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THE INFLUENCE OF DIFFERENT THICKNESS ON THE PHYSICAL PROPERTIES OF TIO_2 THIN FILMS PREPARED BY CHEMICAL THERMAL EVAPORATION

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ABSTRACT

TiO_2 thin films with different thickness on some substrates of glass by using thermal evaporation method. The result of optical properties illustrated that the best transmitted appeared at thickness (100 nm) and 900 nm wavelengths with a value equal to 78.2%. The observed band gap value of the direct transitions energy 3.69 eV for 150 nm, 2.95 eV for 300 nm and 2.45 eV for 450 nm.

KEYWORDS: Thermal evaporation TiO_2, Electrical Properties, D.C. Conductivity,TiO_2 Properties , And Optical Properties

1. INTRODUCTION

Recently much attention has been paid to use of TiO_2 particles for cleaning the environment by the photocatalytic decomposition of waste material, pollutants and harmful bacteria (Fox & Dulay, 1993). In photolysis reaction, TiO_2 powder are used as the photocatalyst (Jacoby, Blake, Noble, & Koval, 1995) [2]. But the powders have some problems and difficulties in the prevention of aggregation in highly concentrated suspensions. To avoid these issues TiO_2 various deposition methods are used to prepare titanium films – physical methods: DC or RF magnetron sputtering, E-beam evaporation, physical vapour deposition (PVD), thermal evaporation, chemical methods: sol-gel method, anodic oxidation, spray pyrolysis, chemical vapor deposition (CVD)(Blanco et al., 1996) [3], etc. Among these CVD is considered a useful way to prepare high quality thin films over a large defect density(Amadelli, Maldotti, Sostero, & Carassiti, 1991)[4]. Many of TiO_2 properties depend on the operation conditions of the CVD growth process. It is very important to control the CVD condition to optimise these characteristics.

TiO_2 can exist in three basic crystalline phases - anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and an amorphous phase. The first two phases have excellent photocatalytic and antibacterial properties when exposed to UVA light (320-400 nm). The rutile phase ($\Delta Eg = 0.3$,1 eV) has a low photocatalytic activity, but is stabled thermodynamic at high temperatures, the phase's anatase (ΔEg = 3,2 - 3,3 eV) is stabilized but has a higher activated photocatalytic and under appropriate conditions it could transform into rutile. Some authors (Valencia, Marín, & Restrepo, 2009; Yamazaki, Matsunaga, & Hori, 2001) [5-7] believe, that the simultaneous presence of three phases - anatase, rutile and amorphous phase leads to better degradation activity, and amorphous TiO_2 films also have a good photocatalytic properties.

In this work some results for electrical and optical properties of TiO_2 thin films deposited by chemical vapor deposition (CVD), and the effect of thickness are presented.

2. EXPERIMENTAL WORK

2.1 The diagram

The diagram below shows the direction of experimental work

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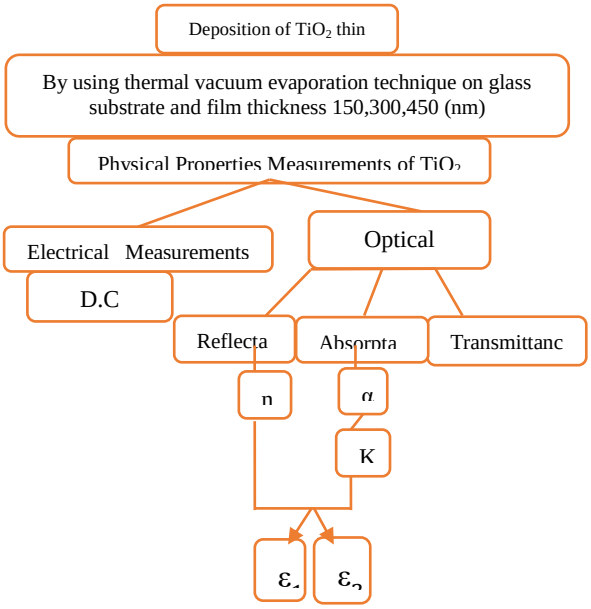

2.2 Method

Deposition method of thermal evaporation consisting in heated until reach evaporation of the mater to get deposits. The vapour of material then constitutes in shapes of thin films on a surface of cold substrate and on the walls of device. The pressures to be uses is around 10^{-6} to 10^{-3}torre to avoid reaction between material vapour and atmosphere. These lower pressures allow a free path of atoms at the same dimensions of vacuum chamber which is mean the particles can be travelling straight from the source to the substrate. The results films have a high order of purity.

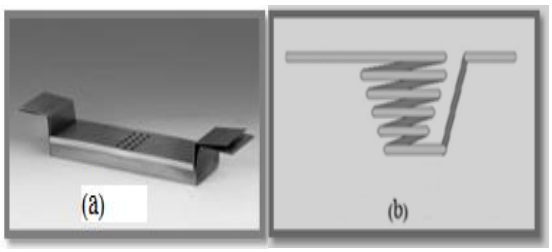

Fig. (1):- Various types of boats a) Molbidnyom boat for TiO_2 , b) spiral boat for Al poles.

A photograph of the device that have been used in this research shown in figure 2. Substrata of a glass was used to prepare TiO_2 under a pressure 10^{-} Torre. A boat of Tungsten uses to place the material in it then heated until the degree of evaporation, the vapour condensed on cooled substrate. Titanium Dioxide thin films formed at 500 ^{0} C substrate temperature and formed by a high annealing temperature.

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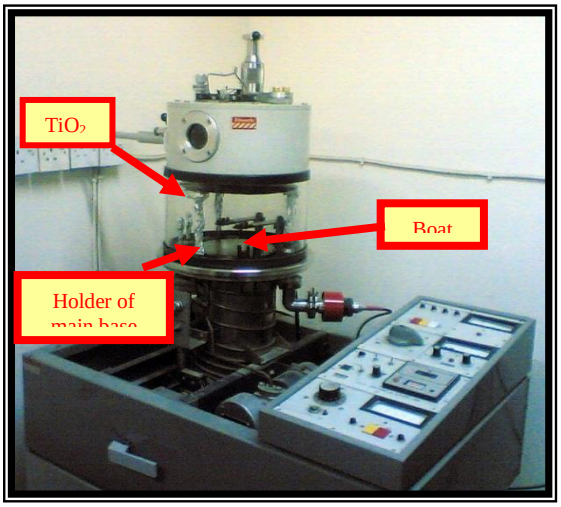

Fig. (2):- Thermal evaporation system type (Edwards).

3. THE OPTICAL INTERFEROMETER METHOD (FIZEAU FRINGES):-

The method is simply light interference of the light reflected from sample surface and substrate bottom. The thicknesses measured using (Chopra, 1969) [8]:

$$t = \frac{\Delta x}{x} \cdot \frac{\lambda}{2}$$

Where x is the fringes spacing, Δx is the displacement and λ is the wavelength of laser light as shown in figure (3).

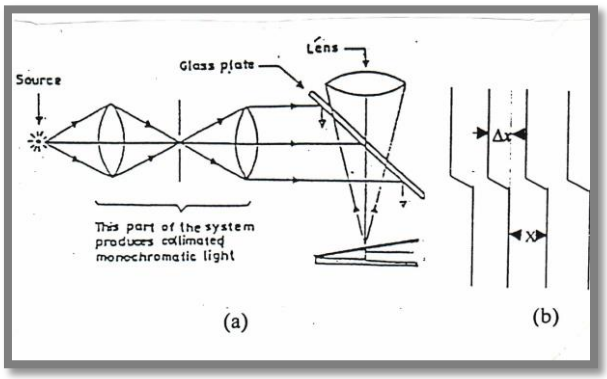

Fig. (3) Experimental arrangement for Fizeau fringes [8].

4. OPTICAL MEASUREMENTS

The optical properties of the prepared TiO_2 has been investigated by using the UV-VIS spectrophotometer SPECTROMOM 195D.

The range of wavelength that used to measure transmittance spectra were between (300 – 900) nm.

4.1

The influence of different thickness of TiO_2 thin films on the optical properties of the prepared films was studied extensively. Figure (4) illustrated the transmission spectra of TiO_2 against the wave length with range from 300nm to 900nm and from this figure TiO_2 films spectra exhibit high visible transmittance, up to 78 %, for 150 nm, which decreased slightly to 61.4 % for 450 nm films, because light losses and the absorption in the films grow up.

The transmission increase with increasing wave length and have maximum transmission at (900 nm), and there is an inverse relation between transmittance and thickness, i.e., it decreases when thickness increases (Sharma, Shukla, & Kumar, 2007) [9], transmittance slight decreased with the thickness films increased. This behaviour is attributed for increase the density of atoms (or concentration) with the thickness which rise the collision number between incident atoms, which then leads to the absorptance increasing of and decreasing transmittance [10]. The crystallographic and optical properties of the results films were dependent on the conditions of deposited like substrate temperature, film thickness and annealing temperature (Bedikyan, Zakhariev, & Zakharieva, 2013)[11].

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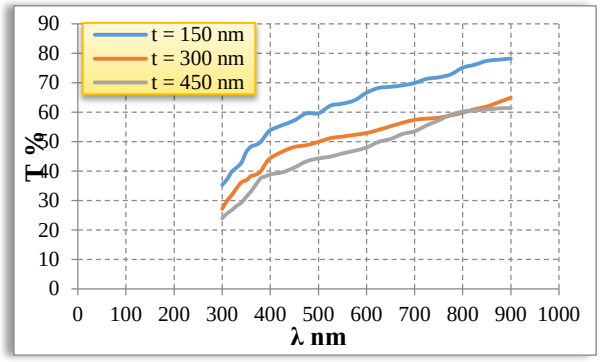

Fig. (4): The relation between transmittance and wavelength for TiO_2 films

4.2

When the thickness of the film is increased, absorptance is also increased and Figure (5) illustrates absorptance spectrum for (TiO_2) films of different thickness.

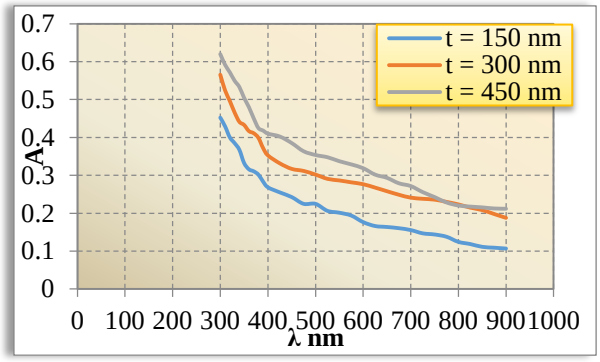

Fig. (5): The wavelength against absorptance of TiO_2 thin films.

At high λ the un enough energy of incident photons made it unable to interact with atoms, the transmission occurs when the wavelength (λ) decreases (photon energy increase). The interaction between incident light and material will occur and then the absorptance will increase(Speyer, 1993) **[12].**

4.3

Study of optical absorption spectra consider one of the most productivity devices for concept and develop the band structure and band gap energy of crystal and amorphous non-metallic material(Pattanaik & Srinivasan, 2003) [13]. The threshold at the low energy side of the optical absorption spectra is called optical absorption edge and corresponds to separation in energy between the bottom of the conduction band and the top of the valance band (Morigaki, 1999)[14].

The measure of absorption coefficient could be found from the formula:

$$\alpha = (2.303 \quad A) / t \text{ [15]}$$

Where: - absorption coefficient (α), thickness (t), and absorptance (A). Figure (6) show the variation of (α) with photon energy (hν) for TiO_2 thin films. From the figure the absorption coefficient (α) increases with increasing photon energy for investigated thin films. It can evidently be see that absorption coefficient having values (α> ⟦10⟧ ^4 cm^(-1)) which leads to increase the probability of occurrence direct transition, whereas the absorption coefficient is increasing with thickness decreasing. This can be linked with the formation stage of anatase and with increase in grain size and density of layers and it may be attributed to the light scattering effect for its high surface roughness (Kushwaha, Kushwaha, Shukla, & Kumar, 2005)[16].

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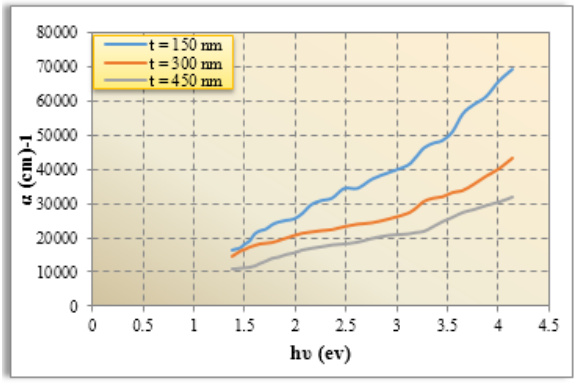


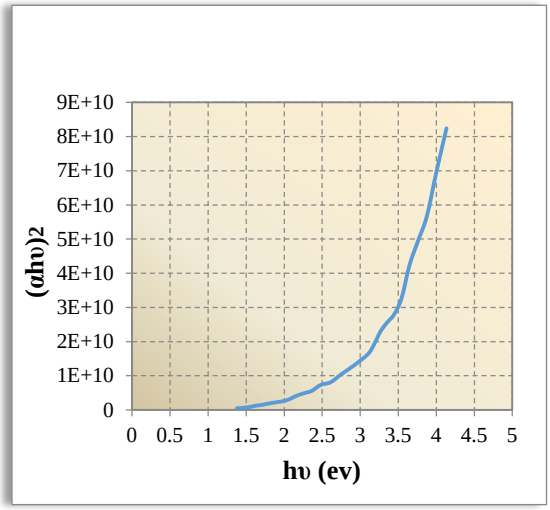
Figure 6: absorption coefficient as function of energy photon for different thickness of TiO_2 thin films.

4.4

Optical energy gap is formally defined as the intercept of the plot of $(\alpha h\nu)^{\wedge 2}$ against (hν). The high absorption region determines the optical energy gap. The strong absorption region involves optical transition between valence and conduction band. The absorption coefficient of amorphous semiconductor in the high-absorption region (α = 104cm-1) can be calculated by using equation:

$$(\alpha h\upsilon)^2 = B^2 (h\upsilon - Egopt.)$$

for allowed direct transition(Neamen, 1992) [17]. figure (7) illustrate allowed direct transition electronic and figure (8) illustrates Variation of optical band gap with thickness of TiO2 thin films.



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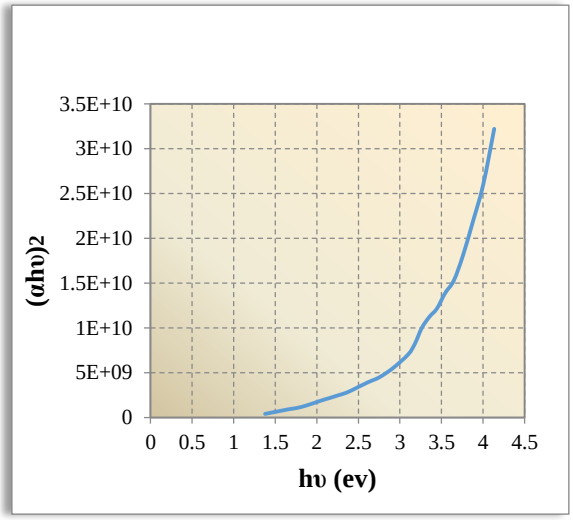

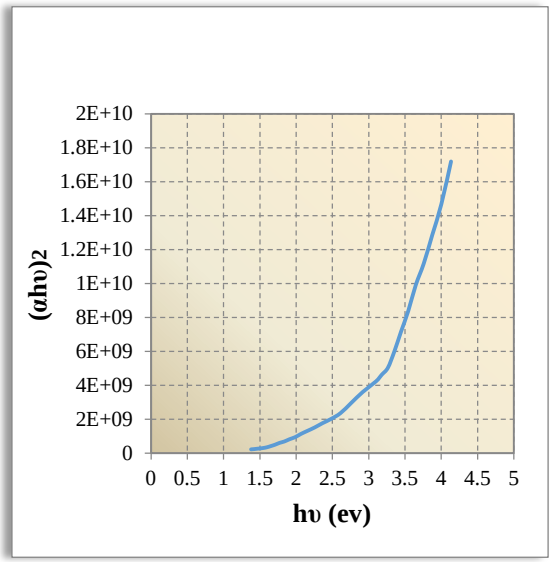

Fig. (7): allowed direct electronic transitions of TiO_2 thin films: (a) t=150nm. (b) t=300nm. (c) t=450nm

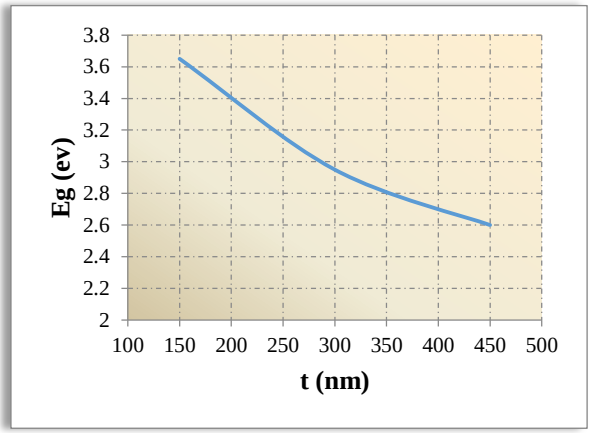

Figure (8):- Variation of optical band gap with thickness of TiO_2 thin films.

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Table (1) shows direct energy gap for allowed for different thickness of TiO_2 thin films

Thickness (nm.)	Allowed photon energy E_g (eV)
150	3.690
300	2.95
450	2.45

4.5

Reflectance is defined as ratio of the reflected intensity rays to value the intensity of incident rays [18]. Reflectance is calculated from spectrum of absorptance and transmittance for all prepared thin films. For all samples the reflectance has a high value that decrease when the wavelength increasing, as in figure (9). We can see an increasing in the value of reflectance by increasing the thickness of the prepared films. However, this result means there is an increase in the surface atom and smoothness of the prepared films.

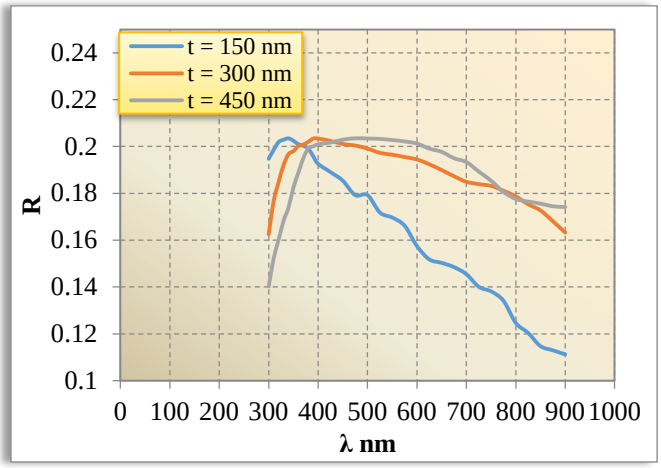

Fig.(9): The relation between reflectance and wavelength of TiO_2 thin films.

4.6

Refractive index is measured by using relation (Tsurumi, Nishizawa, Ohashi, & Ohgaki, 1999)[19]:

It has been shown in figures (10) as a function of wavelength of (TiO_2) films. The shape of the curve with wavelength is similar to the curve reflection curve because the increase in the energy of photon energy cause an increasing in the relation between them, and then decrease, refractive index enhances when the thickness increased. This is may be due to higher packing density and changing in crystal structure, the reason behind that is the enhance in crystalline growth (Maged, Amin, Semarym, & Borham, 2009)[20]

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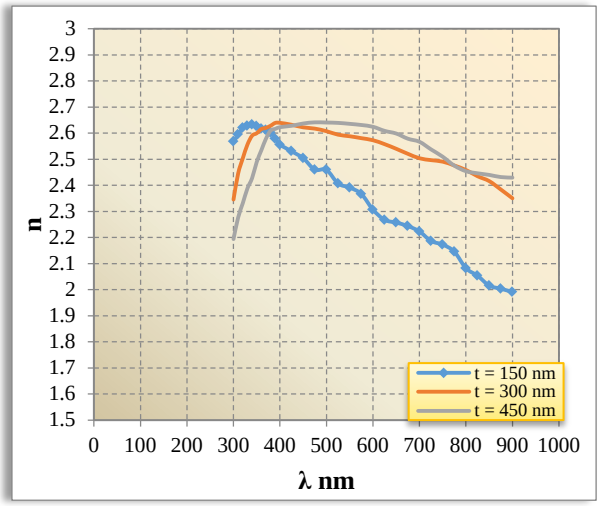

Fig.(10): Refractive index as function of wavelength for different thickness of TiO_2 thin films.

4.7

Excitation coefficient is measured by using equation [19] :

$$Ko = \alpha \lambda / 4\pi$$

Figure (11) illustrates variation of (Ko) as a function of wavelength for (TiO_2) films. Excitation coefficient behaves in the same behavior of absorption coefficient (α) because they are joined by previous relation, extinction coefficient decreasing with thickness increasing.

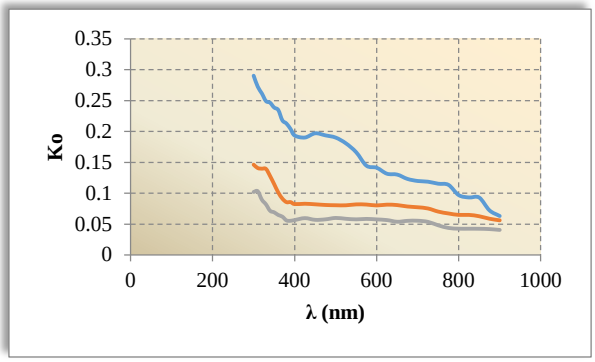

Figure (11): Excitation coefficient with wavelength for different thickness of TiO_2 thin films

4.8

The bellow relations have been used to find the real (ε_1) and imaginary (ε_2) dielectric constant respectively (Maged et al., 2009; Pankove, 1971) [21]:

$$\varepsilon_1 = (n^2 - K_o^2)$$

$$\varepsilon_2 = (2 n K_o)$$

Figures (12) and (13) illustrate variation of (ε_1) and (ε_2) with wavelength. The curves for all thickness shown that their values increasing to maximum value of (ε_1) with wavelength and then decrease [22]

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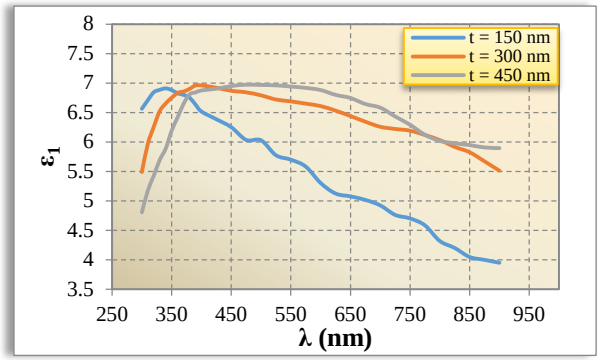

Fig. (12): Real dielectric constant (ε_1) of TiO_2 thin films.

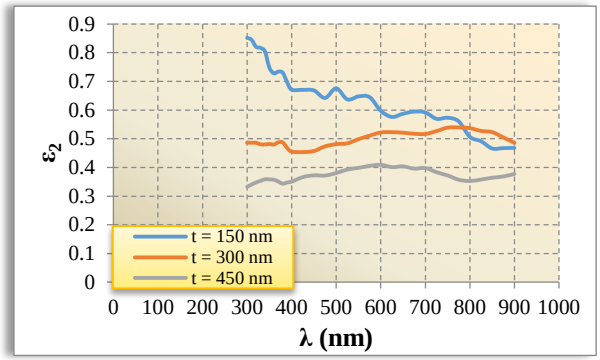

Fig. (13): imaginary dielectric constant (ε_2) of TiO_2 thin films.

5. ELECTRICAL MEASURMENT

The electrical direct conductivity ($\sigma_{d.c.}$) is calculated from equation

$\sigma_{d.c.} = 1/\rho_o$

Figure (14) shows the relation between (ln $\sigma_{d.c.}$) and (1000/T) for (TiO_2) films. Polycrystalline TiO_2 thin films have two activation energies for low and high temperatures within thermal range (20-200 ^{o} C). it has calculated and table 2 shows the results for high and low temperature.

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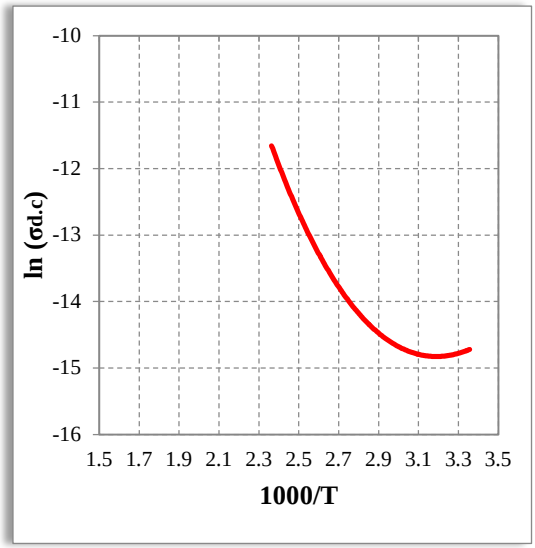

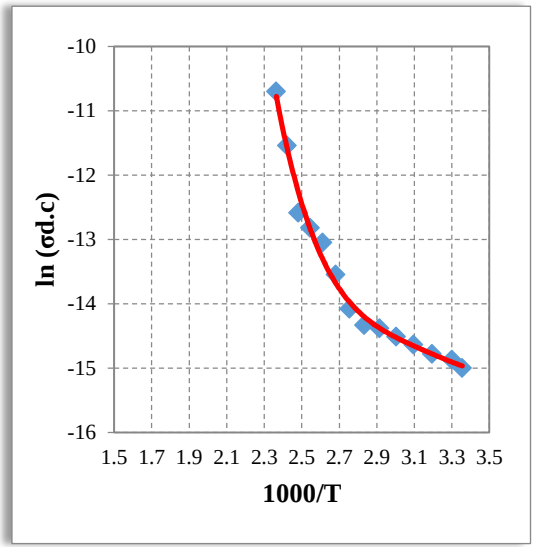

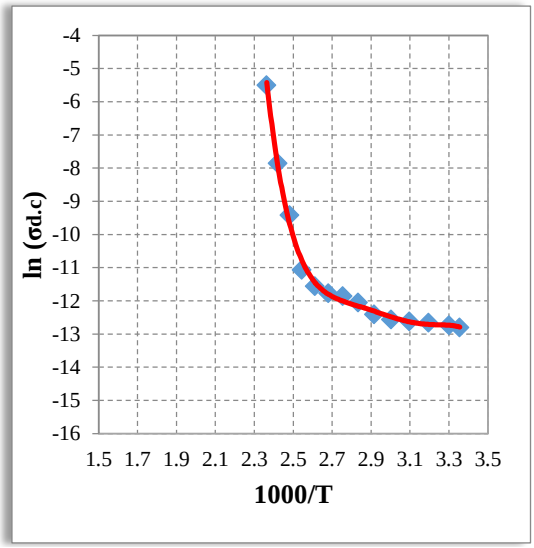

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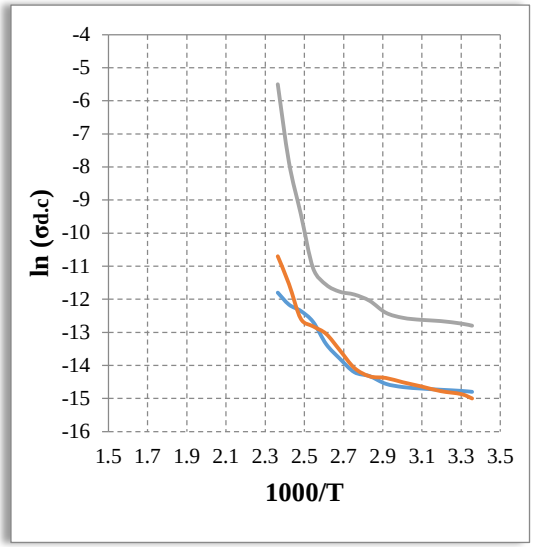

Fig. (14): The relation between ln ($\sigma_{d.c.}$) and (1000/T) for TiO_2 films for different thickness.

Table (2) shows activations energy (E_a) for different method of TiO_2 films with thickness 450 nm, within thermal range (20-200 ° C).

Thickness (nm.)	E_a(eV) (1) at high temperatures	E_a(eV) (2) at low temperatures
150	2.625881	0.413405
300	3.120094	0.490573
450	3.70875	1.035

6. CONCLUSIONS

TiO_2 thin films were deposited on glass substrates by chemical vapor deposition (CVD) with different thickness. The optical properties extensively studied and show that the films have a maximum transmitted value equal to 78.2% for 100 nm thickness at 900 nm wavelengths. The observed band gap value of the direct transitions energy 3.69 eV for 150 nm, 2.95 eV for 300 nm and 2.45 eV for 450 nm. The band gap width differences are connected with increasing of the crystallites dimensions and the surface alterations after annealing. The electrical properties shows that the activated band gab all films decreased with increasing the thickness means an increasing in the number of atoms led to decrease the band gab.

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