The Effect of Different Thickness on The Optical and Electrical Properties of TiO₂ Thin Films

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Abstract: In the recent years TiO₂ films are extensively studied because of their interesting chemical, optical and electrical properties. In the researcher work, TiO₂ thin films have received great attention, because of having excellent photocatalytic and antibacterial properties when exposed to UV light (320–400 nm). TiO₂ films spectra have maximum transmission at (900 nm) and exhibit high visible transmittance, up to 78 %, for 150 nm, which decreased slightly to 61.4 % for 450 nm. When wavelength decreases the absorptance will increase. The absorption coefficient is increasing with thickness decreasing (the probability of occurrence direct transition). From the light scattering effect for its high surface roughness the formation stage of anatase was appear with increase in grain size and density of layers. The refractive index increases with thickness increasing, and then the enhancement of growth crystalline. It have found a wide range of applications in various fields like photocatalysis, antibacterial and protective coatings, antireflecting coatings, etc.

Keywords: TiO₂, thermal vacuum evaporation, electrical properties and optical properties.

Introduction
Recently much attention has been paid to use of TiO₂ particales for cleaning the environmert by the photocatalytic decomposition of waste material, pollutants and harmful bacteria [¹]. In photolysis reaction, TiO₂ powder are used as the photocatalyst [²]. But the powders have some problems and difficulties in the prevention of aggregation in highly concentrated suspensions. To avoid these issues TiO₂ diverse deposition methods are used to prepare titanium thin films. Some physical methods, DC or RF magnetron sputtering, E-beam evaporation, physical vapor deposition (PVD), thermal evaporation, chemical methods (sol-gel method), anodic oxidation, spray pyrolysis, chemical vapor deposition (among these CVD is considered a useful way to prepare high quality thin films over a large defect density)[³,⁴], etc.

TiO₂ can work out in three requisite crystalline phases - anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and an amorphous phase. The first two phases have outstanding photocatalytic and antibacterial properties when exposed to UVA light (320–400 nm). The rutile phase (ΔEg = 3.0–3.1 eV) is thermodynamically stable at high temperatures, but has a lower photocatalytic effectiveness. The anatase phase (ΔEg = 3.2–3.3 eV) is
metastable and has a higher photocatalytic effectiveness but under suitable provision can be modify to the rutile. Some authors [5-7] suppose, that the concurrent participation of three phases - anatase, rutile and amorphous phase leads to better degradation effectiveness. A morphous TiO₂ thin films have a good photocatalytic characteristics. In this research some results for electrical and optical properties of TiO₂ thin films deposited by chemical vapor deposition (CVD) have been studied. The effect of different thicknesses were presented.

**Experimental and Method**

The vacuum thermal evaporation system type (Edwards) was used to evaporate Ti on glass slides at room temperature under low pressure (10⁻⁶ or 10⁻⁵) Torr to avoid reaction between the vapor and atmosphere. Material was placed in Tungsten and Molbidnymo boats then heated to evaporate [thin films (Ti) was fabricated by the material vapor on cooled substrate]. Films produced by evaporation are relatively pure and thus are of interest from a theoretical standpoint. TiO₂ thin films annealed at 500°C [oxidation temperature of (Ti) thin films].

**The Optical Interferometer Method (Fizeau Fringes):**

The method is based on interference of the light reflection from thin film surface and substrate bottom. He – Ne Laser (λ = 632.8) nm is used and the thickness is determined using the formula [8]:

\[
\Delta x \lambda = 2x
\]

Where \( \Delta x \) is the fringes spacing, \( x \) is the displacement and \( \lambda \) is the wavelength of laser light as shown in figure (1).

![Figure (1) Experimental arrangement for Fizeau fringes](image)

**Optical properties measurements**

The optical characteristic of the invented TiO₂ were studied on the basis of transmittance measurements using the UV-VIS spectrophotometer from SPECTROMOM 195D. Transmittance and absorption spectra of the prepared films within the wavelength range (300 – 900) nm.

**1- Optical Transmission Measurements**

The influence of different thickness of TiO₂ films on the optical properties was studied extensively. The transmission spectra of TiO₂ as a function of wave length in the range (300-900) nm is shown in figure (2) and from this figure TiO₂ 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 transmittance is inversely proportional with thickness, i.e., it decreases when thickness increases [9], transmittance decreases slightly with the increasing of film thickness. This behavior is attributed to the increase the number of atoms with the thickness that leads to the increase of the number of collision between incident atoms and crystalline nature of the films throughout the coated area which is obtained due to uniform oxidation and improvement in lattice arrangement which in turn leads to the increase of absorptance and decreasing transmittance [10]. This result is conditional with many other works [  ]. TiO2 films have a good transparency in the visible region. It is known that the sharp decrease in transparency of
TiO2 films in UV and IR regions is caused by fundamental light absorption and by free-carrier absorption respectively. The crystallographic and optical properties of the deposited films were dependent on the deposition conditions: substrate temperature, film thickness and annealing temperature[11].

Figure (2): The transmittance as a function of wavelength for TiO2 thin films.

2- Optical Absorbance Measurements

When the thickness of the film is increased, absorptance is also increased and Figure (3) illustrates absorptance spectrum for (TiO2) films of different thickness.

Fig.(3) relation between wavelength and absorptance of TiO2 thin films.

At high λ the incident photons do not have enough energy to interact with atoms, the photon will be transmitted when wavelength (λ) decreases (photon energy increase). The interaction between incident light and material will occur and then the absorptance will increase[12].

3- Absorption Coefficient (α)

Analysis of optical absorption spectra is one of the most productive tools for understanding and developing the band structure and energy gap of both crystalline and amorphous non-metallic material[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 \[14\].

Absorption coefficient is calculated by using equation:

\[
\alpha = \frac{2.303 \times A}{t} \quad [15]
\]

Where absorption coefficient \(\alpha\), thickness \(t\), and absorptance \(A\). Figure (4) show the
variation of \(\alpha\) with photon energy \((h\nu)\) for TiO\(_2\) thin films. From the figure the absorption
coefficient \(\alpha\) increases with increasing photon energy for investigated thin films. It can
evidently be see that absorption coefficient having values \((\alpha > 10^4 \text{cm}^{-1})\) which leads to
increase the probability of occurrence direct transition, where as 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 \[16\].

![Figure 4: absorption coefficient as function of energy photon for different thickness of TiO\(_2\) thin films.](image)

**Electronic Transitions Measurements and Optical Band Gap**

Optical energy gap is formally defined as the intercept of the plot of \((\alpha h\nu)^2\)against \((h\nu)\). 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 \((\alpha = 10^4 \text{cm}^{-1})\) can be calculated by
using equation:

\[
(\alpha h\nu)^2 = B^2 (h\nu - E_{g opt})
\]

for allowed direct transition \[17\]. figure (5) illustrate allowed direct transition electronic and
figure (6) illustrates Variation of optical band gap with thickness of TiO\(_2\) thin films.
Figure (5) allowed direct electronic transitions of TiO$_2$ thin films: (a) $t=150$nm. (b) $t=300$nm. (c) $t=450$nm.

Figure (6): Variation of optical band gap with thickness of TiO$_2$ thin films.
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                             |

Reflectance Measurements (R)

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. We observed that reflectance have high value which decreasing with wavelength increasing for all films, as in figure(7). 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.

![Figure (7): the reflectance at wavelength range (300-900 nm.) of TiO$_2$ thin films.](image)

Refractive Index

Refractive index is measured by using relation $^{19}$:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$

It has been shown in figures (8) as a function of wavelength of (TiO$_2$) films. The shape of the curve with wavelength is the same curve reflectance curve because the relation between them is increased with photon energy increasing and then decreases, refractive index increases with thickness increasing. The increase may be attributed to higher packing density and the change in crystalline structure, this increase due to the enhancement of growth crystalline $^{20}$.
Figure (8): refractive index as function of wavelength for different thickness of TiO$_2$ thin films.

**Extinction Coefficient Measurements (K$_o$)**

Excitation coefficient is measured by using equation $^{[19]}$:

$$ K_o = \frac{\alpha \lambda}{4\pi} $$

Figure (9) illustrates variation of (K$_o$) as a function of wavelength for (TiO$_2$) films. Excitation coefficient behaves in the same behavior of absorption coefficient (\(\alpha\)) because they are joined by previous relation, extinction coefficient decreasing with thickness increasing.

Figure (9): Excitation coefficient with wavelength for different thickness of TiO$_2$ thin films

**Dielectric Constant Measurements**

Both real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) dielectric constant are measured for prepared films by using following relations respectively $^{[21]}$:

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

$$ \varepsilon_2 = \left( 2nK_o \right) $$

Figures (10) and (11) illustrate variation of ($\varepsilon_1$) and ($\varepsilon_2$) as a function of wavelength. It is observed that their values increase with wavelength to maximum value of ($\varepsilon_1$) and then decrease $^{[22]}$ for all thickness.
D.C. Conductivity Measurements

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

$$\sigma_{d.c.} = \frac{1}{\rho_{0}}$$

Figure (12) 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 °C). It has calculated and table 2 shows the results for high and low temperature.
Figure (12): the relation between \( \ln(\sigma_{d.c.}) \) and \( (1000/T) \) for TiO\(_2\) films for different thickness.

Table (2) shows activation energy (\( E_a \)) for different methods of TiO\(_2\) films with thickness 450 nm, within thermal range (20-200 \(^\circ\)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                                |

Conclusions

TiO\(_2\) thin films were deposited on glass substrates by using thermal vacuum evaporation technique and film thickness 150,300,450 (nm). 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 gap all films decreased with increasing the thickness means an increasing in the number of atoms led to decrease the band gap.

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