Optical Constants of Fe_2O_3 and TiO_2:Fe_2O_3 Thin Films Prepared by Spray Pyrolysis Technique

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Abstract

In the present work, optical constants have been studied for pure and titanium dioxide (TiO_2) doped iron oxide (Fe_2O_3) thin films with different titanium dioxide dopant concentrations (1, 3 and 5 %) prepared by chemical spray pyrolysis technique on glass substrates. The optical properties of the films, which were prepared with thickness of (260±10) nm, have been determined by using Shimadzu spectrophotometer, the optical transmittance measurements in the spectral region from (500- 1100) nm. Direct energy gap for (Fe_2O_3) equal (2.01) eV, it increases with increasing of TiO_2%. The optical constants such as refractive index, extinction coefficient and dielectric constants have been calculated for all prepared films. The results show that all optical constants decreases with increasing of dopant ratios.

1. Introduction:

Over the last decades, semiconductor thin films have attracted considerable attention from the research community because of their wide use in the fabrication of solar cells and other optoelectronic devices. The most spectacular examples are found in microelectronics, which modern electronic devices are based on different thin film technologies combined with methods of microstructuring [1]. Iron oxides are compounds widespread in nature. This class of compounds has a rich palette of possible oxygen to iron ratios, as well as many different phases for each composition [2]. Iron compounds are widely used as pigment, in catalysts, in thermite, and one biological example is hemoglobin. The stability and non-toxic nature of the iron oxides makes them suitable to use as pigments and coatings. Iron oxide can exhibit several crystal structures and compositions but the most important ones are hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) [3]. Hematite, a-Fe_2O_3 has a corundum structure, with a hexagonal unit cell. The structure can be described as: hexagonal close packed (hcp) anion (O^{-2}) arrays with two thirds of the octahedral sites filled with a Fe^{+3} cation. It is the most stable iron oxide and often the end transformation of the oxide when annealed in air [2]. Thin films of iron oxide have attracted considerable attention in last few years due to their interesting magnetic properties. As far as hematite (α-Fe_2O_3) is concerned, it is one of the most stable iron oxide under ambient conditions. Owing to its various interesting properties such as n-type semiconducting behavior, band gap (E_g= 2.1 eV), low-cost synthesis, non-toxic nature, high resistant to corrosion. Because of the high electrical conductivity and high-sensitivity to gaseous environment, α-Fe_2O_3 also used as an efficient material for the fabrication of effective gas sensors [4].

Titanium dioxide TiO_2 material has been attracting a great deal of attention amongst researchers because of its unique properties such as high optical transparency, wide band gap energy, high refractive index, high dielectric constant, non-toxicity, abundance in nature and good chemical stability in undesirable environment conditions [5]. TiO_2 (titania) is a cheap and one of the most efficient semiconductor photocatalysts for extensive environmental applications because of its strong oxidizing power, high photochemical corrosive resistance and cost effectiveness. Due to these inherent properties, TiO_2 is the most suitable candidate for degradation and complete mineralization of toxic organic pollutants in water [6]. Titanium oxide is well known that TiO_2 exists in three crystalline structures: rutile, anatase and brookite. It has one stable phase, rutile and two metastable polymorph phases, brookite and anatase [7]. In this paper, the effect of doping with TiO_2 has been studied on optical constants of Fe_2O_3 thin films have been deposited by chemical spray pyrolysis before and after doping.

2. Experimental Details:

Fe_2O_3 solution is prepared by dissolving of ($FeCl_3.9H_2O$) [purity 97.0%, Sinopharm Chemical Reagent Co., Ltd], which is a powder of brown color, it's molecular weight is (162.20) $g.mol^{-1}$ in (200) mL distilled water at room temperature , a magnetic stirrer is incorporated for this purpose for about (25) minutes to facilitate the complete dissolution of the solute in the solvent. Also, TiO_2 be can prepared of titanium chloride ($TiCl_3$) [AR grade, 99.9% pure, Merck made, Germany], $TiCl_3$ is a liquid material, it's molecular weight is (154.26) $g.mol^{-1}$.

The dissolving weight (W_t) of the above materials respectively were determined by using the following equation [8]:

$$M = (W_t / M_{wt}) \times (1000 / V) \ldots\ldots\ldots\ldots (1)$$

Where: M: is the molar concentration, which taken in this work equaled to 0.2M, M_{wt}: molecular weight, V: volume of distilled water and W_t: weight of powder material.

The TiO_2: Fe_2O_3 ratios calculated on a volume percent (%) used in the starting solution were 1, 3 and 5 %. No additional additives or complexing agent is required to form the precursor solution. The precursor solution was sprayed onto the preheated glass substrates of [(7.5×2.5× 0.1) cm^3] size with substrate temperature of 450 ^oC. While varying the doping percentage, other preparative parameters such as solution percentage (0.2 M), time of deposition is (4s) for each (1min). Restart spraying (20) times for each sample until the desired thickness of thin films is reached. The nozzle-to-substrate distance (30 cm) were kept constant for all experiments.

3. Results and Discussion:

Optical absorption spectra depends on the chemical composition, crystal structure, energy of the incident photon, film thickness, and film surface morphology. Figure (1) displays the variation of absorbance spectra with wavelength from (500 to 1100) nm of the pure Fe_2O_3 and TiO_2:Fe_2O_3 thin films. It appears that α-Fe_2O_3 thin film has high absorbance in the visible region, indicating its applicability as an absorbing material [9]. From the plots, it can be justified that all films have a strong absorption at wavelength less than (640) nm, then the absorbance decreases with the increasing of wavelength. This attributed to the fact that at high wavelength the incident photons don’t have enough energy to interact with atoms, the photon will transmit. When the wavelength decreases, the interaction between incident photon and material will occur, and then the absorbance will increase [10]. It is also noticeable that the absorbance decreases with increasing of TiO_2 ratio. This confirms titanium atoms entry within the crystal structure of the prepared film.

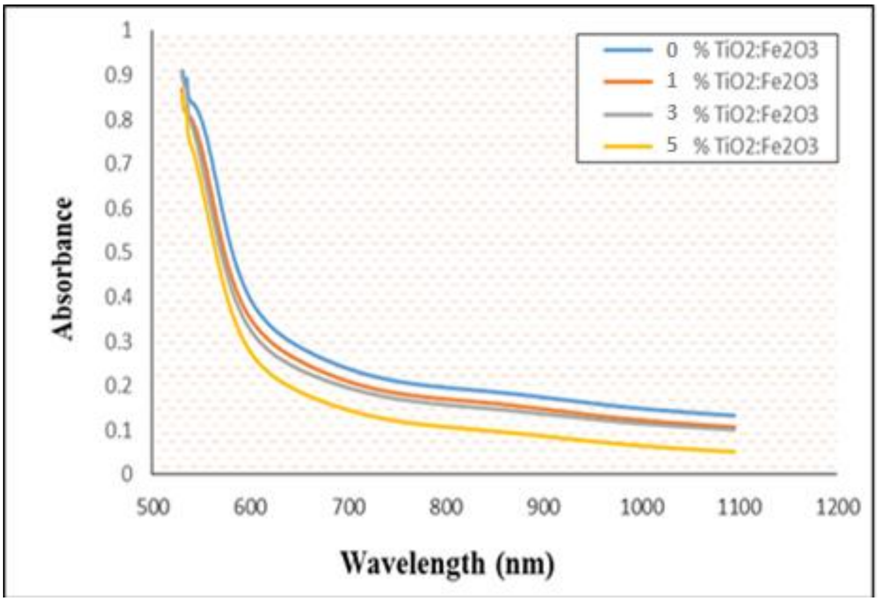

Figure (1): Absorbance spectrum as a function of wavelength for pure and doped Fe_2O_3 thin films.

The transmittance of the Fe_2O_3 thin films deposited with different TiO_2 concentration is calculated by using equation (2) [11].

$$T = \exp[-2.303A] \quad \ldots\ldots\ldots\ldots\ldots (2)$$

From Figure (2), the transmittance spectrum of all deposited thin films increases with the increasing of wavelength (λ). On the other hand, the transmittance spectrum increases with the increasing concentration of TiO_2 and this is due to the decrease of the surface roughness promoting the decrease of the surface scattering of the light.

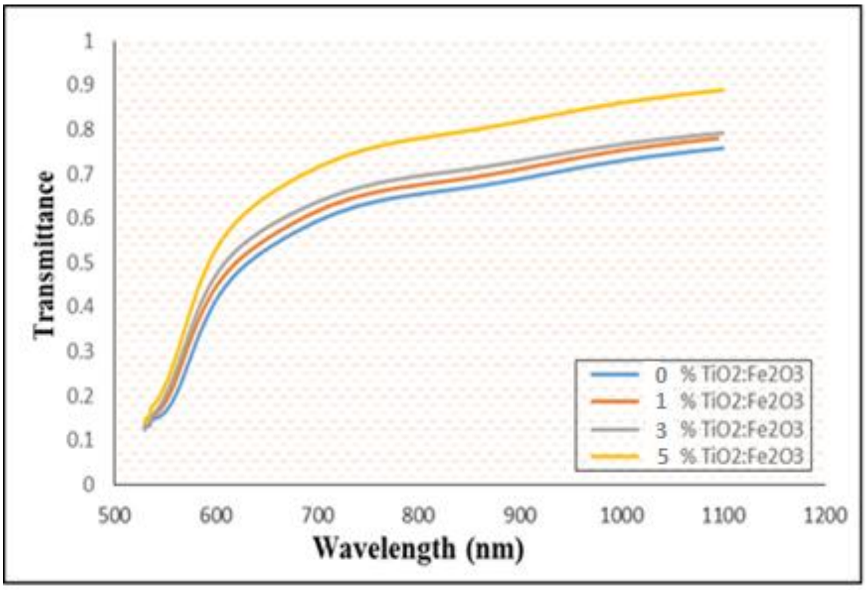

Figure (2): Transmittance spectrum as a function of wavelength for pure and doped Fe_2O_3 thin films.

Absorption coefficient is defined as a ratio decrement in flux of incident rays energy relative to the distance unit in the direction of incident wave diffusion. The absorption coefficient (α) for pure and doped Fe_2O_3 thin films deposited with different concentration of TiO_2 is calculated by using equation (3) [12].

$$\alpha = \frac{2.303 \times A}{t} \quad \ldots\ldots\ldots\ldots..(3)$$

Where: (A) is absorbance and (t) is the thickness of thin films.

From Figure (3), the absorption coefficient exhibits high values ($\alpha > 10^4\ cm^{-1}$) which means that there is a large probability of the direct transition [13], and then (α) decreases with the increasing of wavelength. It is observed that the absorption coefficient (α) decrease with increasing the concentration of TiO_2, and this is due to the increasing of energy gap with increasing of doping ratio.

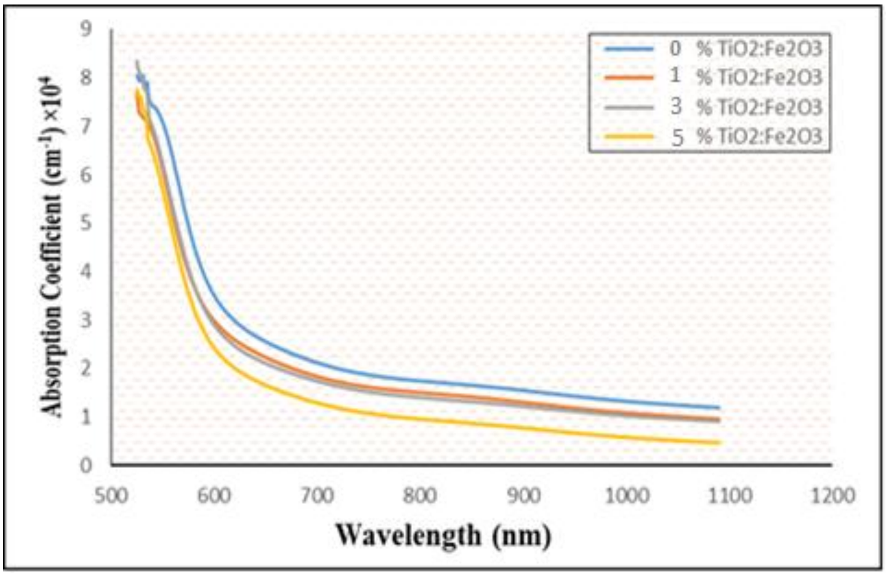

Figure (3): Absorption coefficients as a function of wavelength for pure and doped Fe_2O_3 thin films

The values of optical energy gap (Eg^{opt}) for pure and doped Fe_2O_3 thin films have been determined by drawing between $(\alpha h\nu)^2$ as a function of ($h\nu$) as shown in Figure (4), by extended straight line of the curve and intersection with x-axis that gives the value of the energy gap for prepared thin films. Figure (4) shows the energy gap of pure Fe_2O_3 is (2.1) eV. This result agrees with the result shown by [14]. Also, the energy gap is increased with increasing TiO_2 % because the decreasing of the density of state inside the optical gap, the increasing concentration of TiO_2 leads to decrease from the secondary levels, which lead to the contract tails region and this leads to expand in the optical energy gap that contributed to an increase of energy gap and then decreases the electronic transfer, the values of energy gap of prepared thin films shown in Table (1).

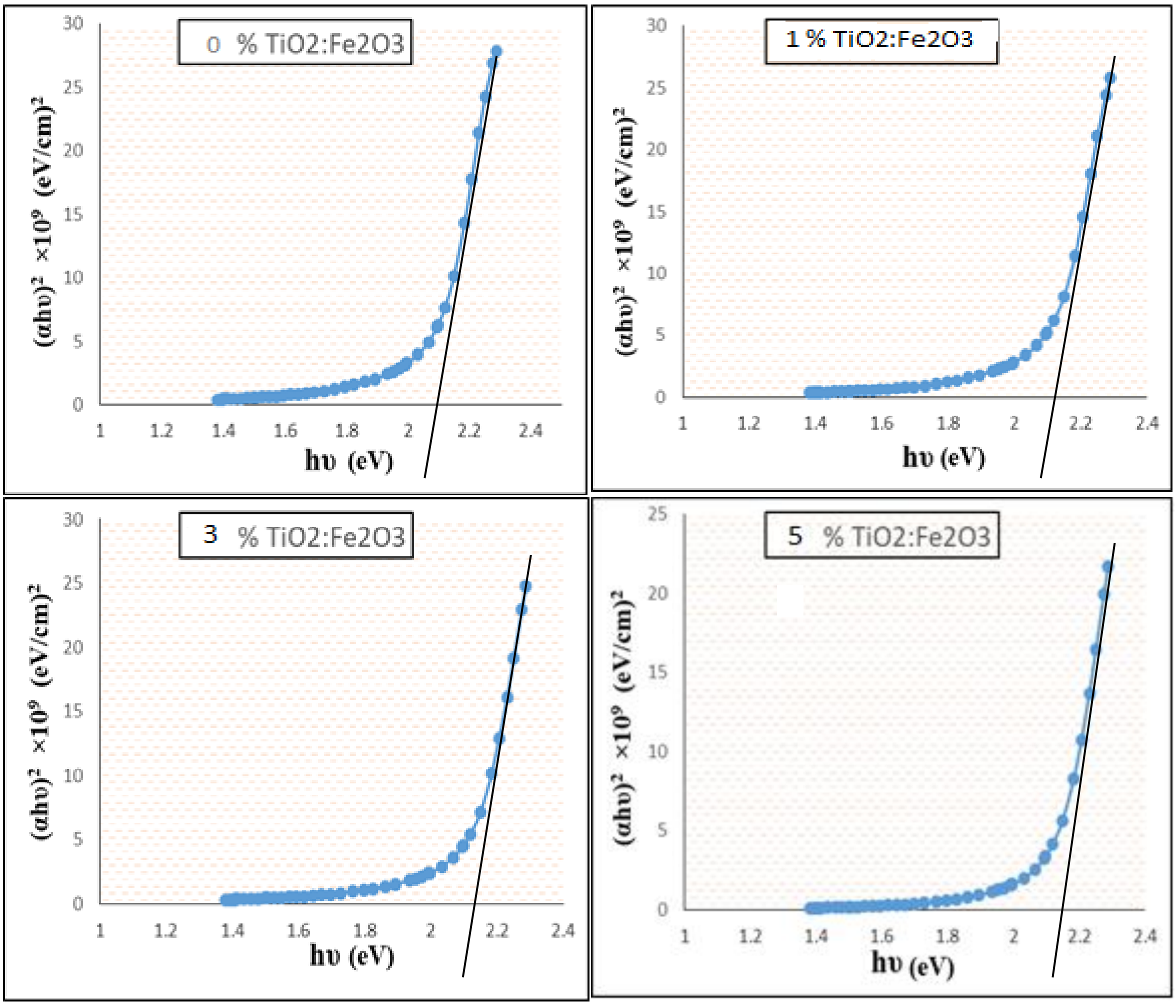

Figure (4): $(\alpha hv)^2$ **as a function of** h_V **for pure and doped** Fe_2O_3 **thin films.**

Table (1): Values of optical energy gap for pure and doped Fe_2O_3 **thin films.**

Sample	E_g **(eV)**
0 % TiO_2:Fe_2O_3	2.1
1 % TiO_2:Fe_2O_3	2.12
3 % TiO_2:Fe_2O_3	2.15
5 % TiO_2:Fe_2O_3	2.17

The refractive index (n) for pure and doped Fe_2O_3 thin films deposited with different concentration of TiO_2 is calculated by using equation (٤) [15].

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - (k^2+1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \quad \ldots\ldots\ldots (4)$$

Where: (R) is reflectance and (k) is extinction coefficient.

The variation of the refractive index versus wavelength in the range of (500–1100) nm for pure and doped Fe_2O_3 thin films at different TiO_2 % are shown in Figure (5). It can be noticed from this figure the refractive index (n) value decreases when concentration of TiO_2 increases. This behavior can be explained on the basic of that increases concentration of TiO_2 leads to make prepared samples less dense (decreasing the packing density) and the change in crystalline structure, which in turn increases propagation velocity of light through the sample which results decreasing of the refractive index (n) values [16].

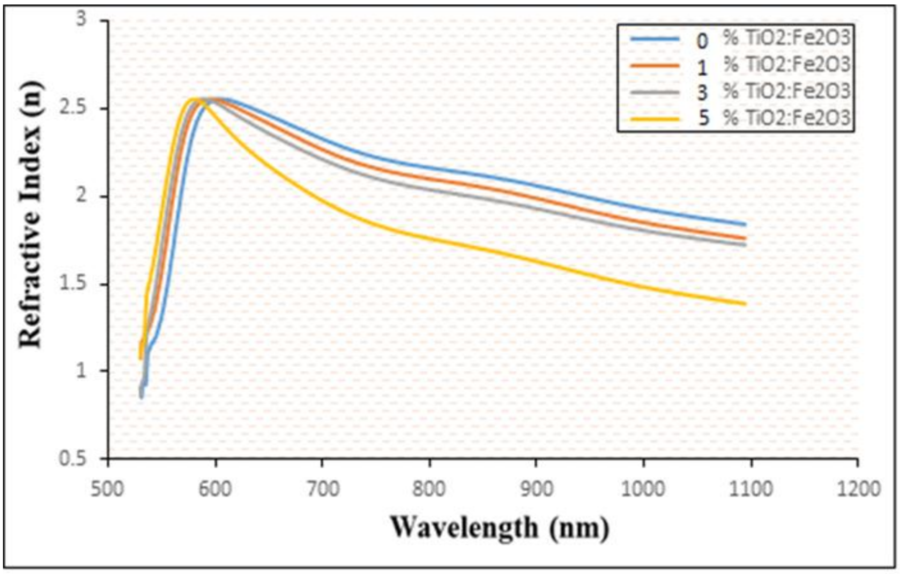

Figure (5): Variation of refractive index as a function of wavelength for pure and doped Fe_2O_3 thin films.

The imaginary part of the complex refractive index N is called the extinction coefficient. The extinction coefficient (k) for pure and doped Fe_2O_3 thin films deposited with different concentration of TiO_2 is calculated by using equation (٥) [15].

$$k = \alpha\lambda/4\pi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (٥)$$

The extinction coefficient (k) represents the amount of absorption energy in the thin film material, which means the attenuation of an electromagnetic wave that is traveling in a material. The values of (k) depend on the density of free electrons in the material and on the structure defects. The relationship between extinction coefficient and wavelength of deposited pure and doped Fe_2O_3 thin films is shown in Figure (6). In general, it is clear that the extinction coefficient (k) decreases with the increasing of wavelength (λ) for all prepared samples. The extinction coefficient (k) decreases with the increasing of doping ratio with TiO_2 for all prepared samples. In general, the behavior of (k) similar to the behavior of α. This is attributed to the same reason mentioned previously, since the increasing of TiO_2 concentration increases the optical energy gap as a result of absorbance decrement. This result agrees with the result shown by [17].

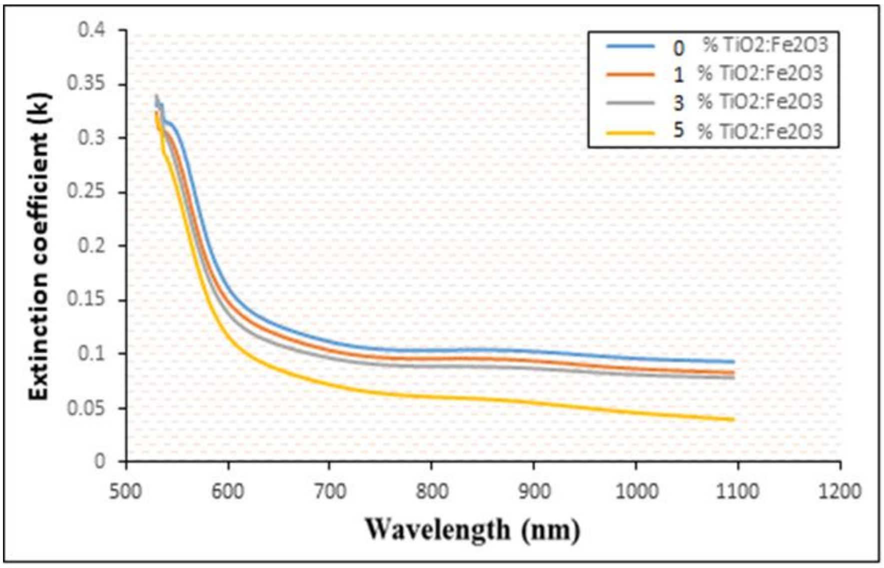

Figure (6): Extinction coefficient as a function of wavelength for pure and doped Fe_2O_3 thin films.

The dielectric constant represents the ability of a matter for polarization. The matter can respond to different frequencies in a complex manner, at optical frequencies represented by light waves the electronic polarity is dominating above other remaining types of polarization. The real and imaginary dielectric constant can be calculated by the following equation [18]:

$\varepsilon_r = n^2 - k^2$ ………………………… (٦)

$\varepsilon_i = 2nk$ ………………………… (٧)

The variation of the real and imaginary parts of the dielectric constant values versus wavelength in the range of (500–1100) nm are drawn in Figure (7) and (8) for pure and doped Fe_2O_3 thin films. The behavior of (ε_r) is similar to that of the refractive index (n) because of the smaller value of (k^2) compared with (n^2), while (ε_i) is mainly depended on the (k) values. It is found that (ε_r) and (ε_i) decrease with increasing ratio of TiO_2. It is seen that the value of real part is higher than the imaginary part. From the above note that the increase in the proportion of concentration of doping leads to rearrange the localized state causing decrease in conductivity film on the account that increases in fixed real isolation [19]. The values of optical constants of prepared thin films at $\lambda_{\text{cut off}}$ shown in Table (2).

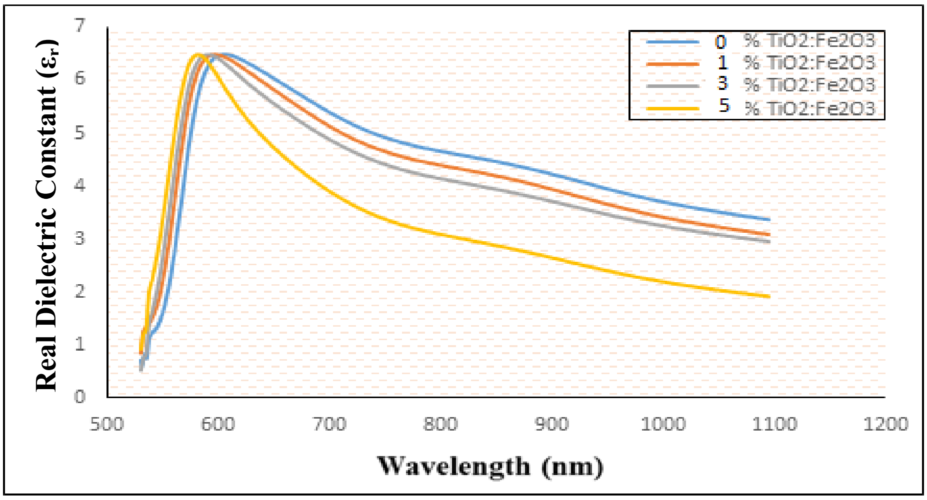

Figure (7): Real dielectric constant as a function of wavelength for pure and doped Fe_2O_3 thin films.

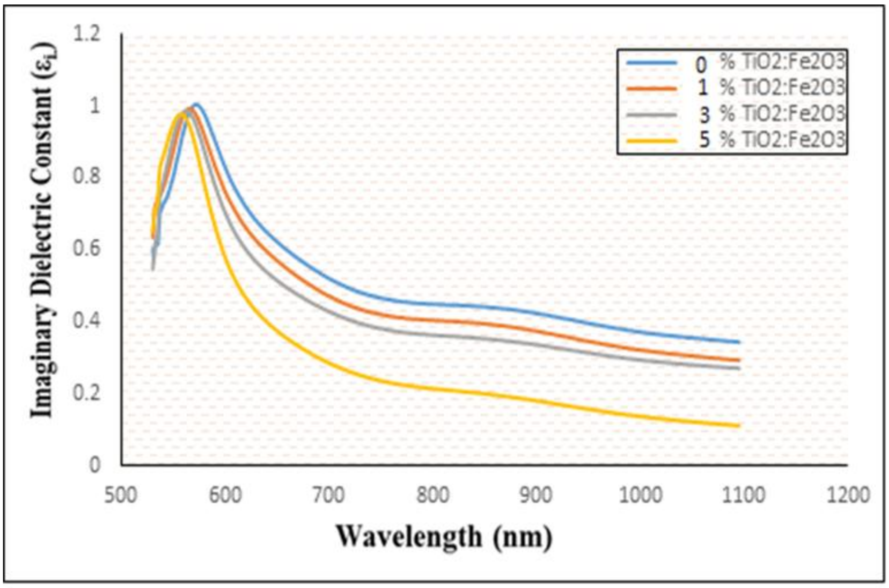

Figure (8): Imaginary dielectric constant as a function of wavelength for pure and doped Fe_2O_3 thin films.

Table (2): Values of optical constants for pure and doped Fe_2O_3 thin films.

Sample	$\lambda_{\text{cut off}}$ (nm)	n	k	ε_r	ε_i
0 % TiO_2:Fe_2O_3	638	2.490	0.131	6.172	0.652
1 % TiO_2:Fe_2O_3	٦٢٩	2.745	0.127	6.126	0.628
3 % TiO_2:Fe_2O_3	٦٢٠	2.459	0.121	6.054	0.600
5 % TiO_2:Fe_2O_3	٦١٦	2.347	0.103	5.531	0.483

4. Conclusions:

Pure and doped Fe_2O_3 thin films have been successfully deposited on glass substrates at 450 °C using spray pyrolysis technique. The optical properties show that the optical energy gap increase with the increasing of TiO_2 concentration, while the photon transition was allowed direct transition and absorption coefficient decreased with increasing TiO_2 doping concentration. The results shows that the optical constants such as refractive index, extinction coefficient and dielectric constants decreases with increasing dopant ratios.

CONFLICT OF INTERESTS

There are no conflicts of interest.

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دراسة الثوابت البصرية لأغشية Fe_2O_3 و $TiO_2:Fe_2O_3$ الرقيقة المحضرة بطريقة الرش الكيميائي الحراري

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الخلاصة

تم في هذا البحث دراسة الثوابت البصرية لأغشية أوكسيد الحديد (Fe_2O_3) النقية والمشوبة بثنائي أوكسيد التيتانيوم (TiO_2) بالنسب % (١,٣,٥) المحضرة بطريقة الرش الكيميائي الحراري على قواعد زجاجية. تم دراسة الخصائص البصرية للأغشية المحضرة بسمك nm (٢٦٠±١٠) باستخدام مطياف Shimadzu قيست النفاذية البصرية في المدى الطيفي nm (٥٠٠–١١٠٠). وجد ان فجوة الطاقة المباشرة لغشاء (Fe_2O_3) تساوي (٢.٠١ eV)، والتي تزداد مع زيادة نسبة (TiO_2). وتم حساب الثوابت البصرية كمعامل الانكسار ومعامل الخمود وثوابت العزل الكهربائية لجميع الأغشية المحضرة. واظهرت النتائج أن جميع الثوابت البصرية تقل بزيادة نسب التطعيم.

الكلمات الدالة: أغشية أوكسيد الحديد، ثنائي أوكسيد التيتانيوم، الرش الكيميائي الحراري، الثوابت البصرية.