

Impact Of Substrate Nature On Optical Properties Of Titanium Dioxide Thin Films

Al-Wardy, Rusul Adnan ^a , Hawraa Hussien Alesami ^a 
^{a, c*} Department of Clinical Laboratory Science, College of Pharmacy,
Al-Nahrain University, Baghdad, Iraq.

Abstract:

In this work, we developed and implemented a numerical model to study the optical properties of TiO₂ thin films, specifically absorption and transmission. Transfer matrix technique was used with different substrates (glass-Boron silicate glass (SiO₂ (80 %) + B₂O₃)-SiO₂-platinum electrode Pt- indium tin oxide ITO) in the range of wavelengths (300-900) nm and thickness (t=100nm). Several significant characteristics were examined, including the absorption coefficient (α) and the energy gap (E_g). The result show that the absorption edge and optical band gap depend on the lattice match between the film and substrate.

Keywords: Boron silicate glass, ITO, TiO₂, thin films, transfer matrix

1.Introduction

An extensive variety of applications can be achieved with transparent and conductive oxides (Elmoula et al., p.1068 ,2020) (Talib et al., p.1, 2021). Titanium dioxide is also known as titanium oxide, titanium V oxide, or titania (Thjeel Al-Ogaili, H., & Al-wardy, R., p.2, 2020). Transition-metal oxide is cheap, harmless (Al-Wardy, R. A., p. 1, 2019), white, non-biodegradable, and versatile. Among its numerous optical and industrial applications are the design of optoelectronic devices (Bouchenak, K. N., & Chabane, N. E., p.23, 2013), multilayer optical coatings (Chudy, P. S. et al., p.4, 2019), gas sensors (Daniel, M. T., & Gregory, A. T., p.1, 2009) and photocatalytic purifiers (Diana, M., et al., p.1-4, 2000). Due to its high dielectric constant, it is frequently used in microelectronic devices (Do Amaral, M., & Barcelly, Y. R., p.3, 2021) . Amorphous, tetragonal, and orthorhombic phases of brookite are known, as well as tetragonal, orthorhombic, and tetragonal anatase, rutile, and amorphous rutile (Dundar, I., Mere, A., Mikli, V., Krunk, M., & Acik, I. O. p. 10,(2020).),(Gopakumar, A., Pal, K., & Wolverton, C., p. 1-3, (2022)), (Habis, C., Zaraket, J., & Aillerie, M., p. 243, (2022)).

At high temperatures over 800°C, anatase is irreversibly converted into rutile, resulting in anatase being metastable (Hossain, M. F., Pervez, M. S., & Nahid, M. A. I., p.186, (2020)), (Ikram, M., et al. p. 24215, (2020)). In addition to its wide bandgap from 3 to 3.2 eV for anatase, TiO₂ is non-toxic, transparent in visible light, and opaque in ultraviolet radiation (Islam, S., et al.p.11 (2024)), (Jaiswal, H. N., et al. p.5762 (2021)). The Anatase refractive index of TiO₂ is (2.26) (Elmoula et al., p.1068 ,2020), (Kabir, I. I., et al. , p.3774, (2020)). Impurities and crystal sizes in TiO₂ are the dominant defects, and they influence the optical properties of the film (Islam, S., et al.p.11 (2024)). TiO₂ is an n-type semiconductor (Magid, H. C., Rasheed, H. S., & Al-Wardy, R. A ,p.118, (2023)). Three of the most essential considerations for assessing glazing lighting and energy efficiency are the transmittances in the UV, visible, and infrared, or IR, ranges. These factors are strongly reliant on the type of film used, as well as the substrate's composition, thickness, surface roughness, and coherence of the film (Sultan and Sultana, 2015) (Marcello, A. B., Correa, V. O., Bento, T. R., & Pillis, F. M.,p.31, (2020)). (Gopakumar, A., Pal, K., & Wolverton, C., p. 1-3, (2022)) has written a lot on the creation and application of TiO₂ thin films in solar cells. He discovered that the highest transmission occurred at 900 nm and that the films had a high visual transmittance of up to 78% for thicknesses of 150 nm, but only 61.4% for 450 nm. The UV-Vis spectra of TiO₂ thin films created on borosilicate glass using the spin coating approach were displayed by (Mohammed, A., & U. M., G.,p. 20, (2018)) as proof that these films were extremely bright (85%) in the visible light spectrum. Through utilizing ultrasonic spray pyrolysis to make TiO₂ thin films on boron silicate glass, (Naceur, J. B., et al. p. 422 (2012)) revealed all of the films of TiO₂ were absorbing light in the UV-A location, which corresponds to wavelengths of 380 nm and lower. In a laboratory inspection (Panepinto, A.,et al. p.15 (2021)) reported that TiO₂ thin films created on ITO media using the sol-gel spinning coating procedures offer transparency over 80% throughout the spectrum of light and remain opaque in the range of ultraviolet radiation. One of the things that renders TiO₂ thin films attractive for usage in solar cell production is their excellent transparency. (I. I. T. Venkatachalam et al. p. 11 (2011)) saw

significant transparency (more than 75%) detected in the spectral band of 400 nm to 2500 nm as TiO₂ thin films were coated onto well-cleaned substrates composed of glass using a naturally invented original dipodrive coating procedure.

In the study by Cornelia (Sima and Constantin Grigoriu, p.10 (2009)), films produced through a modern pulsed laser deposition process (PLD) on ITO bases exhibited optical transfer in the visible range of from forty percent to sixty percent. The resulting films were designed to be utilized like effective sensors for the manufacture of solar cells. A valuable technique of generating thin film equipment for uses including chosen sunlight is mathematical simulation. It saves both time and money by offering an exact and quick evaluation of the task, avoiding the need for exploratory resources as well as time. Numerous studies have tried to replicate an optical thin film's transparency and reflectance.

(Sultan and Sultana, p.9 (2015)) use Fresnel's parameters to calculate the optical transparency of three unique films. The optical simulations of zinc oxide on the BK7 glass substrate and zinc oxide on the sapphire substrate were generated by (Khelladi and Chabane, p.12(2013)) using the Sellmeire laws. A transmission system concept examining thin-film optical filter materials was offered by (Pieper et al., p.9 (2006)). On the other hand, (Topasna and Topasna, p.8 (2009)) utilised a Transfer array technique for easy-to-understand, rapid, trustworthy modelling. This approach allows a more in-depth review of all potential material mixes, so numerous variables can be evolved to satisfy demands, such as the film's dimension, coating type, and their position in connection with substrate type.

In this work, the contribution of the type of accumulation substrate (glass-Boron silicate glass-SiO₂- platinum electrode Pt-indium tin oxide ITO) on the visual characteristics of TiO₂ films was studied applying the transfer matrix method, and the results have been compared with those obtained via actual studies.

2. Method for analysis

Visualizing a uniform, isotropic layer with refraction index (n_1), created on a substrate that has a refraction index (n_s), and covered in a medium having (n_0), At the first interface (a), the incident beam experiences an

exterior reflection, and at the second interface (b), the transmitted beam experiences an internal reflection and transmission. The tangential components of the resulting electric and magnetic fields are continuous across the contact, as determined by solving several equations using boundary equations^{19, 27}:

$$E_a = E_b \cos \delta + B_b \frac{i \cdot \sin \delta}{\gamma_1} \quad (1)$$

$$B_a = E_b (i\gamma_1 \sin \delta) + B_b \cos \delta$$

The transfer matrix is used:

$$\begin{pmatrix} E_a \\ B_a \end{pmatrix} = \begin{pmatrix} \cos \delta & \frac{i \cdot \sin \delta}{\gamma_1} \\ i\gamma_1 \sin \delta & \cos \delta \end{pmatrix} \cdot \begin{pmatrix} E_1 \\ B_1 \end{pmatrix} = M_1 \cdot \begin{pmatrix} E_1 \\ B_1 \end{pmatrix} \quad (2)$$

Assume,

$$M_1 = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \quad (3)$$

And

$$M = \prod_{i=1}^N M_i \quad (4)$$

So that,

$$\begin{pmatrix} E_0 + E_{r1} \\ \gamma_0(E_0 - E_{r1}) \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \cdot \begin{pmatrix} E_{t2} \\ \gamma_s E_{t2} \end{pmatrix} \quad (5)$$

The coefficient of reflection and transparency are defined as $r = \frac{E_{r1}}{E_0}$ and

$t = \frac{E_{t2}}{E_0}$ (Macleod, 2001)¹⁹:

$$tr_\lambda = \frac{2\gamma_0}{\gamma_0 m_{11} + \gamma_0 \gamma_s m_{12} + m_{21} + \gamma_s m_{22}},$$

$$rf_\lambda = \frac{\gamma_0 m_{11} + \gamma_0 \gamma_s m_{12} - m_{21} - \gamma_s m_{22}}{\gamma_0 m_{11} + \gamma_0 \gamma_s m_{12} + m_{21} + \gamma_s m_{22}} \quad (6)$$



$$R_{\lambda} = (|rf_{\lambda}|)^2, \text{ and } T_{\lambda} = (|tr_{\lambda}|)^2,$$

To run the simulations of the following parameters must be provided (as shown in Fig. 1 displays the steps to work with the program) by using a Mathcad version 14 computer program. Using the range of wavelength from (300-900) nm and taking the thickness ($t=100\text{nm}$) of the films and refractive index of TiO_2 and air is ($n_1=2.42$, $n_0=1$) respectively, meanwhile the optical properties thin film deposition was studied using five types of substrate (glass-Boron silicate glass- SiO_2 - platinum electrode Pt- indium tin oxide ITO) with refractive index (1.52, 1.51, 1.55, 1.34, 1.8270) respectively.

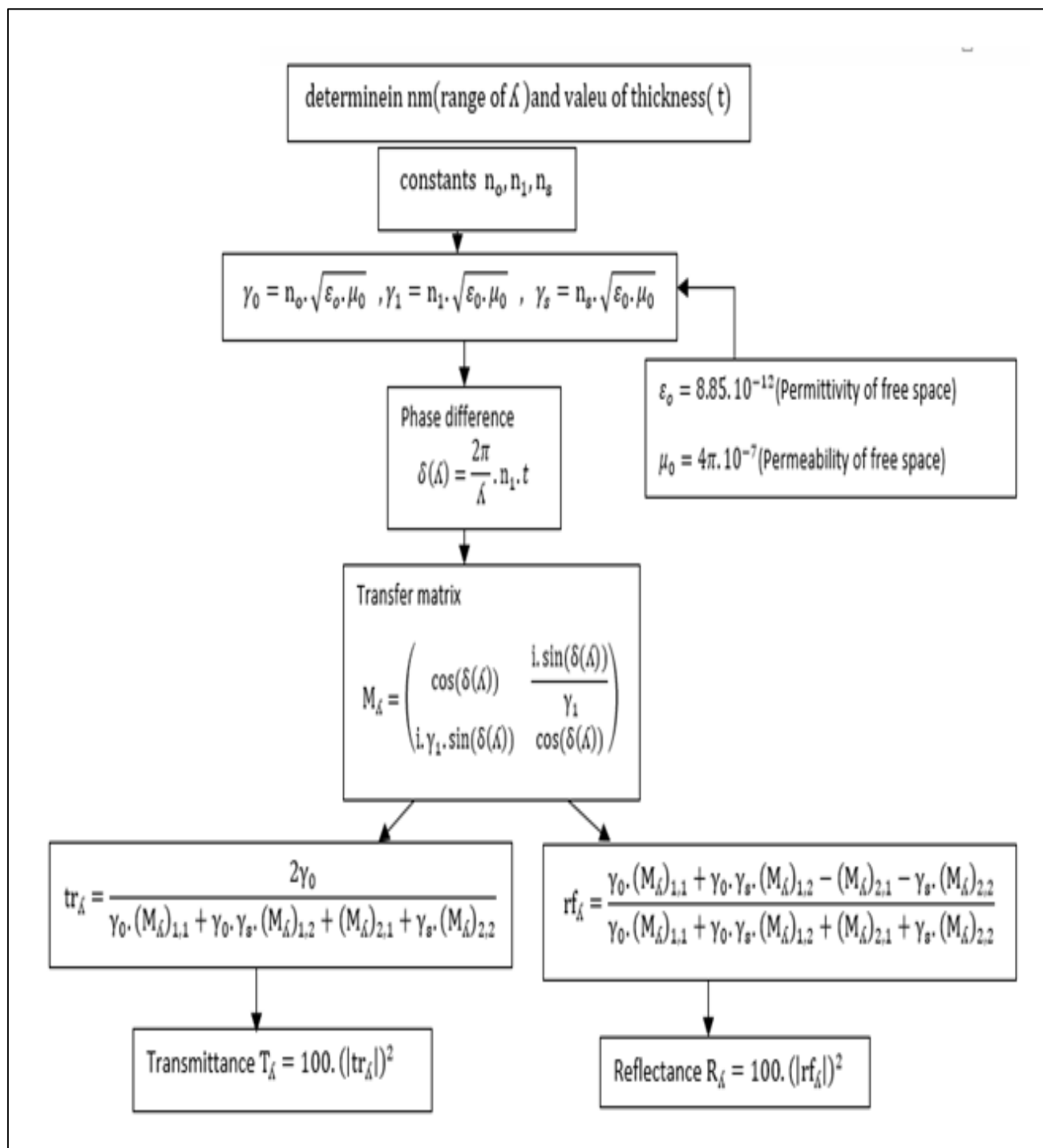


Figure 1. Shows the steps to work with the Mathcad program.

3. Results and Discussion

3.1 Transmission coefficient:

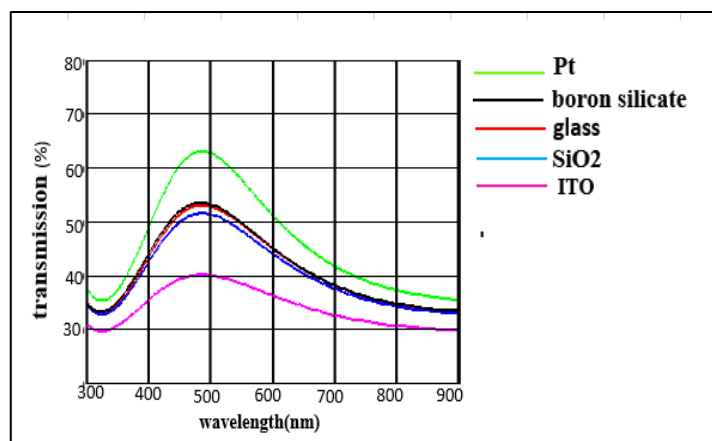


Figure 2. Transmission Vs. wavelength of TiO_2 thin film for different substrates.

Fig. 2 displays the transmission (%) versus wavelength in rang (300-900) nm, Generally, the transmittance increases within the wavelength range of 481-500 nm. the transmittance computed at 484nm in the visible range for different deposition substrates (73.0% for PT, 63.4% for boron silicate glass, 62.9% for glass, 61.5% for SiO_2 and 48% for ITO), were presented in table1 in addition comparing the transmittance of our theoretical work with other practical research of TiO_2 thin films.

Table 1. Comparison of this work of TiO₂ thin film with other experimental research

reference	Visible transmittance (%)	Thickness (nm)	Type of substrate	Method employed
[21](2020)	70	150	Borosilicate glass	Ultra spray pyrolysis
[22](2015)	80	70.63	ITO	Sol-gel coating
[12](2018)	70	50	glass	Sol-gel
[4](2020)	89	20	glass	Electron-beam evaporation
[24](2009)	85-86	100	ITO	Pulsed laser deposition
This work	73.034	100	Platinum electrode	theoretical
	63.49	100	Borosilicate glass	
	62.987	100	Glass	
	61.515	100	SiO ₂	
	48.446	100	ITO	

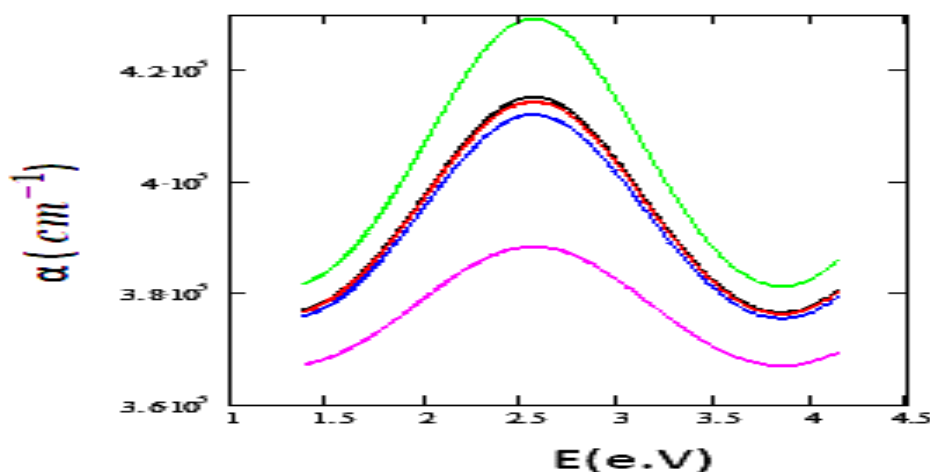
The deposition substrate affects the optical response of TiO₂ film with thickness(100nm). The transmittance in the visible light region of about 484nm of the film using Pt and boron silicate glass substrates is higher than substrates of glass, SiO₂ and ITO, owing to that better of lattice match between substrates and films (Pt: $a=0.3923\text{nm}$, boron silicate glass: $a=0.399\text{nm}$, TiO₂: $a=0.3876\text{nm}$ for anatase) and the magnitude of adhesive forces increases due to the chemical bonding between TiO₂ film and substrate increase²⁸ which results in heterogeneous stages nucleation causes the film to generate a lower stress level and is good to growth building and grain development as it results in greater sizes of grains. In addition, the substrate's external situation, specifically the texture, has a major effect on the stability of the film that is formed²⁹. As limitations within grains are what enable the film to grow, more grains equal more limitations, which means more the scattering effect. The gain both structural and optical qualities (the greater permeability) occurs by the rise in grain size. P. Sawicka-chudy et.al³¹ conclude from AFM 2D

images that the surface roughness of coating TiO_2 films (200nm) was (0.5) while it (1.2) for (250nm) of TiO_2 film.

while the transmittance in the visible light region of the film go down using glass, SiO_2 and ITO substrates showed an asymmetrical constant of lattice among the thin film and platform ($a=0.405$ nm for glass, $a=0.491$ nm for SiO_2 , and $a=1.009$ nm for ITO). That led in a decreased size of the grains and elevated film stress, which could lead to cracking or instabilities in the film. Glass and SiO_2 both showed an amorphous structure. substrates between substrates and films [3, 29]. This result is not consistent with ³² observed that transmission increase for TiO_2 film deposited on (ITO) substrate by R.F sputtering rather than deposited on glass substrate, He explained that TiO_2/ITO film has spaces that allow light to pass through easily, thus causing permeability.

3.2. Absorption coefficient and energy gap:

Fig. 3 shows the absorption coefficient vs. photon energy for the studied substrate (Pt- Boron silicate glass-glass- SiO_2 - ITO), we notice from the figure the increased value of absorption coefficient with photon energy



for all types of substrate, we also find a clear convexity. The reason for this convexity is the presence of

Figure 3. Absorption coefficient with photon energy for TiO_2 thin films with different types of substrates.

Table 2 .The optical band gap, E_g for TiO_2 films deposited on Pt, glass, boron silicate, glass, SiO_2 and ITO substrates, respectively.

Parameters	TiO_2/Pt	$\text{TiO}_2/\text{boron silicate}$	$\text{TiO}_2/\text{glass}$	$\text{TiO}_2/\text{SiO}_2$	TiO_2/ITO
$\alpha \text{ (cm)}^{-1}$	4.292×10^5	4.152×10^5	4.144×10^5	4.12×10^5	3.881×10^5
$E_g \text{ (eV)}$	2.578	2.568	2.567	2.562	2.48
T(E)%	70.034	63.49	62.987	61.515	48.446
$\lambda \text{ (nm)}$	481	483	483	484	500

absorption peaks between (2.48-2.578) eV. This means that photons with energies equivalent to the energy gap are absorbed, as seen in Table 2. This is in agreement with ³³ when showing the maximum absorption at (420nm) for TiO_2 thin film obtained by electrospinning, following was discovered and noted that the visible-light penetration across several visible light spectrum regions may be related to the bandgap values of the sample.

The absorption coefficient of amorphous semiconductor in the high-absorption region ($\alpha = 10^4 \text{ cm}^{-1}$) can be calculated by using the equation for allowed direct transition ^{3, 11, 12}:

$$(\alpha h\nu)^2 = A^2(h\nu - E_g^{opt}) \quad (1)$$

Fig. 4 shows $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for TiO_2 thin films with different types of substrates, a straight line is a conclusive line for $(\alpha h\nu)^2 = 0$, The cut-off point represents the value of the optical energy gap E_g^{opt} . Table 2 predicted the value of optical energy gap decrease for TiO_2 thin films (2.578, 2.568, 2.567, 2.562, 2.48) eV with (Pt- Boron silicate glass-glass- SiO_2 - ITO) substrate, respectively. Explain that lattice match and adhesion force caused heterogeneous phase nucleation to make the film generate smaller stress and beneficial to the nucleation formation and grain growth due to bigger grain size influences the absorption edge of the thin film, this result is in agreement with the experimental study by Seham Hassan Salmana et. Al ³ and X. Zhu et.al ³⁰. The different values of the energy gap of TiO_2 thin films for other researchers are shown in Table 3.

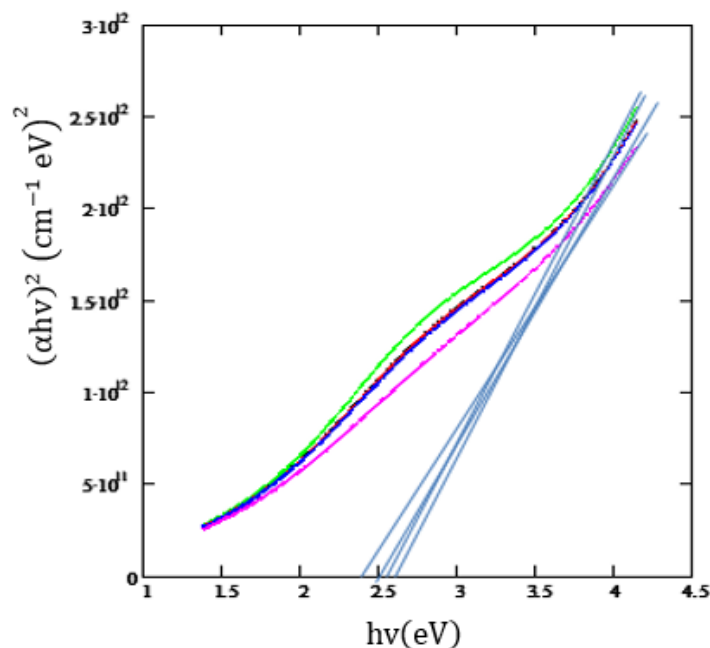


Figure 4. shows $(\alpha hv)^2$ vs photon energy for TiO_2 thin films with different types of substrates.

Table 3. The different values of the energy gap of TiO_2 thin films for other researchers.

Reference	Eg (eV)	Thickness (nm)	Type of substrate	Method employed
[21](2020)	3.4	150	Borosilicate glass	Ultra spray pyrolysis
[22](2015)	3.92	70.63	ITO	Sol-gel coating
[17](2021)	2.76		glass	Sol-gel
[11](2021)	2.45	450	glass	Chemical vapor dep.
	2.95	300		
	3.690	150		
[12](2018)	3.788	50	glass	Sol-gel
	3.687	150		
	3.753	100		
[4](2020)	4	20	glass	Electron-beam evaporation
	3.95	80		
[3](2018)	3.4	80	glass	R.F magnetron sputtering

	3.2	80	ITO	
[31](2019)	3.5	200	glass	DC magnetron sputtering
	3.1	250		
This work	2.52	100	Platinum electrode	theoretical
	2.5	100	Borosilicate glass	
	2.4	100	Glass	
	2.31	100	SiO ₂	
	2.25	100	ITO	

4. Conclusion

the analysis of optical properties of TiO₂ films taking the thickness (t=100nm) with different type of substrate using transfer matrix technique, with the range of wavelengths from (300-900) nm. The resulting that the films have a maximum transmitted value equal to (73.0, 63.4, 62.9, 61.5, 48) % for (PT, boron silicate glass, glass, SiO₂ and ITO) substrates respectively. The band gap width depends on the lattice match size and phase structure of substrate. TiO₂ films deposited on PT substrate is better by crystallization from other studied substrates.

Authors' declaration:

- "Conflicts of Interest": None.
- "The Figures and Tables in the manuscript belong to me and us "

Ethical Clearance: "The local ethical committee at Al-Nahrain University approved the project".

"Authors' contributions statement":

"The idea presented by R.A. was conceived, designed, developed, and computationally analysed by H.A. to investigate algorithms and compare different approaches to the service problem in future networks. H.A. and RA supervised the findings of this work. The authors wrote the article, checked carefully, discussed and contributed to the final version"

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تأثير طبيعة الركيزة على الخواص البصرية لأغشية ثاني أكسيد التيتانيوم الرقيقة

رسل عدنان الوردي¹، حوراء حسين²

2.1 قسم العلوم المختبرية السريرية، كلية الصيدلة، جامعة النهرين، بغداد، العراق

مستخلص البحث:

في هذا العمل، قمنا بتطوير وتنفيذ نموذج عددي لدراسة الخصائص البصرية لأغشية TiO₂ الرقيقة، وخاصة الامتصاص والنفذية. استُخدمت تقنية مصفوفة النقل مع ركائز مختلفة (زجاج - زجاج سيليكات البورون - (SiO₂ (80%) + B₂ O₃) - SiO₂ قطب بلاتيني Pt ، أكسيد قصدير الإنديوم، (ITO) ضمن نطاق أطوال موجية (300-900) نانومتر وسمك 100 نانومتر. تم فحص العديد من الخصائص المهمة، بما في ذلك معامل الامتصاص (α) وفجوة الطاقة (E_g). أظهرت النتيجة أن حافة الامتصاص وفجوة النطاق الضوئي تعتمدان على تطابق الشبكة بين الغشاء والركيزة.

الكلمات الافتتاحية: زجاج سيليكات البورون، أكسيد الإنديوم، ثاني أكسيد التيتانيوم، الأغشية الرقيقة، مصفوفة النقل