clearly shown that the enlarge annealing temperature causes a strong decrease in transmittance for all TiO thin films samples in the UV region, which indicates high light-absorbing and existence of bandgap of TiO thin film samples that can be attributed to the semiconductor nature and enchantment in the performance of devices that requires a thin coating and high transparency (Arunachalam *et al*, 2015). Have been reported that the thin films of TiO deposited on glass had a transmittance nearly ≈ 70%. Furthermore, Fig. 2 (b) illustrates the plot of $(\alpha h\upsilon)^2$ versus bandgap energy ($h\upsilon$) for TiO thin films deposited at different annealing temperature. Where, the optical band gap can be obtained from extrapolating the straight line of the plot to $\alpha = 0$ (direct transition) and calculated using Tauc's relation as following: 34

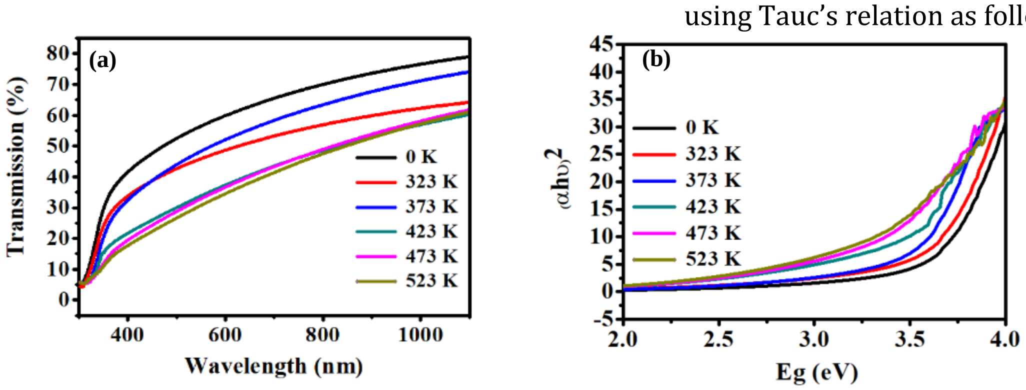

Fig. 2. (a) Transmittance spectra of TiO thin films prepared via chemical spray pyrolysis at different annealing temperature, (b) $(\alpha h\upsilon)^2$ versus bandgap energy

Fig. 3 exhibits the absorption coefficient as a function of wavelength at different annealing temperature. It showed that the values of the absorption coefficient at high wavelengths are lower in terms of short wavelengths as well as the probability of electronic transitions appeared lesser. All measured values of α are limit (α>104), that refers to the direct transition due to the influences of annealing temperature incensement. Besides, the behavior of the absorption coefficient α of the films has been determined from equation (3), where t is the thickness of the films. The consequence showed the thickness of all films are found to be 109.9 nm (Aziz *et al*, 2019).

$$\alpha = ln(1/T)/t \quad (3)$$

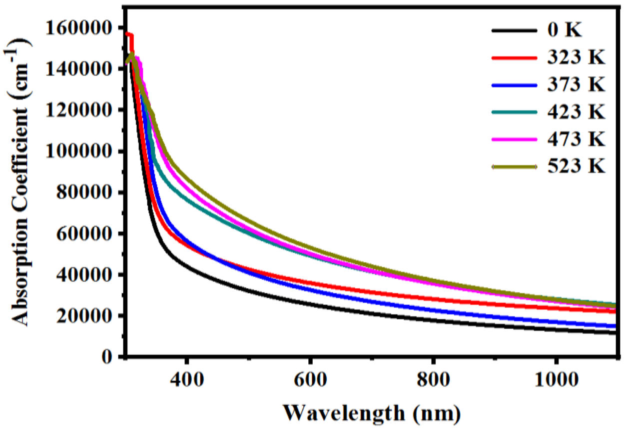

Fig. 3. Absorption coefficient of TiO thin films prepared via chemical spray pyrolysis at varied annealing temperature.

The extinction coefficient (k) spectra of TiO thin film samples dependent various annealing temperatures are shown in the Fig. 4. The extinction coefficient values of the prepared titanium oxide thin films are gradually increasing at short wavelength and decrease with longer wavelength due to its association with the absorption coefficient (Arunachalam *et al*, 2015). These obtained values of the extinction coefficient of the films has been measured from equation (4), showing that the extinction coefficient deepened annealing temperature.

$$k_0 = \alpha\lambda/4\pi t \quad (4)$$

Where, the Extinction coefficient (K_o) represents the inertia of the electromagnetic wave within the substance. While, λ is wavelength, α is absorption coefficient, and t is the thickness.

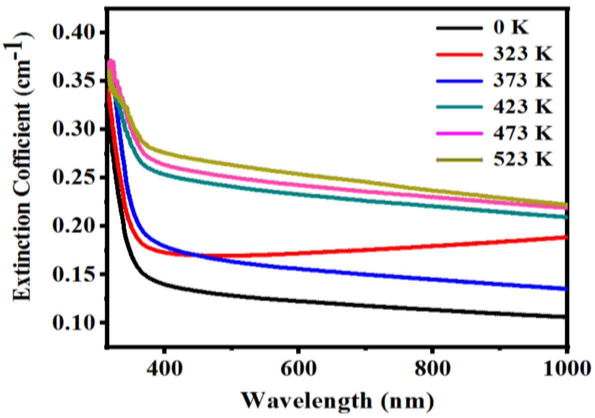

Fig. 4. Extinction coefficient of TiO thin films at different annealing temperature

Figure 5 exemplifies the change optical refractive index as function of the wavelength of TiO thin films. Where, the refractive index values were steadily increased in the short wavelengths until reaching a peak value of 2.6. Afterward, they begin slightly decreasing at longer wavelengths due to reflectivity values and increasing the annealing temperatures. The values were calculated from the equation (5) as following.

$$n = \left[\frac{1+R}{1-R}\right] + \sqrt{\frac{4\times R}{(1-R)^2} - K^2} \quad (5)$$

Where (λ) represents the absorbed photon wavelength, the refractive index (n) is defined as the ratio between the speed of light in the vacuum and its velocity within the substance, wherein R is the reflectivity (Filipovic *et al*, 2014).

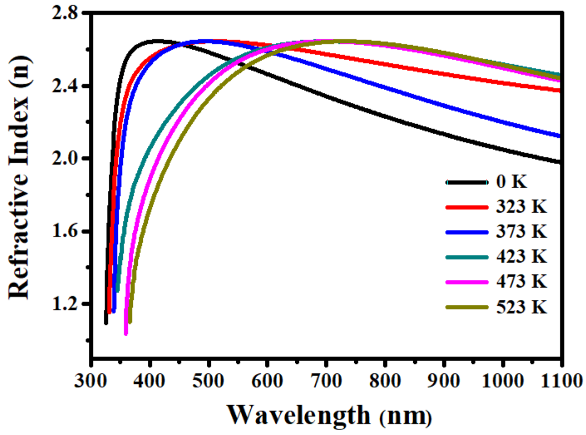

Fig. 5. Refractive index of TiO dependent various annealing temperature

Fig. 6 shows the PL spectra of TiO thin films at the different annealing temperatures, observed in the range of 310–470 nm with excitation wavelength of 300 nm. Prior exposing to the temperature at 0 K, the film unveils the characteristic band corresponding to trap-based emission of TiO at 350 nm. Upon increasing the temperatures, the emission bands were slight shifted into higher wavelength accompanying a growth in intensity that occurred due to the excited electron from valence band to conduction band with presence of photon. Thus, the excitation can be simply obtained through process of an electron with an amount of energy over the energy gap that caused to the electron release the energy through jumping over the crystal of TiO while the hole capture by localized electron. It is noticed that the intensity incensement of emission peak for all samples were due to the radiative recombination of trap exciting of TiO films. These observed PL emission peaks of annealed films were attributed to enhanced defect trapped excitons which enhances the presence of states in the TiO band gap and recombination centers electrons and holes. Besides, it is clearly presented the bandgap of TiO films through the PL peaks was decreasing because of the inversely proportional to the wavelength as tabulated in Table 1. The maximum intensity which observed at 523K is coherent with the lowest band gap value of the matrix.

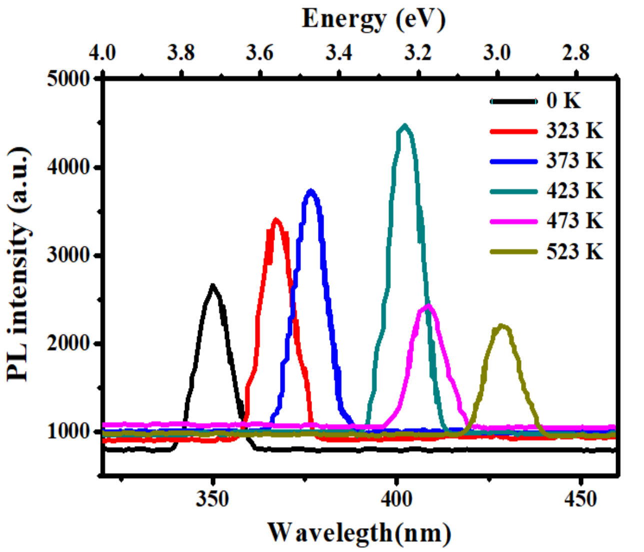

Fig. 6. Photoluminescence spectrum of TiO thin film prepared via chemical spray pyrolysis at different annealing temperature

Table 1. The bandgap values of TiO thin films with the different annealing temperature

Sample Code of TiO Thin Film	Annulling Temperature (K)	Emission Peak (nm)	Energy Gap (eV)
S0	0	350.13	3.54
S1	323	367.03	3.37
S2	373	376.35	3.29
S3	423	401.88	3.08
S4	473	408.00	3.03
S5	523	428.50	2.89

Conclusion

In this report we synthesized TiO thin films at different annealing temperature via spray pyrolysis technique. Appropriate formation of the TiO thin film was established via FTIR measurement. The change in the intensities and slight shifting of absorption bands of FTIR spectra indicated the effect of the annealing temperature on the film. The optical properties of the TiO samples revealed good transmittance properties (> 70%) for all films. Absorption coefficient α and extinction coefficient K increased with an increase in the annealing temperature. Through the values of α, we estimate that the electronic transition in the bandgap has a direct transition. The luminescence behavior of TiO film was verified using photoluminescence (PL) measurement where the PL intensity changed with various annealing temperatures. The optical bandgap of the TiO films decreased from 3.5 to 2.8 eV as temperature increased from 303K to 523 K. these obtained features may be prospective candidate for photonic applications.

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