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Effect of Gamma Ray on the Optical Properties of TiO_2 and ZnO Thin Films

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ABSTRACT

In this work, the zinc oxide (ZnO) and dioxide titanium (TiO_2) thin film were prepared by using the method of spry pyrolsis chemical with different thickness on glass substrate at temperature of 60º C. Thees different thickness of the deposited films were measured by using mass approximations weighting different method. The thickness for Tio_2 films are (3.1, 0.24, 0.12)µm and for ZnO films (3.5, 4)µm. The samples coated have been irradiated by gamma ray to 21.5 kGy dose from Co-60 source. The optical properties such as the absorbance spectrum, transmittance, reflectance, and optical constant (absorption coefficient, extinction coefficient, refraction index and coefficient finesse with different thickness as function wave length of films but energy gap and urbach energy as function photon energy) were studied before and after irradiation dose. From experimental work show that the color of these films were changed after irradiated, at the result all optical properties spectra thin films changed with different thicknesses. The absorption**,** reflectance absorption coefficient, extinction coefficient, refractive index, coefficient finesse are increases after irradiation but the transmission, urbach energy and energy gap decreases after dose for all thicness of TiO_2 films. Whereas absorption and absorption coefficient, extinction coefficient increases after irradiation for thiknsss of ZnO thin films but reflectance, transmission, refractive index, coefficient finesse urbach energy and energy gap decreases after dose for Zno. These effect of optical properties may be due to change of structure properties for Tio2, Zno thin films after irradiated.

1. Introduction

Among these promising materials ZnO and TiO_2 are the most versatile ones, since their non-toxicity[1], stability and ease to prepare[2,3]. ZnO has been recently used in UV LEDS light emitting materials and in solar cell as transparent conductive oxide, the large scale uses of conductive transparent films for optoelectronic device and displays have led to the development of a variety of film preparation techniques [4]. TiO_2 thin films find a wide range of applications in various field like photo catalysis, gas sensing, antireflective and protective coatings, antibacterial and optical coatings, dielectric films for new generate on field effect transistors, ect. TiO_2 is photosensitive semiconductor, when it is illuminated with the light of energy higher than the ban gap, on inter-band transition can be induced and electron-hole pairs. TiO_2 can exist in three basic crystalline phase- anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic), and an amorphous phase. Thin films of ZnO and TiO_2 can be deposited by many methods, e.g chemical bath deposition, spray pyrolysis, RF magnetron sputtering[5][6]. In the last year emerged numerous from researcher attempted treatment and improvement properties of thin film. One of these evaluation in bulk materials films by use irradiation technique, when solid materials exposure to ionizing radiation (such as x-ray, gamma radiation, beta particles, alpha particles, ect.) produce change in the microstructure properties, which in turn affects the optical, electrical and physical properties of the solid material. The effects of the gamma radiation dosimeter. Naturally, a deep understanding of the effects of gamma irradiation on different physical properties of these films is a quite vital from the viewpoint of the physics of the metal oxides and polymers as well as from design and development of novel radiation sensors and dosimeters [7].

2. Literature Review

In the last few year a great deal of work has been done on the effect of the irradiation by gamma ray on the optical properties for thin films.

The some work has been done on the effect of gamma irradiation on the structural and optical properties of ZnO thin films by N. Al-Hamdani, et al. [8]. At Physics Department, Education College, Al-Mustansiriyah University, Baghdad-Iraq in February 2014. His work describes effect of gamma ray investigation on optical properties, ZnO thin films were exposed to gamma ray result from Cs137 source with active radiation (0.36µci) and gamma emission energy is 0.662MeV for 21 day at room temperature, the absorption and transmission spectra recorded in the UV/VIS/NIR region for the as deposited and irradiated films, the band gap is decreased and absorption coefficient (α) is increased after irradiation. Optical constants (refractive index, extinction coefficient, dielectric constant) the films are affected by irradiation.

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Also another work has been done by S. Al-Sofiany, H .Hassan, A.H. Ashour and M. Abd El-Raheem on the study of γ-rays enhanced changes of the ZnO:Al thin film structure and optical properties at Physics Department, Faculty of Science, Taif University, Al-Hawiah, Taif, Saudi Arabia in 2014 [9]. Has work investigations were also done for the effect of the heat treatment of the samples for comparison with gamma irradiation. The samples were irradiated by three gradual gamma rays doses using CO-60 source. Optical properties of the investigated samples were measured using UV-Vis spectrometer. The transmission spectra of irradiated samples were compared with that of un-irradiated ones for comparison. In general, it was found that the optical parameters of the samples decrease in the transmittance after irradiation and the calculated optical energy gap was decreased.

Also work has been done on the effect of gamma-ray on structural and optical properties of cadmium sulfide (CdS) thin films by F. Antar at Physics Department Education College for Pure Sciences, Anbar University ,Iraq in September 2014. Has work describes the effect of gamma radiation from Co-60 by with ray dose 20 Mrad on the optical properties of the CdS thin films was investigated, The optical transmittance measurements were recorded by using a double beam spectrophotometer, the result was found the transmittance and optical band gap energies of the prepared CdS thin films decreases after irradiation[10].

Another work has been done by M. Hassouni, K. Mishjil, S. Chiad and N. Habubi at Physics Department, College of Education, Al_Mustansiriyah University, Baghdad, Iraq in 2013, on the Effect of gamma irradiation on the optical properties of Mg doped Cdthin films deposited by spray pyrolysis [11]. Has work The effect of γ-ray irradiation on the optical properties has been investigated, Films were irradiated by gamma ray form Cs-137 (0.4.9 μCi) for 30 days . The absorption coefficient for the CdO films increased after irradiation and the absorption coefficient for the (CdO : 9 % Mg) films decrease after irradiation and can conclude that γ–ray irradiation was effecting all the parameters such as (reflectance, extinction coefficient, refractive index, real and imaginary parts of the dielectric constant and the electrical conductivity) under investigation.

3. Theoretical Background

The absorbance spectrum (A) results from the loss of energy resulting from interaction between the light and the charged contained in the material if the drop beam intensity I_0 on the film, hence transmittance beam is the intensity can be integrated to obtain Beer's law

$$I_{(z)} = I_{\circ} e^{-\propto t} \qquad (1)$$

Where I_0 is the optical intensity incident, I(z) incident at position z.

transmissivity (T) is defined likewise as the ratio of the transmitted power to the incident power give by

$$T = e^{-2.303} \qquad (2)$$

reflectivity is usually given symbol (R) and is defined as the ratio of the reflected power to the power incident on the surface give by

$$R = 1 - A - T \qquad (3)$$

The absorption of the light an optical medium is quantified by its absorption coefficient ($\propto$) give by

$$\propto = \frac{2.303A}{t} \qquad (4)$$

The extinction coefficient(K) given by equation.

$$K = \frac{\propto\lambda}{4\pi} \qquad (5)$$

The propagation of the beam through a transparent medium is described by the refraction index (n) according to [4][5].

$$n= \sqrt{\frac{(1+R)^2}{(1-R)^2} - \sqrt{K^2+1} + \frac{1+R}{1-R}} \qquad (6)$$

The parameter F is called the coefficien finesse, the coefficient finesse is sensitive function of the reflection R the finesse F is the ratio the separation between transmittance peaks to the full width at hail minimum of the peaks give by [12].

$$F = \frac{4R}{(1-R)^2} \qquad (7)$$

The Urbach tail (Eu) is used to describe exponential dependence of the absorption coefficient at the optical absorption edge give by equation (7).

$$E_u = \left(\frac{In\propto}{h\upsilon}\right)^{-1} \qquad (8)$$

Optical energy gap(Eg)(8) For direct transition, the absorption coefficient relates to the photon energy as

$$(\propto h\upsilon)^2 = B(h\upsilon - Eg)^r \qquad (9)$$

4. Preparation Samples

The zinc oxide (ZnO) and dioxide titanium (TiO_2) thin film were prepared by using the method of spry pyrolsis chemical with different thickness on glass substrate at temperature of 60º C.

4.1. Preparation TiO_2 Samples

C-doped TiO_2 nanocrystals (C-doped) were prepared by partial oxidation [POX] of Tic. In atypical process 3.0 g titanium carbide Tic powder was loaded in a ceramic curible and then placed in the middle of muffle furnace which was open to the a atmosphere. after that Substrate preparation TiO_2 films were deposited on glass substrate was cut into (25.4x76.2)mm and (1-1.2)mm thick. The glass was then cleaned using detergent for one minutes because to eliminate the impurities residue at the glass substrate. Thin films deposited Powder C-TiO_2 was added in mixture of ethanol thin films TiO_2 have been prepared by chemical deposition (spray pyrolysis method). Design glass substrate on the heater, at 60 ^{0}C substrate temperature. Solution spray on the rules , adjusted solution quantity on substrate because to get most homogeneous film. sit film on the heater between 1-2 minutes.

4.2. Preparation ZnO Samples

Prepared using zinc acetate (ZAD) 0.1mg, dissolved in 300ml of ethanol in glass beaker. Then the solution was stirred for 60 min at 80 ^{0}C until became milky solution. Drop from 2-methoxyethnol (2-ME) was added to the solution as stabilizer to get a transparent solution. Substrate preparation zno films were deposited on glass substrate was cut into (25.4x76.2)mm and (1-1.2)mm thick. The glass was then cleaned using detergent for one minutes because to eliminate the impurities residue at the glass substrate. Thin films Zno have been prepared by chemical deposition (spray pyrolysis method). Design glass substrate on the heater, at 60 ^{0}C substrate temperature. Solution spray on the rules , adjusted solution quantity on substrate because to get most homogeneous film. sit film on the heater between 2-3 minutes.

Calculating the Thickness of thin films by the weight different method

The thickness was calculated by:

$$t = \frac{\Delta m}{A.\rho} \quad (10)$$

The mass (Δm) of the film has been measured by digital electronic balance before and after coating [7].

5. Determination of the Optical Properties

Absorption spectrum was determining by Uv-vis spectrophotometer over wavelength range (190-800)nm for TiO_2 and range(280-800)nm for ZnO films. After that absorption coefficient films were calculating by equation (4), the value of (∝) plays an important role to the limitation of the type of transition, from the some figures appears the value of the absorption coefficient up than ((⟦10⟧^4) ⟦cm⟧^(-1)) so that the transition was direct transition(r=1/2), but the absorption coefficient has value less ((⟦10⟧^4) ⟦cm⟧^(-1)) means that indirect transition (r=2). Figures result were relationship curve between absorption coefficient and wave length. measured transmittance (T) and reflectance(R) by using equations (2),(3) respectively, all films were describing the absorption of light as it travels thought the material (extinction coefficient) was calculating by relationship(5).The refractive index (n) was determining from the (R)and (K) by using the relation(6) then it were measuring sharply cilium interference(airy function or finesses coefficient (F)) by equation (7).calculated urbach energy (E_u) of through relation (8) films were calculating energy minimal for needed electron cause transition from valance band to conduct band (energy gap Eg),the optical energy gap value could be determined using equation (9), we a plotted curve between (∝hυ)^(2)versus hυ the determined Eg by extrapolating the linear portion of the curve to zero absorption (the straight portion to the energy axis at(∝hυ)^(2)=0). Measurements were carrying at before and after irradiation of the sample with different thickness by gamma ray from CO^{6o} source with radiation does 21.5 kGy for 21 hours at room temperature.

6. Result and Discussion

Table 1. shows that different thickness for the samples TiO_2, and ZnO which were measured by using mass approximations weighting different method.

Table1. Thickness of thin films samples.

Samples	Thickness (µm)
TiO_2, sample (a)	3.1
TiO_2, sample (b)	0.24
TiO_3, sample (c)	0.12
ZnO, sample(a)	3.5
ZnO, sample(b)	4

The absorption (A) spectra of TiO_2 films and ZnO films with different thickness before and after irradiation were shown in figure1.and figure2. The absorbance was increase as the wave length decrease, but decrease as the thickness increase of TiO_2 films and ZnO films that due to Beer's law.

From figure.1 and figure.2 it clear that the value of (A) for irradiation samples was upper than without irradiation samples. This increasing may be due to increase the number of charge carries, as increase absorption possibility when increasing concentration charges free carries into matter after irradiation by gamma rays. and also show that the lambda cut off for TiO_2 and ZnO films shifted toward long wave length UV region.

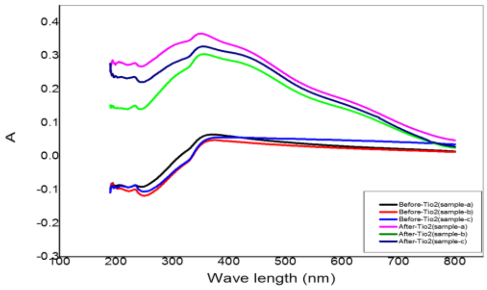

Figure 1. absorbance spectrum Tio2 films before and after dose.

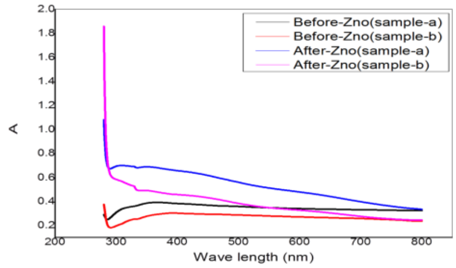

Figure 2. Absorbance spectrum ZnO films before and after dose.

The optical transmittance (T) was calculated for the prepared samples, the transmittance spectra of Tio_2 films and ZnO films with different thickness before and after irradiation were shown figure3 and figure4 respectivly, they were observed that the transmittance of TiO_2 and ZnO films samples were decrease after iradiadition by dose of gamma rays. The dose of gamma rays may be cause increase in the grain size of these films or formation of color centers in the film which cause more darkness in comparison with the unirradiation

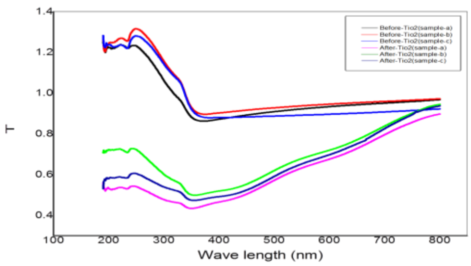

Figure 3. Transmittance spectrum TiO_2 films before and after dose.

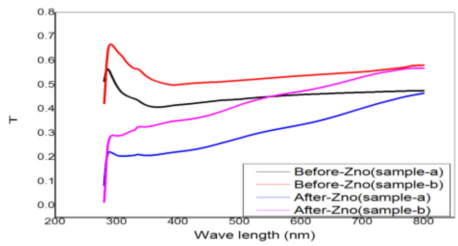

Figure 4. transmittance spectrum TiO_2 films before and after dose

Figure 5. show that the optical behavior reflectance(R) increases when the TiO_2 was irradiated with gamma dose. Whereas ZnO prepared in the form of the display of the reflection spectrum of the oscillation in the between the decrease and non-effect irradiation that shown in figure 6 and figure 5 respectively.

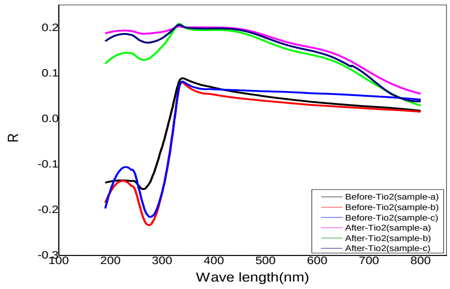

Figure 5. Reflectance spectrum Tio2 films before and after dose.

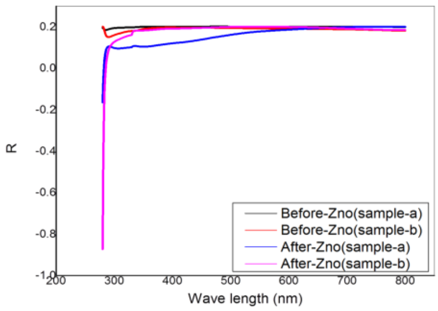

Figure 6. Reflectance spectrum Zno films before and after irradiation.

Figure 7 and figure 8, they show the dependence of the absorption coefficient (α) as function of the wave length for samples before and after irradiation. From these figures they clear that the absorption coefficient for the films increased after irradiation.

These increasing in absorption coefficient due to increasing in absorption which was described by equation (4) and figures 1and 2.

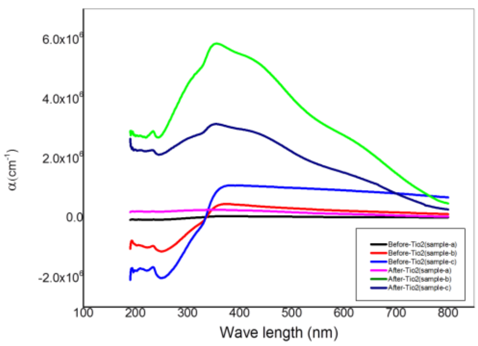

Figure 7. Absorption coefficient Tio2 films before and after dose.

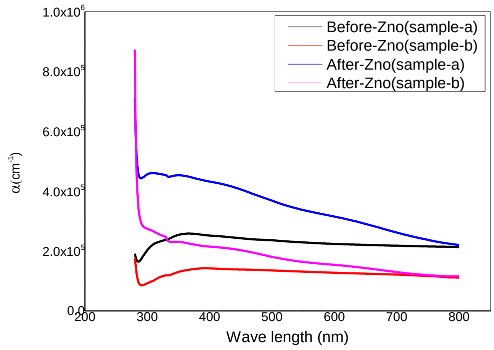

Figure 8. Absorption coefficient Zno films before and after dose.

From figure 9 and figure 10 they clear that excitation coefficient for different thicknees of TiO_2 and ZnO was incresed after irradiation samples by gamma rays. These icrease in excitation coefficient attributed to incresing in absorption coefficient, it clear in equation(5), figure 7 and figure 8.

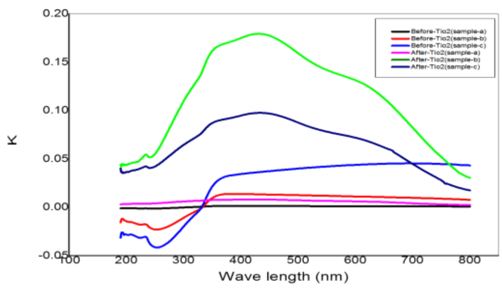

Figure 9. Extinction coefficient TiO_2 films before and after dose.

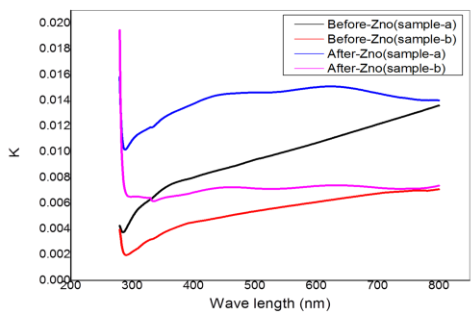

Figure 10. Extinction coefficient Zno films before and after dose.

The Refraction index for TiO_2 and ZnO films with different thicknees as function of the wave length which can be considered normal dispersion behavior. The refractive index after irradiation for TiO_2 films was increased after irradiated by gamma rays as shown in figure 11, whereas the refractive index for ZnO films was decreased after irradiation as show in figure 12. This variatition in the refractive index due gamma doe attributed to structal of mateial of TiO_2 and ZnO.

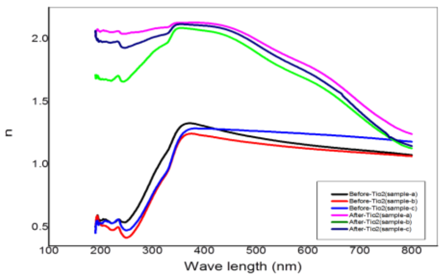

Figure 11. Refraction index TiO_2 films before and after dose.

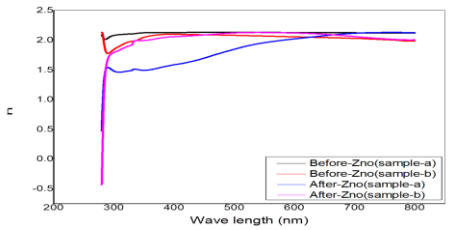

Figure 12. Refraction index Zno films before and after dose.

Figures 13 shows the variation of coefficient finesse (F) with the wave length of TiO_2 films. The coefficient finesses increases after irradiated. From figure 14 it clear that the variation of (F) with the wave length of ZnO films vibrated between the non-effected and decreased to the irradiation, same behavior as the reflection spectrum of Zno.

These of all changes in the optical constant cause due to the change in absorption and transmission of the films irradiated by gamma rays.

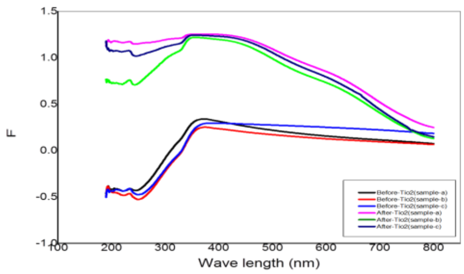

Figure 13. Coefficient finesse Tio2 films before and after dose.

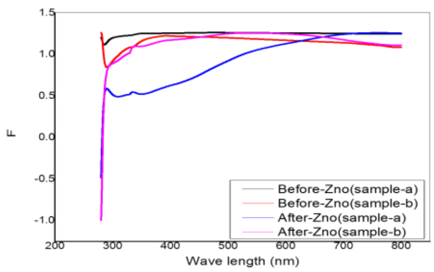

Figure 14. Coefficient finesse Zno films before and after dose.

Figure 15, 16 shows the variation of urbach energy V.s photon energy for TiO_2 and ZnO thin films, urbach energy values of for unirradiated films are less than those irradiated films.

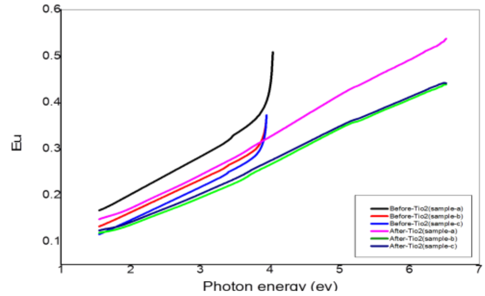

Figure 15. Urbach energy TiO_2 films before and after dose.

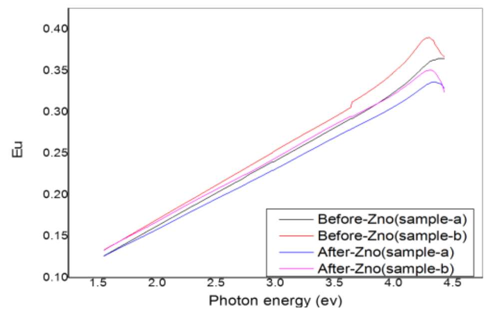

Figure 16. Urbach energy Zno films before and after dose.

The energy gap was plotted as function of photon energy show table 2. For TiO_2 and ZnO. It clear that the band gap was decreased after irradiation the for all different thickness films prepared. This decreased on Energy gap could may be attributed to formation of localized states due the structure defect. The increase of carriers localized state lead to decrease in transition probabilities into the extended state, thus reduce the band.

Table 2. Energy gap before and after irradiation.

Samples	Energy gap (ev)	
	Before	After
TiO_2 (a)	3.90	3.01
TiO_2 (b)	3.71	2.96
TiO_2 (c)	3.84	2.87
ZnO (a)	2.19	1.88
ZnO (b)	2.07	1.96

7. Conclusion

TiO2, Zno are synthesized through spry chemical evaporation technique at different thickness, sample thickness of the deposited films was measured using weighting different method. The UV-VIS spectrophotometer pattern shows that TiO2, ZnO thin film is absorption before and after irradiation by gamma ray.with different thickness films were changed of the optical properties.

The effect of gamma ray irradiation has been investigation on the table 3 from exsamples sample (c) for TiO2 and sample (a) for ZnO.

Table 3. Optical behavior TiO_2(sample c) and ZnO (sample –a) before and after irradiation in the visible region (540 nm).

Optical properties with 540(nm) wave length				
Properties	Tio_2, sample(c)		Zno, sample(a)	
	Before	After	Before	After
A	5%	18%	34%	51%
T	88%	64%	54%	30%
R	6%	16%	20%	17%
$\propto$	$\mathbf{9.5 \times 10^5}$	$\mathbf{1.8 \times 10^6}$	$\mathbf{2.2 \times 10^5}$	$\mathbf{3.3 \times 10^5}$
K	0.043	0.077	0.009	0.014
N	1.2	1.8	2.1	1.9
F	0.27	0.92	1.2	1
E_u	0.16	0.15	0.21	0.17

This effect of irradiation on thin films therefore improves the behavior of these films. It was found that irradiation led to the formation of localized levels within the energy gap, which led to decreases in transmission and energy gap, urbach energy, also increasing in absorption and absorption coefficient, extinction coefficient for all thin films. but when properties reflectance, refraction index and coefficient finesse for sample TiO_2, ZnO , there was fluctuation between the increase and decrease after irradiation, including the difference of radiation interaction of material for another substance.

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