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## **Titanium Dioxide Thin Film Prepared By Sol-Gel Technique**

*Ali A. Abed, Ahmed R. AL-Mathloom<sup>1</sup>*

*<sup>1</sup>College of Education for pure Sciences, University of Thi-Qar, Thi-Qar, Iraq.*

### **Abstract:**

A titanium oxide thin film was prepared by Sol-gel technique, deposited on glass substrates using TiO<sub>2</sub> precursor Titanium (IV)butoxideTi(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>. The surface topography and structural properties of these films were studied by using scanning electronic microscopy (SEM) and X-ray diffraction techniques. According to the X-ray diffraction spectra, TiO<sub>2</sub> thin films were formed with an anatase type phase and tetragonal unit cell with a preferred orientation along (110) plane. Optical and electrical properties of these samples were analysed. Parameters such as band gap (E<sub>g</sub>), extinction coefficient (k), absorption coefficient (α), dielectric constant (ε), refractive index, (n) and resistivity (ρ) were calculated using the data obtained from different measurements. The optical band gaps found to be 3.56 eV and 3.26 eV for direct and indirect process, respectively. And The optical and structural characterizations showed that the samples have good transmission in the visible and near infrared (NIR) region of the spectrum. The samples have very low reflectance within the visible region and the absorption coefficient decreases with increasing thickness.

**Keywords:** sol-gel technique, Titanium dioxide, thin film.

## 1. Introduction

Titanium oxide (TiO<sub>2</sub>) coatings have been extensively studied and used owing to their great potential in optical device application, such as planar waveguides [1][2][3], antireflective coatings [4], and solar cells [5]. Various methods are available for preparation TiO<sub>2</sub> coatings. These are including electron-beam evaporation [6][7], DC reactive magnetron sputtering [8], ALD process [9], screen printing [10], DC sputtering technique [11], flat-flame chemical vapor condensation Method [12], sputtering [13][14], electrospinning procedure [15], pulsed laser deposition [16][17][18][19], using the ultrasonic spray pyrolysis technique [20], chemical spray pyrolysis [21], ICP chemical vapor deposition [22][23], hydrothermal Method [24], the electro phonetic deposition technique [25] and the sol-gel method [26],[27],[28]. Among the different techniques, the sol-gel method seems to be the most promising one as it offers the advantages of macro-porous coatings prepared at a comparatively low cost, capability of large coating size, and relatively easy process to control [29].

It is well known that TiO<sub>2</sub> occurs in nature in three distinct crystallographic phases: anatase, rutile, and brookite [30]. Anatase and rutile have a tetragonal structure, whereas brookite has an orthorhombic structure [31]. Anatase TiO<sub>2</sub> is the most widely used photocatalyst for oxidative decomposition of organic compounds, and an excellent photocatalyst for photodecomposition [30],[32]. Moreover, TiO<sub>2</sub> remains one of the best candidate materials in the development of dye solar cells due to its high efficiency, chemical inertness and photostability [33]. The major obstacle for its wide practical application in photocatalysis and photoelectrochemical energy conversion is the wide band gap that limits the photogeneration of electrons and holes to the UV region (comprising only ~5% of the solar radiation reaching the Earth) [34].

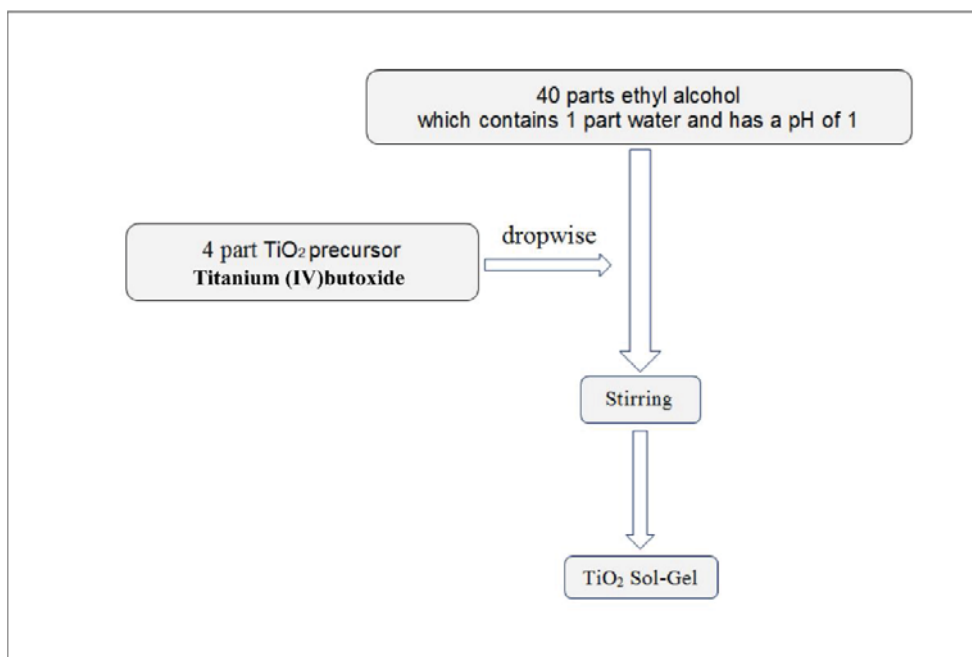
The aim of the present work is preparing thin films of TiO<sub>2</sub> using Sol-Gel technique and study the effect of number of layers (increase thickness), SEM and AFM. The impact on number of layer on optical properties such as absorbance (A) and transmittance (T) and reflectivity (R) and absorption coefficient ( $\alpha$ ) and refractive index (n) and extinction coefficient (K) and the Urbach energy (E<sub>U</sub>) and the direct and indirect optical energy (E<sub>g</sub>) and The real ( $\epsilon_r$ ) and imaginary ( $\epsilon_i$ ) parts of the dielectric constant. Has also been investigated.

## 2. Experimental

The TiO<sub>x</sub> sol-gel is prepared using the TiO<sub>2</sub> precursor Titanium (IV) butoxide Ti(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> (Aldrich). By volume, 4 parts of Titanium (IV) butoxide is added dropwise to a solution of 40 parts ethyl alcohol, which contains 1 part water and has a pH of 1, adjusted with the addition of hydrochloric acid (Aldrich), as shown in scheme (1).

These reagents hydrolyses the Titanium (IV) butoxide, forming –OH bonds, which may then polymerize, leading to gelation [35]. The sol-gel is stored on a stirplate to maintain the suspension and reduce the possibility of precipitation of large particles. The glass substrate were cleaned with ethanol and acetone in ultrasonic cleaner.

In either case, the material is spin-cast at ~1000 rpm for 20 second to produce a uniform film with 1.5  $\mu$ m thickness, and we then drained the thin film which coated on glass using the hot plate for 10 minutes 75 °C and then we depositing another layer to the previous layer the same way for a multi-layered thin film. then sintered for this a multi-layered thin film at 450°C for 30-60 minutes to convert the material to a crystalline anatase phase. The TiO<sub>x</sub> film is transparent and smooth relative to the nanoparticle layer.



### 3. Result and discussion

#### 3.1 Surface Morphology

##### 3.1.1 XRD characterization

shows X-ray diffraction peaks of titania film as a function of  $2\theta$  between 20 and 60 degrees. The peaks have been identified from standard diffraction data [36] and the  $2\theta$  peaks at  $25.19^\circ$ ,  $37.81^\circ$  and  $47.90^\circ$  confirm its anatase structure and tetragonal unit cell with a preferred orientation along (110) plane. [37]. The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite, as shown in fig.2.

In order to determine the variation of the crystallites size with increasing the thickness of thin films, we used the Scherrer formula neglecting peak broadening due to residual stresses in the films is given by [38]:

$$D = \frac{0.9 \lambda}{\beta \cos(\theta)} \dots\dots\dots(1)$$

where D is the size of crystallite,  $\lambda$  is wave length of X-Ray (0.1540 nm),  $\beta$  is the broadening of the diffraction line measured at half its maximum intensity in radians,  $\theta$  is a Bragg's angle

and Inter-planar spacing between atoms (d-spacing) is calculated using Bragg's Law [39] and enumerated in Table.1.

$$2 d \sin(\theta) = n \lambda \dots\dots\dots(2)$$

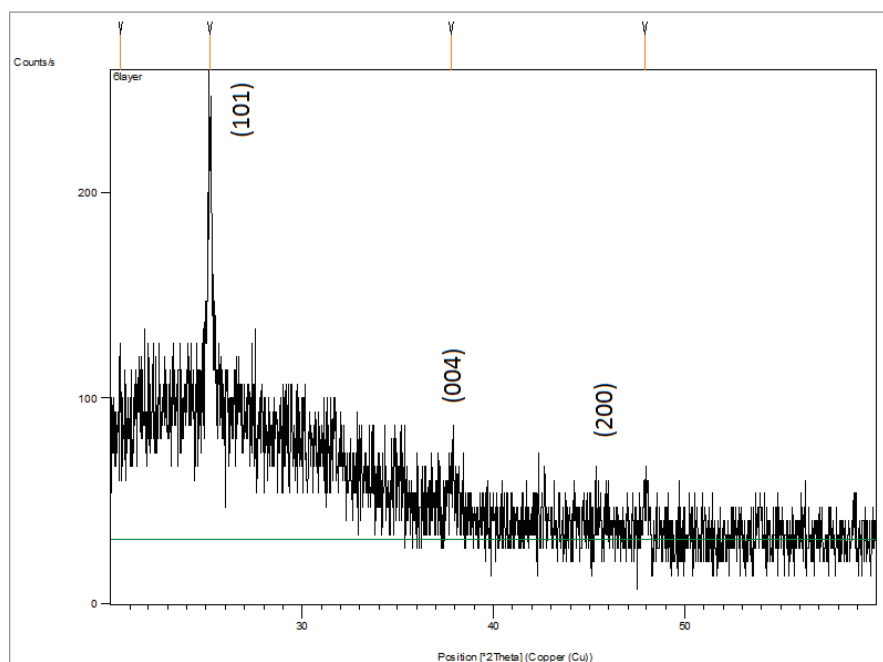


Fig.2 Figure 1. X-ray diffraction patterns of as prepared TiO<sub>2</sub> thin film. And take it on (X ' Pert PrMPD- Philips (Nether land) XRD with Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm) source.

Table.1. XRD Data of TiO<sub>2</sub> thin film

Pos. [°2Th.]	Theta	theta (rad)	cos(theta)	sin(theta)	FWHM [°2Th.]	FWHM (2theta(radius))	$\beta\cos(\theta)$	D(nm)	d-spacing[Å <sup>o</sup> ]
25.1958	12.59	0.2198	0.9759	0.2181	0.1574	0.00274	0.00268	51.696	3.534
37.8183	18.90	0.3300	0.946	0.3240	0.4723	0.00824	0.00779	17.773	2.378
47.9047	23.95	0.418	0.9138	0.4059	0.576	0.01005	0.00918	15.085	1.897

### 3.1.2 SEM studies

Fig.3.a shows a SEM image of the TiO<sub>2</sub> sample deposited at Ts = 450°C which is confirmed by the anatase crystalline structure. From this micrograph, it is possible to observe that as-deposited material consists of Porousstructures of agglomerated platelets of TiO<sub>2</sub> radially arranged [40]. To the best on our knowledge, this is the first time that such fascinating nanostructures of anatase have been reported hitherto. From the XRD pattern, it is possible to conclude that these TiO<sub>2</sub>nanoplatelets structures grow preferentially along the (101) planes and provide reactive edge sites to the Porous structures. We believe these particles could display enhanced sensing capabilities due to the large amount of edges within each platelet[20].

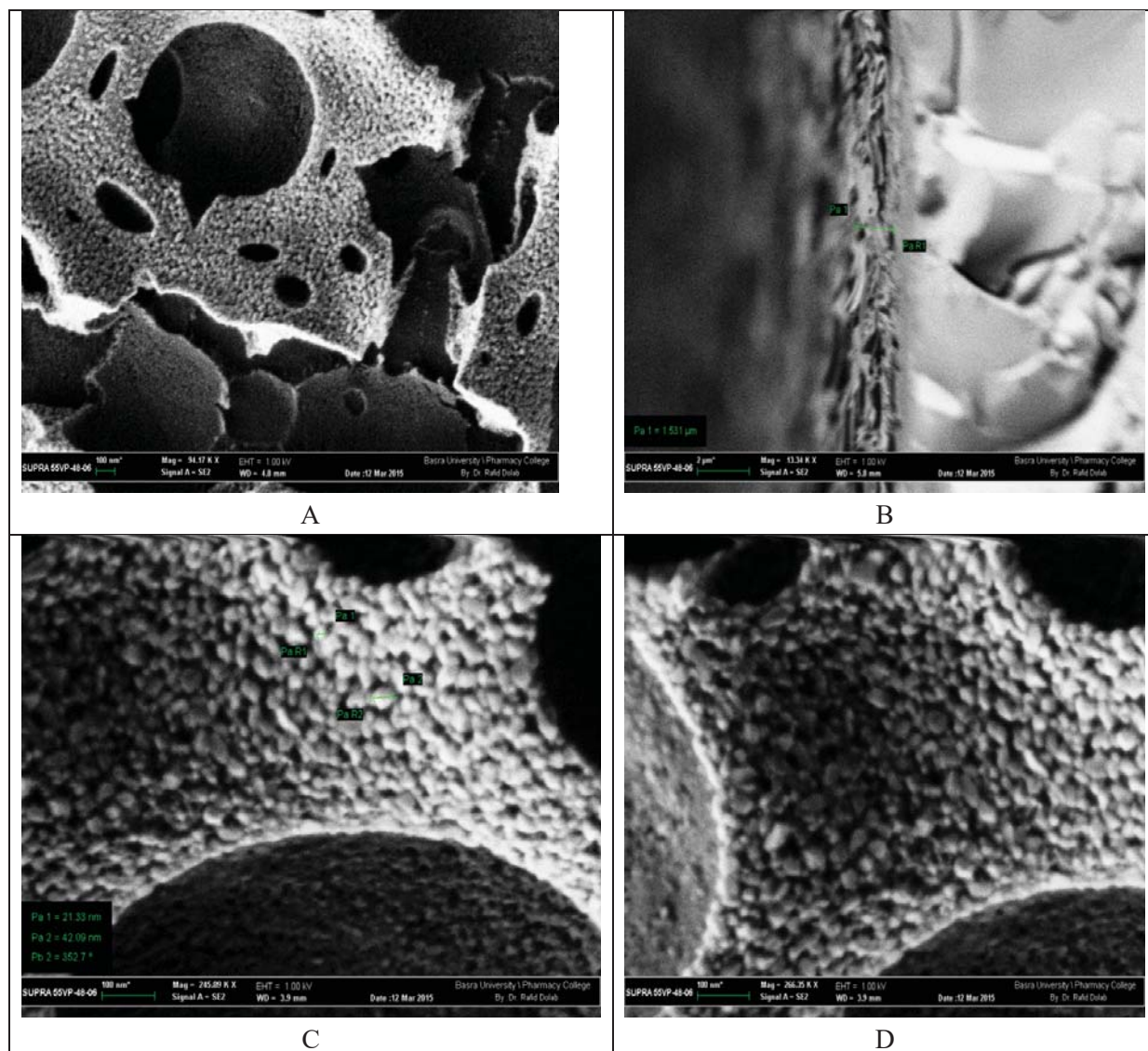
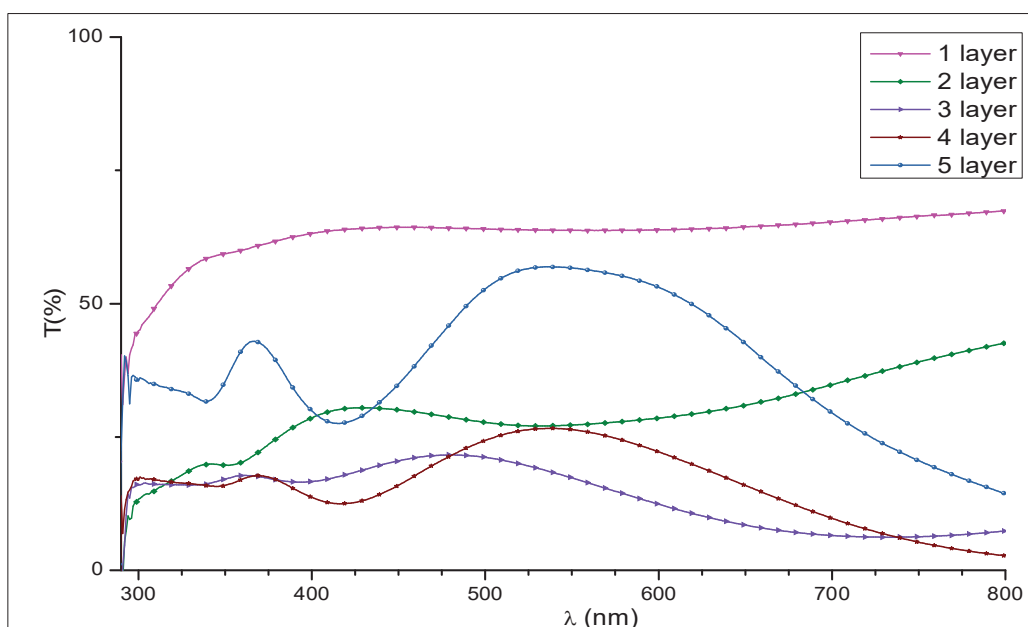


Fig.3 Images of rutile phase. (a) SEM image of 1-layer of  $\text{TiO}_2$ Sol-Gel; (b) SEM image of 1-layer cross section of  $\text{TiO}_2$ Sol-Gel; (c) SEM image of 2-layer of  $\text{TiO}_2$ Sol-Geland (d) SEM image of 2-layer of  $\text{TiO}_2$ Sol-Gel.

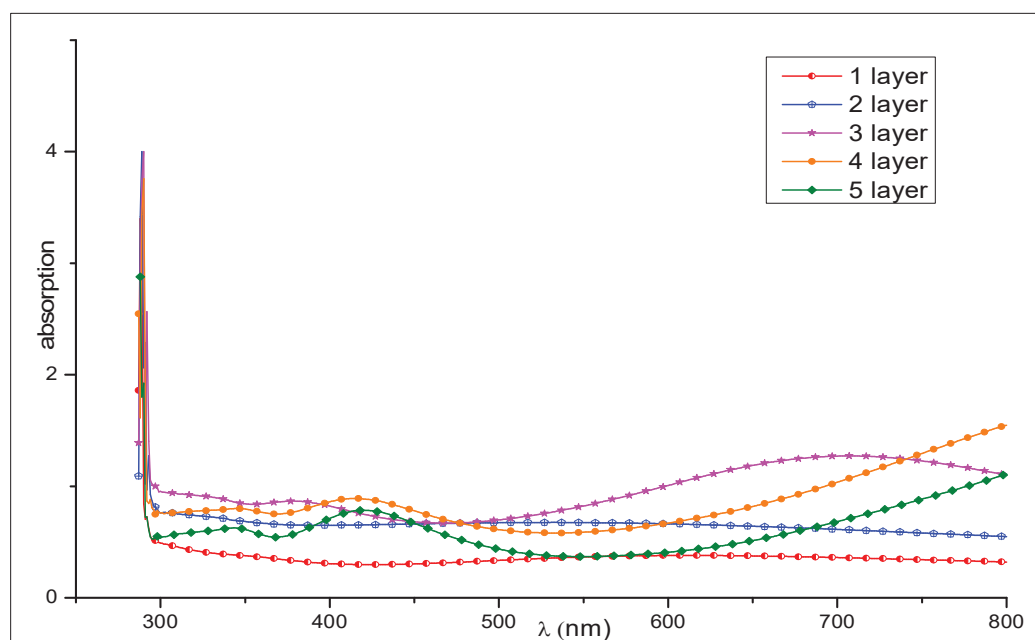
### 3.2 Optical Properties

Transmittance spectra of the coatings annealed at multilayer in the wavelength region from 250 to 800 nm are presented in Fig.4. glasses were used as the substrate in these experiments to avoid the influence of the absorption edge of the substrate. As shown in Figure 3, the average transmittance of 400 °C annealed  $\text{TiO}_2$  coatings is about 60% in the visible region. It is observed also that the number of layer increases as the film thickness increases, Besides, the maximum values of the transmittance decreased with increasing the film thickness as seen in Fig.4, the optical properties were studied using aUV-VIS-NIRspectrophotometer shimazdu 1800.

It can be attributed to the densification and the crystalline transformation that increase the refractive index of the TiO<sub>2</sub> coatings. Then the refractive index has been determined to see the direct effect of densification and crystalline structure. The results of reflectance verify the transmittance one as shown in Fig.4,



**Fig. 4. transmittance spectra of TiO<sub>2</sub> coating annealed at multilayer**



**Fig. 5. absorption spectra of TiO<sub>2</sub> coating annealed at multilayer**

The absorption coefficient ( $\alpha$ ) at frequency ( $\nu$ ) of radiation was calculated using

the formula [41]

$$\alpha(\nu) = 2.303 \frac{A}{d} \dots\dots\dots(3)$$

where d is the film thickness and A is the optical absorbance. Also,  $\alpha(\nu)$  is related to the optical transmission (T) and reflection (R) as follows [42]:

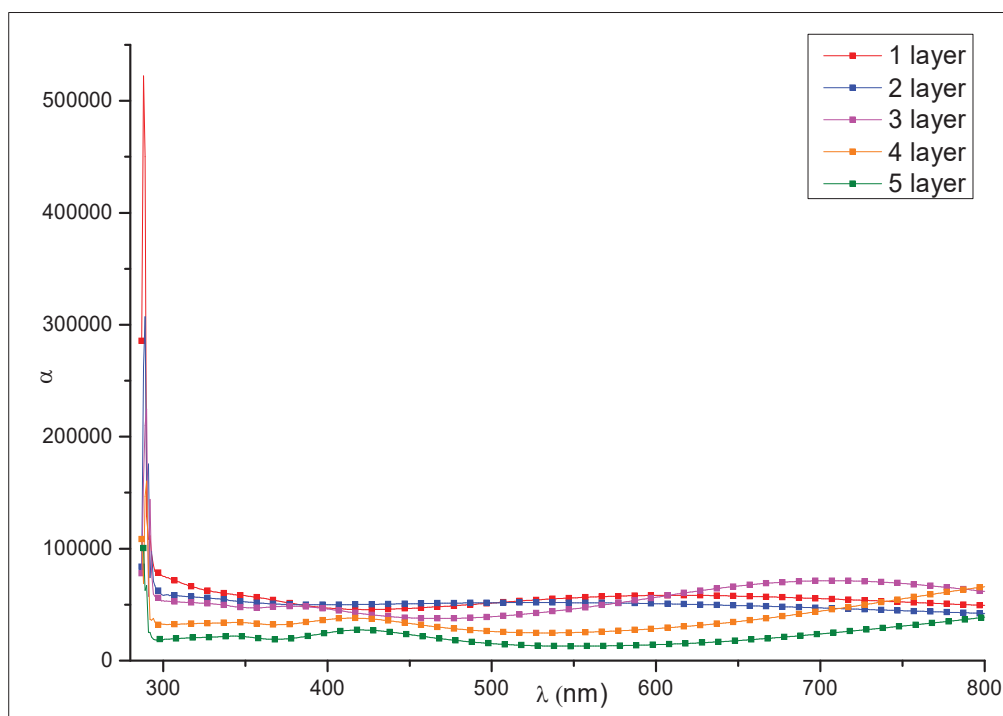
where k is the extinction coefficient which is related to the absorption coefficient and the wavelength as[41]

$$K = \alpha \frac{\lambda}{4\pi} \dots\dots\dots(4)$$

and the refractive index was obtained from the equation [41]

$$n = \frac{1+R^{1/2}}{1-R^{1/2}} \dots\dots\dots(5)$$

The calculated values of refractive index (n) and extinction coefficient (k) were plotted as a function of the wavelength as shown in Fig. 8 and Fig. 9.



**Fig. 6. The variation of absorption coefficient with wavelength**

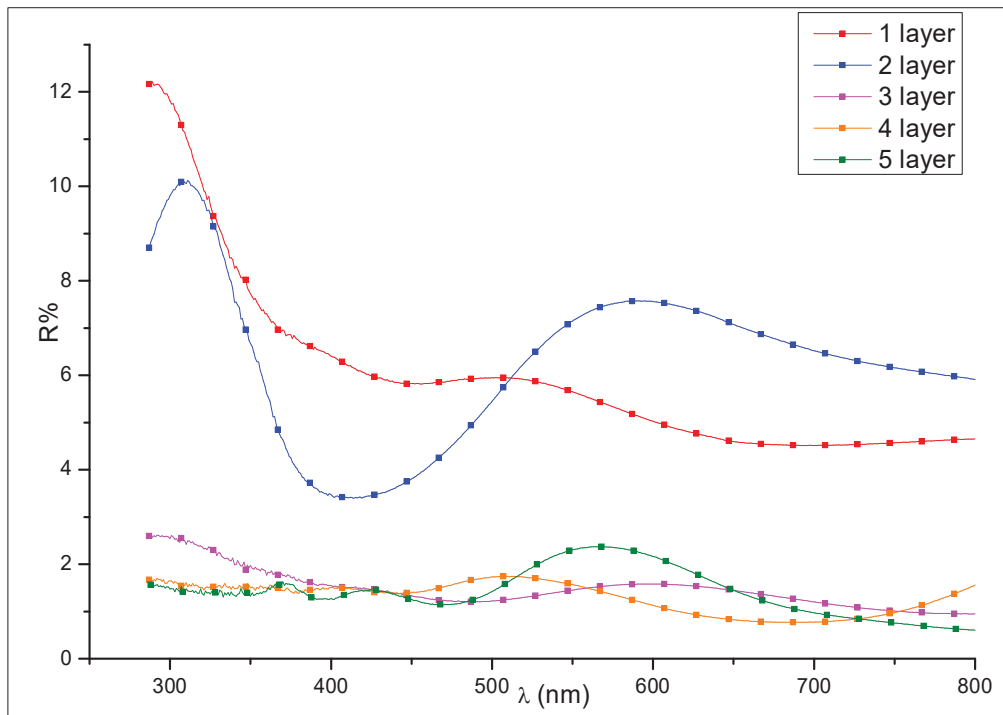


Fig. 7. The variation of Reflection index with wavelength

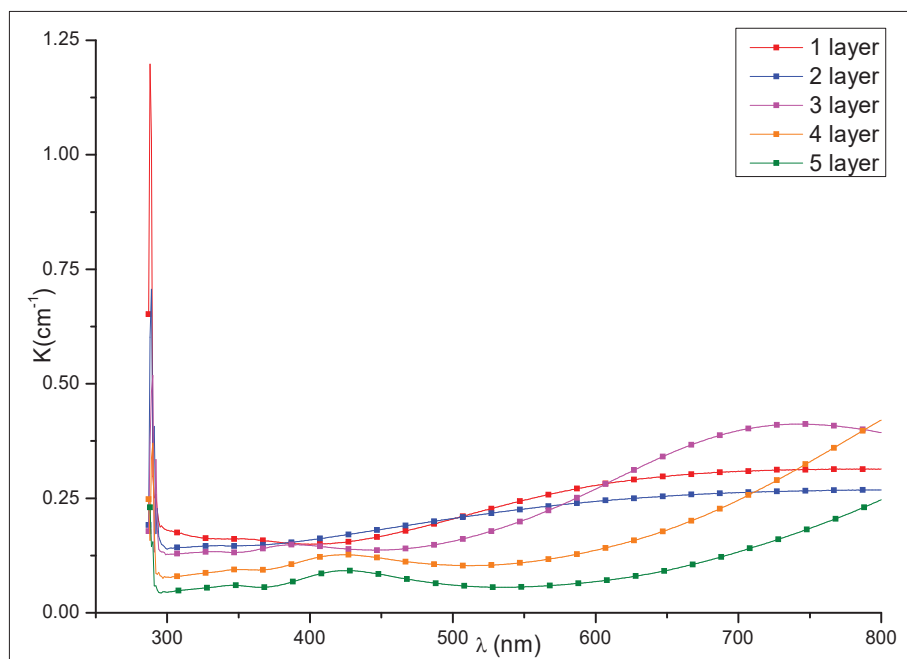
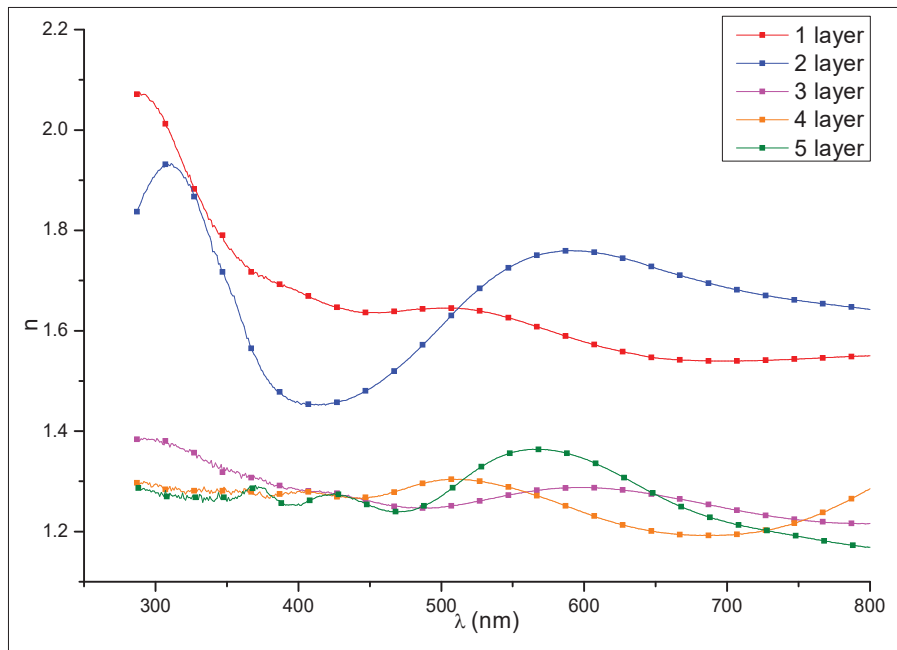


Fig. 8 The variation of extinction coefficient with wavelength





**Fig. 9. The variation of refractive index with wavelength**

We also calculated the imaginary and real parts of the dielectric constant are expressed as [43].

$$\epsilon_r = n^2 - k^2 \dots\dots\dots(6)$$

$$\epsilon_i = 2nk \dots\dots\dots(7)$$

The real ( $\epsilon_r$ ) and imaginary ( $\epsilon_i$ ) parts of the dielectric constant of the films are respectively shown in Fig.10 and fig.11. It is seen that both  $\epsilon_r$  and  $\epsilon_i$  decreases with increasing wavelength. The real and imaginary parts follow the same pattern and it is seen that the values of the real part are higher than the imaginary parts. Increasing indium content causes important changes in these optical constants.

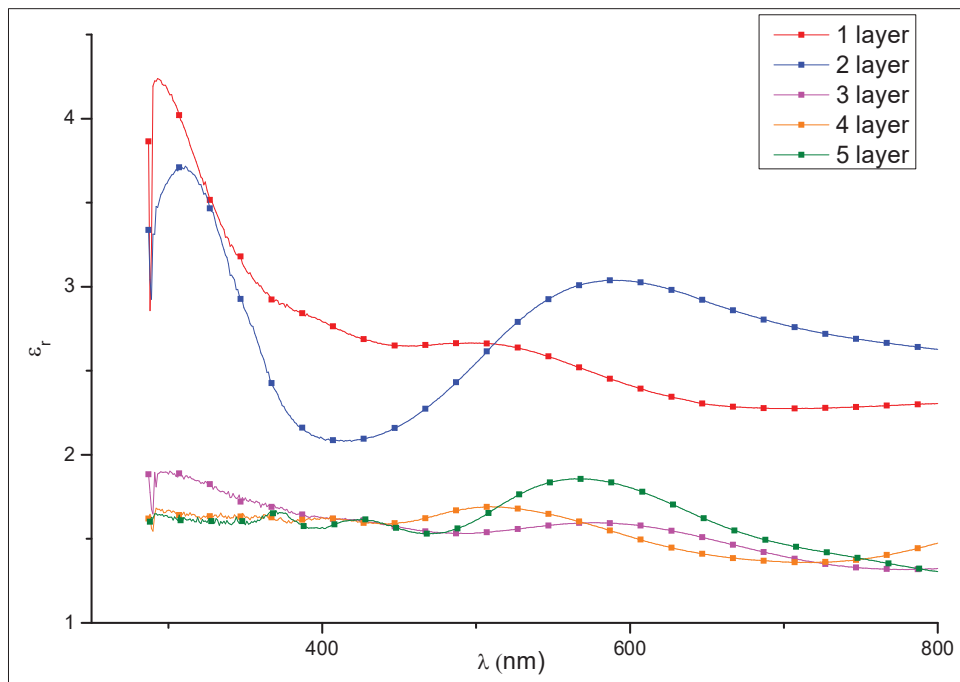


Fig.10. The real part of the dielectric constant the prepared  $\text{TiO}_2$  thin film

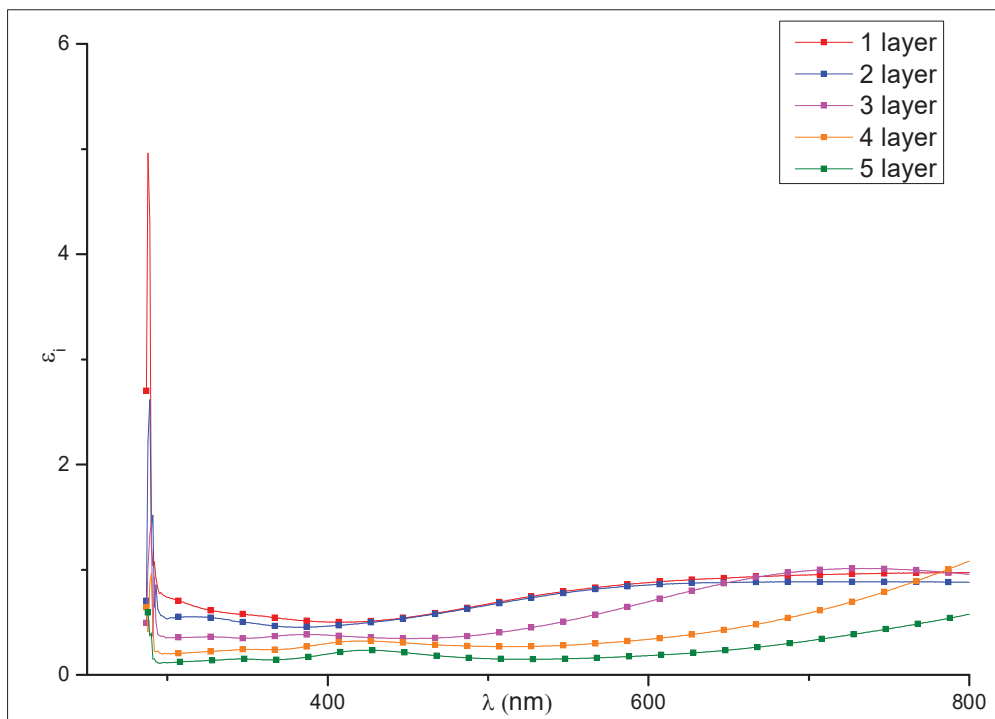


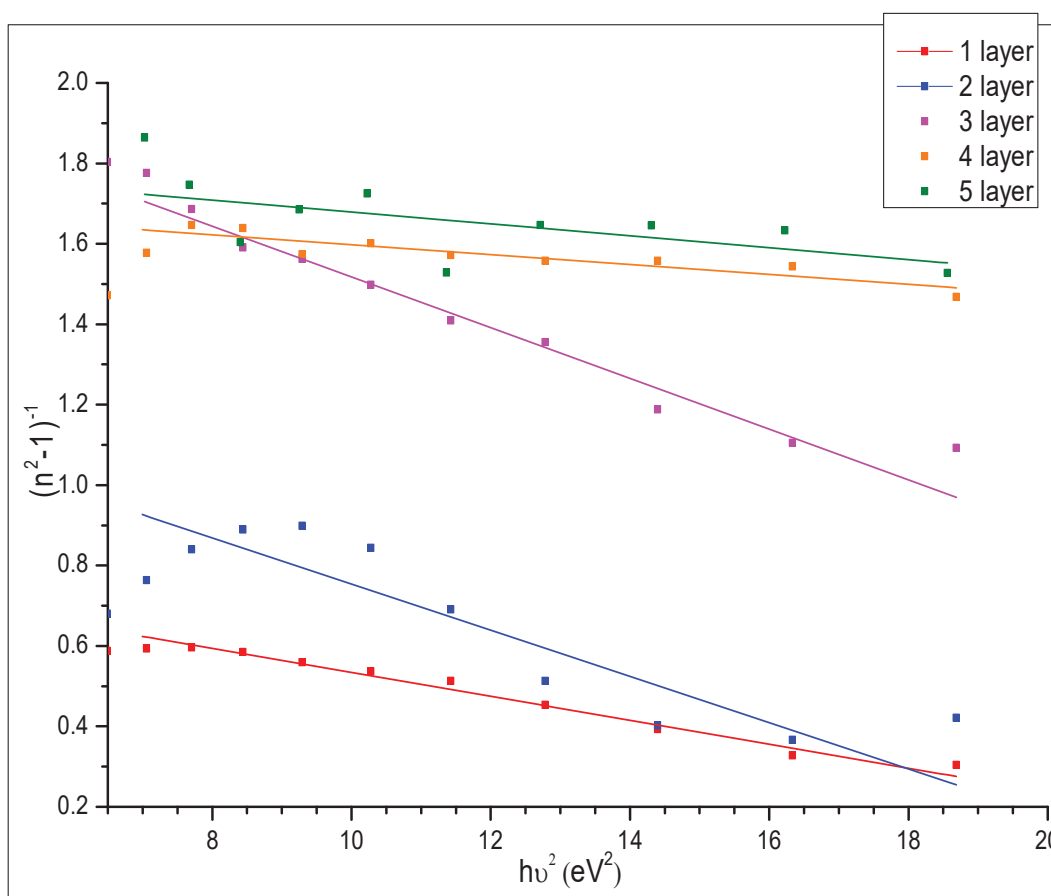
Fig.11. The imaginary part of the dielectric constant the prepared  $\text{TiO}_2$  thin film

The dispersion data of the refractive index can be calculated by single-oscillator method Which developed by Wemple and DiDomenico [44]:

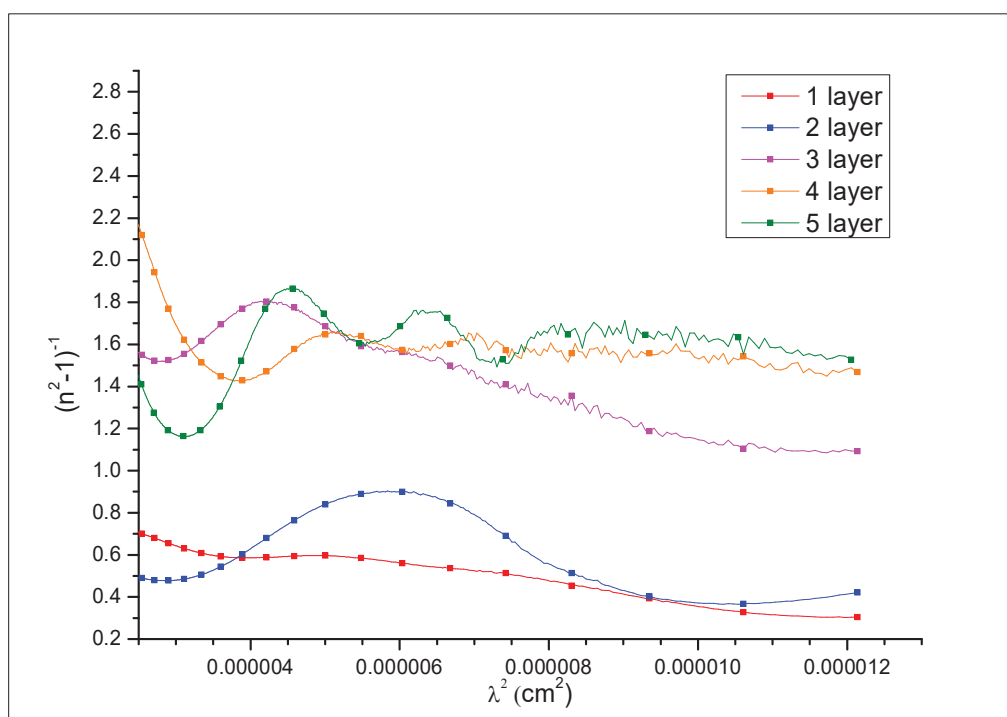
The single-oscillator parameters were calculated and discussed in terms of the Wemple–DiDomenico model. The dispersion parameters of various materials were investigated by using this model in the literature [45]– [47]. This model describes the dielectric response for transitions below the optical gap. It plays an important role in determining the behaviour of the refractive index. The dispersion data of the refractive index can be described by a single-oscillator model [48]:

$$(n - 1)^{-1} = \frac{E_0^2 - (hv)^2}{E_d E_0} \dots\dots\dots(8)$$

where  $E_0$  and  $E_d$  are single-oscillator constants.  $E_0$  is the single oscillator energy



**Fig.12. Plots of  $(n^2-1)^{-1}$  vs.  $(h\nu)^2$  for TiO<sub>2</sub> thin films of different thicknesses**



**Fig.13. Plots of  $(n^2-1)^{-1}$  vs.  $(\lambda)^2$  for  $TiO_2$  thin films of different thicknesses**

and  $E_d$  is the dispersion energy which is a measure of the strength of interband optical transitions. By plotting  $(n^2-1)^{-1}$  versus  $(h\nu)^2$  and fitting a straight line shown in Fig. 12,  $E_0$  and  $E_d$  are determined directly from the gradient,  $(E_0 E_d)^{-1}$  and the intercept  $(E_0/E_d)$ , on the vertical axis. The values of the single-oscillator parameters for the titanium dioxide  $TiO_2$  thin films are given in Table 2. The oscillator energy,  $E_0$  is an average energy gap as pointed out in many references [49]–[52].

The moments of the optical spectra  $M_{-1}$  and  $M_{-3}$  can be obtained from the relationship [53]:

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \dots\dots\dots(9)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \dots\dots\dots(10)$$

It is found that the calculated values of the moments  $M_{-1}$  increase with increasing the thickness of the films, whereas the moments  $M_{-3}$  decrease. and Table 2. is Review The  $M_{-1}$  and  $M_{-3}$  moments values of the optical spectra.

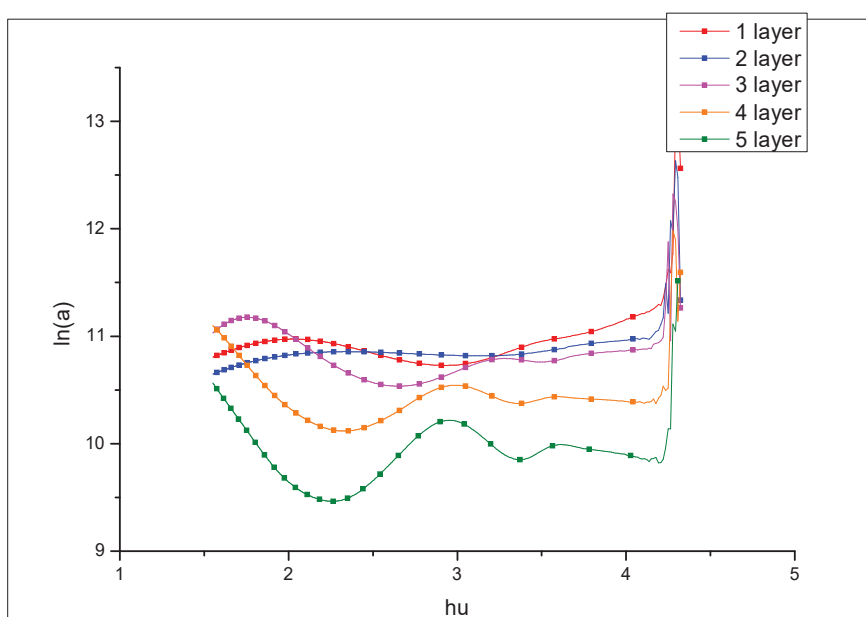
Beside that, it is well known that The absorption coefficient near the band edge show an exponential dependence with the photon energy [54]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right) \dots\dots\dots(11)$$

where  $E_U$  is Urbach energy which corresponds to the width of band tail and can be evaluated as the width of localized states,  $(\alpha)$  is a constant.

The  $E_U$  was calculated from the slope of Fig. (14) by using the relation:

$$E_U = \left(\frac{d(\ln(\alpha))}{d(h\nu)}\right)^{-1} \dots\dots\dots(12)$$



**Fig.14. Plots of Ln( $\alpha$ ) vs. ( $h\nu$ ) for TiO<sub>2</sub> thin films of different thicknesses**

**Table 2. The Urbach energies and the dispersion parameters for TiO<sub>2</sub> thinfilms.**

no. of the layer	Thickne ss ( $\mu\text{m}$ )	Slope	intercept	$E_u$ (ev)	$E_d$	$E_0$	$M_{-1}$	$M_{-3}$	F
1	1.5	0.039 7	0.8	1.7206	5.60490 2	4.4839	1.25	0.0621 7	25.131
2	3	0.057 4	1.3286	5.4110	3.61957 7	4.8089	0.7526 7	0.0325 4	17.406
3	4.1	0.035	1.92	6.0405	3.85758 4	7.4065 6	0.5208 3	0.0094 9	28.571
4	5.4	0.012 3	1.7212	12.095	6.86162 1	11.810 2	0.5809	0.0041 6	81.037
5	6.6	0.013 2	1.82687	3.7788	6.42987	11.746 5	0.5473	0.0039 6	75.528

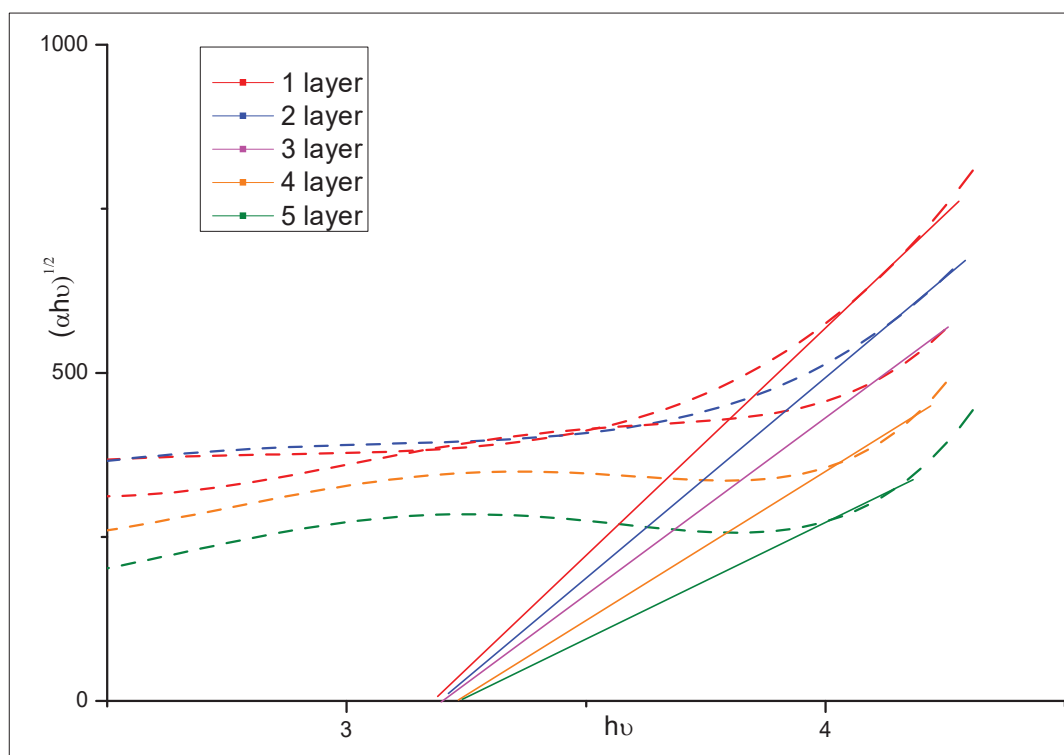
The optical band gap,  $E_g$ , can be determined from the experimental spectra of the absorption coefficient,  $\alpha$ , as a function of the photon energy  $h\nu$ , using the following equation[55]:

$$\alpha h\nu = (h\nu - E_g)^m \dots\dots\dots(13)$$

where  $m$  is equal to  $\frac{1}{2}$  and  $2$  for direct and indirect transitions, respectively, and  $A$  is a constant.

Fig. 15 shows the relation  $(\alpha h\nu)^{1/2}$  vs.  $(h\nu)$  for as-prepared  $\text{TiO}_2$  thin films with different thicknesses. The values of the allowed indirect optical energy gap  $E_g$  can be obtained from the plots of  $(\alpha h\nu)^{1/2}$  versus  $(h\nu)$  by extrapolating the linear portion of the plots of  $(\alpha h\nu)^{1/2}$  versus  $(h\nu)$  to  $\alpha=0.0$  as shown in Fig 3. The estimated values of the indirect optical energy gap were found to be independent on the film thickness where it had the same value 3.26 eV for all the considered film thickness. This value 3.26 eV of the indirect optical gap of the thin films under test is very close to the reported one 3.27 eV [56].

And Fig. 16 shows the relation  $(\alpha h\nu)^2$  vs.  $(h\nu)$  for as-prepared  $\text{TiO}_2$  thin films with different thicknesses. The values of the allowed direct optical energy gap  $E_g$  can be obtained from the plots of  $(\alpha h\nu)^2$  versus  $(h\nu)$  by extrapolating the linear portion of the plots of  $(\alpha h\nu)^2$  versus  $(h\nu)$  to  $\alpha=0.0$  as shown in Fig 3. The estimated values of the optical energy gap were found to be independent on the film thickness where it had the same value 3.56 eV for all the considered film thickness. This value 3.56 eV of the direct optical gap of the thin films under test is very close to the reported one 3.37 eV [57].



**Fig.15. Plots of  $(\alpha h\nu)^{0.5}$  vs.  $(h\nu)$  for  $\text{TiO}_2$  thin films of different thicknesses**

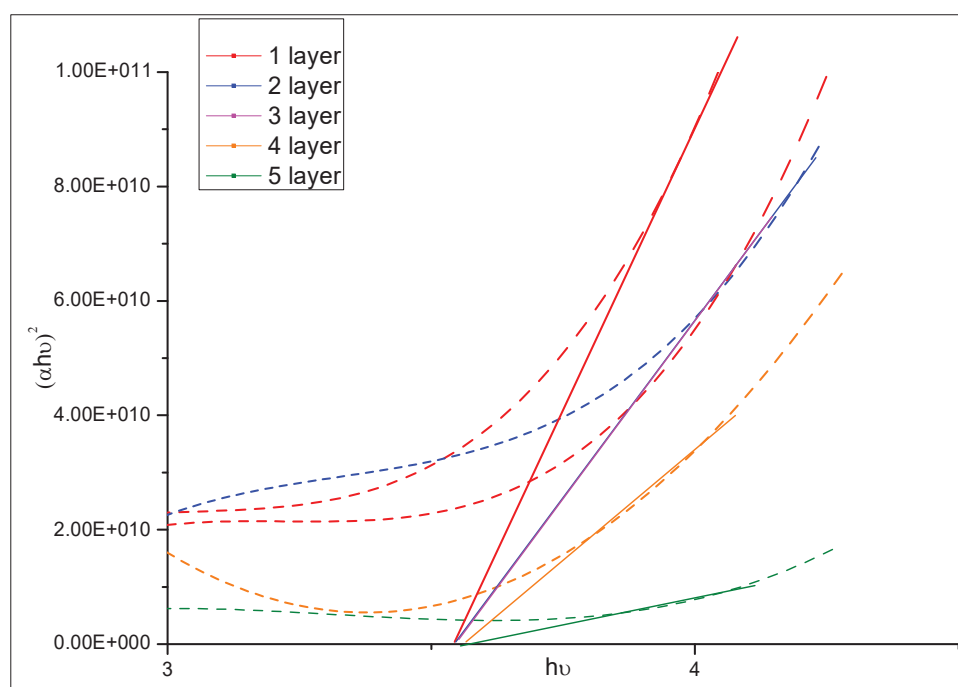


Fig.16. Plots of  $(\alpha h\nu)^2$  vs.  $(h\nu)$  for  $\text{TiO}_2$  thin films of different thicknesses

### 3.3 Conclusion

The optical properties of amorphous  $\text{TiO}_2$  thin films under test have shown that, changing the thickness of the films has not affected the optical energy gap and Urbach tails. The average value of the single oscillator energy has a value that is very close to that of optical energy gap.

The moments  $M_{-1}$  has shown an increase with number of layer from 1 layer to 5-layer nm, whereas, the moments  $M_{-3}$  showed a decreasing with increasing number of layer.

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