Preparation of high transmittance TiO$_2$ thin films by sol-gel technique as antireflection coating

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Abstract. In this present work sol–gel technique with spin coating method is used to deposit Titanium dioxide thin films on glass substrates as anti-reflection coating (ARC) films. Nano crystalline TiO$_2$ (anatase phase) is obtained after heating at 550°C for 2 h. The optical properties of TiO$_2$ films were studied by UV-Vis absorption/reflection spectroscopy, the average transmittance of monolayer coated on glass substrates was greater than 95% in the wavelength range of 300–1000 nm.

Keywords. Sol-gel technique, spin coating method, thin films, antireflection coating.

1-Introduction
Thin film is a layer of material (molecular or element) which ranging thickness of the nanometer region (fractions of a nanometer to a few micrometers) [1-3]. Films are first made by (Busen and Grove) in 1852 A.D by using chemical reaction deposition. In 1857 A.D, Faraday was able to deposit a thin metal film by using thermal evaporation vacuum [4]. Thin films have many applications in several fields like protective films, electrically operating coatings, solar cells, batteries, decorative coatings, and many optical applications [5,6]. Deposition techniques are classified into two kinds, depending on the state materials, chemical or physical [7]. Chemical deposition methods are depending on phase of the precursor, the techniques that come from chemical processes are as follow: dip coating, chemical vapor deposition, chemical solution deposition, plasma enhanced CVD, atomic layer deposition, Langmuir-Blodgett and spin coating [8-10]. Physical deposition method uses mechanical, electromechanical or thermodynamic means to make a thin layer of solid material. Chemical reactions are not used here; physical deposition technique tends to require a low pressure evaporation (high-vacuum). The techniques that come from chemical processes are as follow: electron beam evaporator [11], molecular beam epitaxy (MBE) [12], sputtering [13], pulsed laser deposition [14], cathodic arc deposition or Arc-PVD [15] and electrohydrodynamic[16]. In this research, TiO$_2$ thin films prepared via spin coater which is branch of chemical deposition. One of the most important applications of thin films is anti-reflective which is considered optical applications of high optical transmittance. Anti-reflective coatings (ARC) are applied in a several wide of applications where light passes through a surface with low optical reflection. For examples anti-glare or anti-brightness coating on corrective lenses, cameras lenses elements, and windows of photo voltaic cells. The first and simplest form of antireflective coating was discovered by Rayleigh in 1886 AD. [17]. Single-layer interference is the simplest anti-reflective coatings (ARC$_s$) consist of a single thin film (mono layer) of transparent materials like Titanium dioxide (TiO$_2$) thin film with refractive index equal to square root of substrate's refractive index in air, such a coatings theoretically give zero reflectance for light with wavelength (in the coating) equal to four times the coating's thickness. Reflectance is also decreased...
for wavelengths in a broad band around the center. A layer of thickness equal to a quarter of some design wavelength is called a "quarter-wave layer". TiO$_2$ film is important material with wide applications like optoelectronic devices, photocatalytic systems and anti-reflection coatings [18, 19].

2. Experimental part.

2.1. Preparation of sol-gel solution.

The sol-gel was prepared by using Titanium isopropoxide TIP Ti(OCH(CH$_3$)$_2$)$_4$, ethanol C$_2$H$_5$OH-EtOH and acetic acid CH$_3$COOH as a catalyst, all materials were obtained from (Sigma Aldrich) with purity=99%. The sol-gel was obtained by dissolving 3.15 ml TIP in 25 ml ethanol and 5 ml acetic acid, the solution was stirred for 1h.

2.2. Preparation and characterizations of samples.

The optical glass substrates (1 mm*25.4 mm*76.2 mm) were ultrasonically cleaned by the mixture of acetone and propanol and then dried at 50°C. The spinning process by spinner ((Mod- 4000 Electronic Micro System) was carried out at (T=25°C) and normal atmosphere with the different speeds (1000, 2000, 3000, 4000 and 5000 rpm) on the cleaned substrates, after that treated (annealed) gradually escalating at heat temperature 550°C for (1h) and then let the samples inside the oven cool down as well.

![Diagram](attachment:image.png)

Table (1) shows the samples codes which annealed at 550°C.

| Sample code | Spin speed (rpm) | Thickness (nm) |
|-------------|-----------------|----------------|
| S1          | 1000            | 116            |
| S2          | 2000            | 92             |
| S3          | 3000            | 79             |
| S4          | 4000            | 62             |
| S5          | 5000            | 46             |

TiO$_2$ films were characterized by absorption, transmission and reflection properties as well as by spectrophotometer (UV-VIS).
3. Results and discussions.

3.1. Absorbance Measurements (A).

Fig. (1) refers to absorbance of (TiO$_2$) thin films of different thickness. At the visible regions absorption is decreased, it is excellent to be antireflection layer. At high wavelength the incident lights have not enough ability (energy) to make interaction with materials so photons will be transmitted, when ($\lambda$) decreases (photon energy increase). The interaction between incident photons and material will occur and then the absorbance will increase [20]. Absorption is direct proportional to the film thickness; this means that optical absorptions are inversely proportional to the rotational deposition speed.

![Graph](image.png)

**Figure 1.** Relation between wavelength and absorptance of TiO$_2$ thin films.

3.2. Transmittance Measurements (T).

Fig. 2. Illustrates that the optical transmittance of Titanium dioxide thin films. It is observed that maximum transmittance at (S3, S4 and S5) at thicknesses (79, 62 and 46 nm) respectively for wavelength range (420-900 nm) which is suitable for solar cell window. As showed in figure (4) transmittance is inversely proportional with thickness [21]. This behavior can be attributed to the increasing of thicknesses which lead increasing the atoms number per film and thus observe that optical transmittance is decreased because most of the photons have been absorbed by atoms [22].
3.3. Reflectance Measurements (R).

Reflectance of the surface of a material (thin film) is the fraction of incident light that is reflected at an interface [23]. Fig. 3 below shows the spectral reflectance curve as a function of wavelength. Reflectance is calculated from absorptance and transmittance by using eq. (1). We observed that reflectance have high value which decreasing with wavelength increasing for all films.

\[(R) = 1 - (A + T) \ldots \ldots (1)\]

When \(R\) is reflectance, \(A\) is absorbance and \(T\) is transmittance.

Figure 3. The reflectance at wavelength range (300-990 nm) of TiO\(_2\) thin films for different rpm.
3.4. Absorption Coefficient Measurements ($\alpha$).

Absorption coefficient is defined as (the ratio decrement in flux of incident electromagnetic energy relative to the distance unit in the direction of incident wave diffusion. Its depends on incident light energy ($hv$) and on semiconductor characteristics (n or p) type, [24]. Absorption coefficient can be seen in figure (4) that the absorption coefficient is the smallest at high wavelength, this means that the possibility of electron transition is little because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band ($hv < E_g$), at short wavelength, absorption is bigger; this means that a great possibility for electron transitions consequently, the energy of incident photon is enough to move the electron from the valence band to the conduction band. The energy of the incident photon is greater than the forbidden energy gap, this shows that the absorption coefficient assists in figuring out the nature of electron transition, when the values of the absorption coefficient are high ($\alpha > 10^4$) cm$^{-1}$ at high energies. It is expected that direct transition of electron occur, the electrons and photons maintain the energy and moment. However, when the values of the absorption coefficient are low ($\alpha < 10^3$) cm$^{-1}$ at low energies, it is expected that indirect transition of electron occurs, and the electronic momentum is maintained with the assistance of the phonon [25].

$$\alpha = \frac{(2.303 \times A)}{t} \ldots (2)$$

When $\alpha$ is absorption coefficient, A is absorbance and $t$ is thickness.

![Figure 4](image-url)  

**Figure 4.** Absorption coefficient as function of wavelength for different thickness of TiO$_2$ thin films for different rpm.
3.5. Extinction Coefficient Measurements ($K_0$).

Extinction coefficient ($k_0$) is calculated by using equation (3). The change of the extinction coefficient, as a function of the wavelength, is shown in figures (5). It can be noted that ($k_0$) has same behavior of absorption coefficient, absorption coefficient has a direct related with ($k_0$) as in the equation (3) [26].

$$k_0 = \frac{\alpha \lambda}{4\pi} \quad \text{……….. (3)}.$$  

![Figure 5](image-url).

**Figure 5.** Excitation coefficient as a function of wavelength for different rpm.

3.6. Refractive Index ($n$).

Refractive index is measured by using relation (4). It has been shown in figure (6) as a function of wavelength of ($\text{TiO}_2$) 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 [27].

$$n = \sqrt{\frac{4R - k_0}{R - 1}} - \frac{(R+1)}{(R-1)} \quad \text{……………… (4)}.$$
**Figure 6.** Refractive index as function of wavelength for different thickness of TiO$_2$ thin films.

### 3.7 Dielectric Constant Measurements.

Both real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) dielectric constant are measured for prepared films by using relations (5) and (6) respectively. Figures (7) and (8) 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 [60]. It can be seen that $\varepsilon_1$ considerably depends on ($n^2$) due to low value of ($k_0^2$) so.

$$\varepsilon_1 = (n^2 - k_0^2) \quad \ldots \quad (5)$$

$$\varepsilon_2 = (2nk_0) \quad \ldots \quad (6)$$
**Figure 7.** Real dielectric constant ($\varepsilon_1$) of TiO$_2$ thin films for different rpm.

**Figure 8.** Imaginary dielectric constant ($\varepsilon_2$) of TiO$_2$ thin films for different rpm.
3.8. Energy gaps of allowed direct transition \((E_g)\)

The energy gap can be calculated from equation (7), the relation is drawn between \((\alpha h\nu)^2\) and photon energy \((h\nu)\), as in figure (9) illustrates allowed direct transition electronic.

\[
\alpha h\nu = B(h\nu - E_g^{opt})^r \quad \text{…… (7)}
\]

Where \(E_g^{opt}\) the energy gap between direct transitions, \(B\) is the constant depended on type of material, \(r\) is the exponential constant; its value depended on type of transition. When \(r = 1/2\) for the allowed direct transition.

Table 2. Shows direct energy gap for different thickness of TiO\(_2\) thin films

| Sample code | Thickness (nm) | Allowed energy gap \(E_g\) (eV) |
|-------------|----------------|---------------------------------|
| S1          | 116            | 3.66                            |
| S2          | 92             | 3.7                             |
| S3          | 79             | 3.8                             |
| S4          | 62             | 3.6                             |
| S5          | 49             | 3.56                            |

From previous table and the following figure, it can be observed that \((E_g)\) is decreasing slightly with the increasing of thickness for all films. This is because of the increasing in the carrier concentration, which results in filling the bottom of the conduction band that leads to the decrease in hole between (C.B.) level and (V.B.) level that leads to zoom out the energy gap band [28].

Figure 9. Shows allowed direct electronic transitions of TiO\(_2\) thin films for different rpm.
4. Conclusion

According to a result above we have been concluded an important points, the best transmittance of (TiO$_2$) film is (95%--99%) for thickness (49nm.), within wavelength range (400-900nm.), the film is good to be windows of solar cell. But absorbance (A) is high at short wavelength, therefore; the film is good to be photo detector at ultra-violet range and The values of refractive indexes (n) of films are good ranges. This means that the films are good to be antireflection coating. Also we noticed that, Absorption coefficient ($\alpha$) of (TiO$_2$) film is about ($\alpha$>10$^4$cm$^{-1}$); thus absorption coefficient has higher increase at wavelength. This converts to a large probability that direct electronic transition will happen and Energy gap for allowed direct transition has been calculated as shown in table (2). This proves that the transitions happen from the close points in the top of valance band to the close points in the bottom of conduction band.

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