The Optical Properties Of Nanocomposite SnO_2/Fe_2O_3 Films Of Binary Oxides Obtained Deposited By Chemical Spray Pyrolysis

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***Abstract*—In this study, nanocomposite SnO_2/Fe_2O_3 films have been successfully deposited on glass substrates by chemical spray pyrolysis (CSP) technique at substrate temperature of (400°C), and the thickness of the prepared films were about (300nm),and different composite concentration (20,30,40,50) %. The absorbance and transmittance spectra have been recorded by (UV-VIS) spectrophotometer in the wavelength range of (340-1100) nm in order to study the optical properties. The transmittance for all thin films increases with the increases in the wavelength range, and decreases with the increase in the Fe_2O_3 concentration, The absorbance increase with increased Fe_2O_3 concentration and decreases rapidly at short wavelengths (high energies) corresponding to the energy gap of the film, (when the incident photon has an energy equal or more than the energy gap value). The absorption coefficient was estimated for all samples and due to its high values (<10^4cm^{-1}), it was concluded from this result that the thin films material has a direct allowed band gap. The optical energy gap for a nanofilm was calculated for allowed direct electronic transition. It was found that the band gap decreases when the Fe_2O_3 concentration increases and the band gap values ranges between 3.4eV and 2.62eV. The optical constants including (absorption coefficient (α) and optical conductivity (σ)) for all films were also calculated as a function of photon energy, (reflectance (R), Refractive index (n), extinction coefficient (K_o) and real and imaginary parts of dielectric constant (ε_r,ε_i)) were estimated as a function of wavelength.**

Keywords*—*band gab , SnO_2, Fe_2O_3 , optical measurements

1.Introduction

Nanometer-sized materials have recently attracted a considerable amount of attention due to their unique electrical, physical, chemical, and magnetic properties, these materials behave differently from bulk semiconductors. With decreasing particle size the band structure of the semiconductor changes; the band gap increases and the edges of the bands splits into discrete energy levels. These so-called quantum size effects occur. These quantum size effects have stimulated great interest in both basic and applied research [1-5].

Tin oxide (SnO_2) thin film is well known as a wide band gap n-type semiconductor (Eg = 3.6-3.8 eV), with high simultaneous electrical conductivity and optical transparency in visible region of the spectrum. On the other hand, iron oxide (Fe_2O_3) thin film is a n-type semiconductor (Eg = 2.2 eV). So far, there are only a few reports on optical properties of SnO_2/Fe_2O_3 binary thin films [6.7]. The coupling of Fe_2O_3 with SnO_2 can affect the electronic structure and can thus be used to control and enhance to some extent the surface chemical and physical properties of these systems [8]. A long time ago, composite materials of semiconductors have been studied extensively owing to their unique optical and electric properties [9-12]. SnO_2 and Fe_2O_3 are both important inorganic semiconductors and have potential applications in Li-ion batteries, gas sensors, chemical-catalyst, and magnetic storage devices [13-15]. Their composites also attracted great attention owing to their stable, outstanding gas-sensitive properties and potential application in Li-ion battery electrode [16-18]. Although some groups have synthesized and studied thin films and nanopowders of SnO_2/Fe_2O_3 composite [16,17].

The aim of study is to prepare SnO_2/Fe_2O_3 Nanocomposite films on glass substrate by chemical spray pyrolysis technique and to study the effect of the composite concentration on the optical properties of these films. The optical properties will include: transmittance, absorbance, reflectance, optical constants, energy band gap and optical conductivity.

2. Experimental

Firstly prepared the Fe_2O_3 pure from hematite chloride Hydrated ($FeCl_3.6H_2O$) diluted with distilled water, in order to prepare the solution of 0.1 molar concentration from these material, 0.811 gm weight of ($FeCl_3.6H_2O$), melted in 50 ml of distilled water Secondary prepared the SnO_2 pure from 0.1M concentration precursor solution of the pure Stannic Chloride Hydrated, it chemical symbol ($SnCl_4.5H_2O$) by Purity 99.9, molecular weight (350.58g / mol), it has been prepared by dissolving a solute quantity of 1.753g of $SnCl_4$ in 50 ml of distilled water. The both solutions were added into a round-bottom flask with stirring.

SnO_2 / Fe_2O_3 nanocomposite with different SnO_2 and Fe_2O_3 contents were deposited on a glass substrate by spray pyrolysis technique under ambient atmosphere. Two kinds of aqueous solution, Stannic Chloride $SnCl_4$ and Hematite Chloride $FeCl_3$ were chosen as the sources of Stannic and Hematite respectively. In order to obtain SnO_2/Fe_2O_3 nanocomposite with different contents see Table 1. The deposition parameters were the same for the series of SnO_2/ Fe_2O_3 films. The pure Stannic Chloride $SnCl_4$, pure Hematite Chloride $FeCl_3$ and distilled water were mixed thoroughly to get the solution with a concentration of 0.1 M. the substrate temperature was set at 400°℃ during the film growth.

Table 1: the percentage of SnO_2 and Fe_2O_3.

percentage	SnO_2	Fe_2O_3
Pure –SnO_2	100	Zero
20%	80	20
30%	70	30
40%	60	40
50%	50	50
Pure –Fe_2O_3	Zero	100

Thickness (t) of the samples was calculated using the weighting method, by using the relationship

$$t = \frac{\Delta m}{A.\rho} \quad (1)$$

Where (t) is the thin film thickness , (Δm) is the change in weight (The difference between the substrate weight before and after the deposition) , (ρ) The density of the thin film material (the density of Ferric oxide material equal to 5.24g /cm^3, Tin oxide material equal to (6.95 g/cm^3), and substrate surface area equal (625cm^2).

where the use of the thickness of (300 nm) .

The optical measurements and study the electronic transfer of the prepared films has been examined by use the spectrometer (UV- Visible-NIR Spectrophotometer) equipped of the company (Shimadzu), (UV-1600/1700 series), Japanese.

3. Results and discussion

The optical properties of deposited nanocomposite SnO_2/Fe_2O_3 films on glass substrate at temperature of 400°C are measured by UV-VIS spectrophotometer. The optical transmittance is at normal incidence in the wavelength range (340-1100) nm.

The transmittance spectra of the SnO_2/Fe_2O_3 films coated with different Fe_2O_3 concentration are shown in Fig 1 .The figure shows that films coated with SnO_2 have a maximum transmittance of 88% in the near-infrared region. The transmission of films increases with the increase in the wavelength range, and decrease with the increase in the Fe_2O_3 concentration. where observed that least transmittance was 64% at the Fe_2O_3 pure.

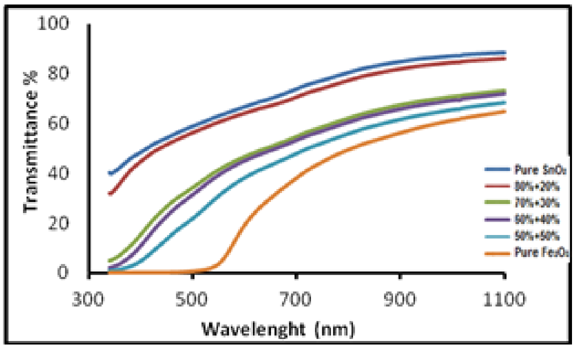


Fig 1. The optical Transmittance of SnO_2/ Fe_2O_3 nanocomposite.

Therefore using the fundamental relation of photon transmission and absorbance, the absorbance (A) is defend as the logarithm of the reciprocal of the transmittance[19]:

$$A = \log\frac{1}{T} \quad (2)$$

The absorbance spectra of the thin films SnO_2/Fe_2O_3 nanocomposite, are shown in Fig. 2. The absorption spectrum takes in exponential decay with increasing wavelength because the energy of photons falling is low. It has been observed that the maximum absorption peak shifts towards the longer wavelength with increasing Fe_2O_3 concentration. Generally, the absorption of films decreases with the increase in the wavelength range, and increase with the increase in the Fe_2O_3 concentration**.**

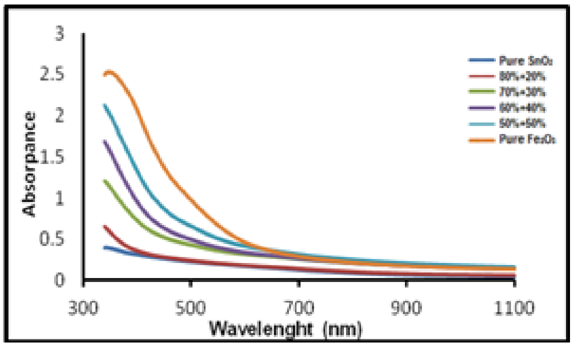


Fig. 2. The optical Absorption of of SnO_2/ Fe_2O_3 nanocomposite .

The optical absorption coefficient (α) as a function of photon energy of SnO_2 /Fe_2O_3 nanocomposite determined from absorbance measurements using equations [20]:

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

Where A is the absorptance of film and (t) is the sample thickness.

Fig.3. shows the absorption coefficient of SnO_2/Fe_2O_3 nanocomposite films increasing with the increasing of photon energy. The absorption coefficient of nanocomposite films increased in the UV/VIS boundary, and then increased gradually in the visible region .as well as, the values of absorption coefficient greater than ($\alpha \geq \geq 10^4 cm^{-1}$) at energies high photonic than likely occurrence of electronic transitions directly.

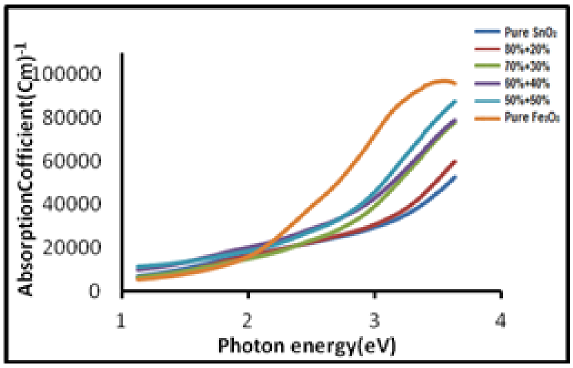


Fig.3.The absorption Coefficient of of SnO_2/ Fe_2O_3 nanocomposite.

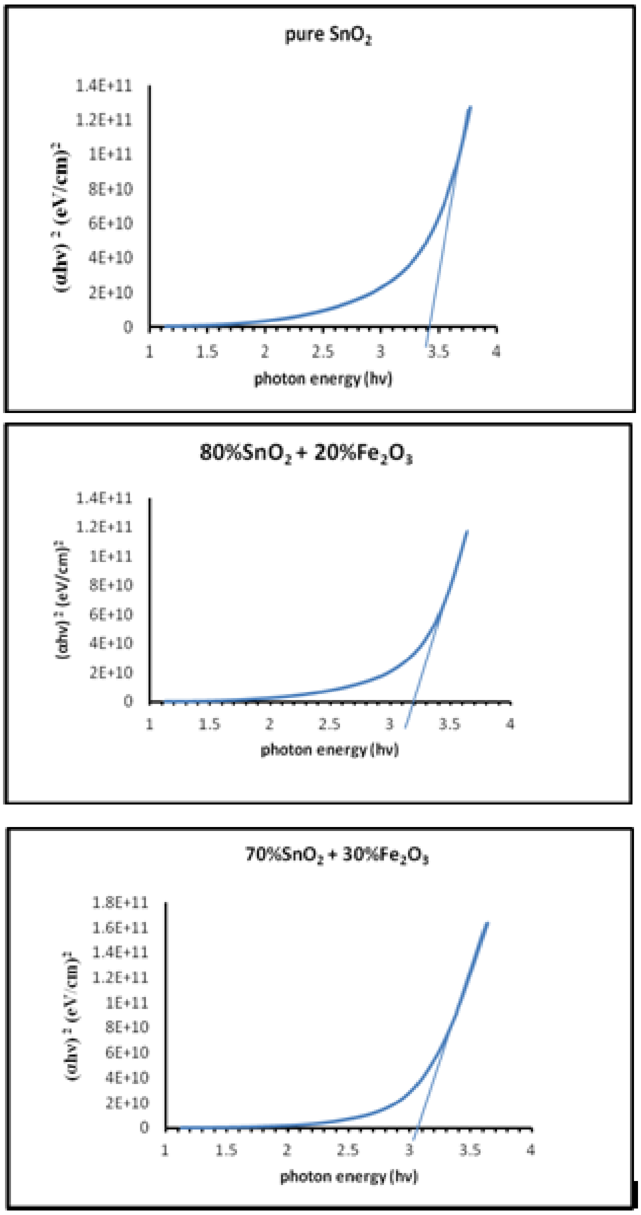
The optical energy gap (Eg) was determined by Tauc equation [21]

$\alpha h\upsilon = B[h\upsilon - Eg]^r$ (4)

Where B is Taue constant, hυ is the photon energy, α is the absorption coefficient, for r = ½ a linear relation dependence, which describe the direct allowed transition, the optical energy gap where calculated by plotting $(\alpha h\upsilon)^2$ versus (hυ) and extrapolating the straight Line portion of this plot to photon energy axis (hυ) (i.e αhυ =0).

Fig.4. show the SnO_2/Fe_2O_3 nanocomposite thin films have band gap in the range (3.4-2.62 eV) as shown in table (2). The band gap of SnO_2 films decrease with increasing Fe_2O_3 concentration

This may be to increase the density of localized allowed states near the conduction band in the energy band gap and consequently decrease the energy gap. According to which increase of the carrier concentration due to Fe_2O_3 addition results in a shift of the Fermi level and block some of the lowest states [22].



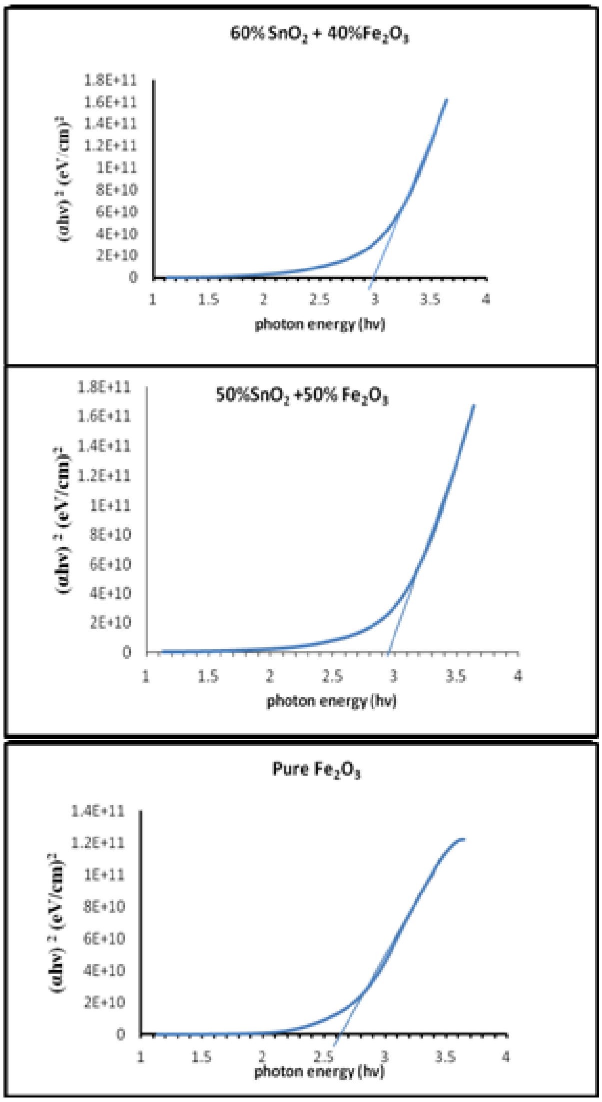


Fig.4.Variation of band gap for Fe_2O_3/ SnO_2 nanocomposite thin films prepared at different Fe_2O_3 concentration.

Table 2 the value of optical energy gap for SnO_2/Fe_2O_3 nanocomposite.

Preparation condition	Band gap energy (eV)
pure SnO_2	3.4
80%SnO_2+20% Fe_2O_3	3.2
70%SnO_2+ 30%Fe_2O_3	3.12
60%SnO_2+ 40%Fe_2O_3	3
50%SnO_2+50% Fe_2O_3	2.91
Pure Fe_2O_3	2.62

The reflection of the films has been found by using relationship [23]:

R+T+A=1 (5)

Fig.6. shows the verity in reflectivity as function to the wavelength of the SnO_2/ Fe_2O_3 nanocomposite. To note that the reflectivity gradually increased to the maximum value at certain wavelengths, and then decreases with increasing wavelength, The overall reflectance of the film increases with increases Fe_2O_3 concentration.

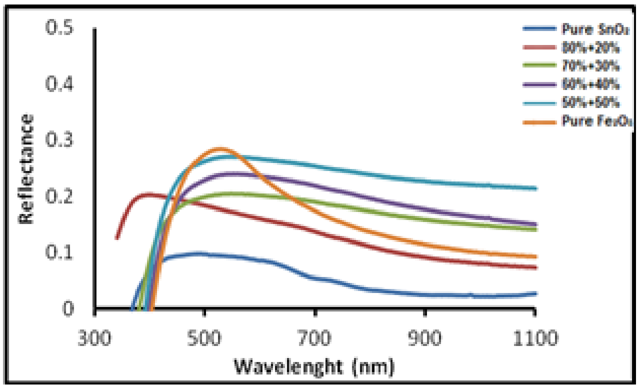


Fig.6 :The Reflectance of SnO_2 /Fe_2O_3 nanocomposite.

From the reflection of the thin film, the refraction index can be calculated from the relationship [24]:

$$n = \frac{1+R^{1/2}}{1-R^{1/2}} \quad (6)$$

Fig.7. shows the relationship between the Refractive Index and wavelength at range about (900-1100) , The increase in the Fe_2O_3 concentration results in the overall increase in the refractive index. This increase is due to the overall increase in the reflectance with the Fe_2O_3 concentration.

Note from the figure that the highest value in the refractive index increases with Fe_2O_3 concentration, Which means that the increase in iron concentration has affected on the nature of the film surface Which happens upon reflectance which leads to verity the refractive index.

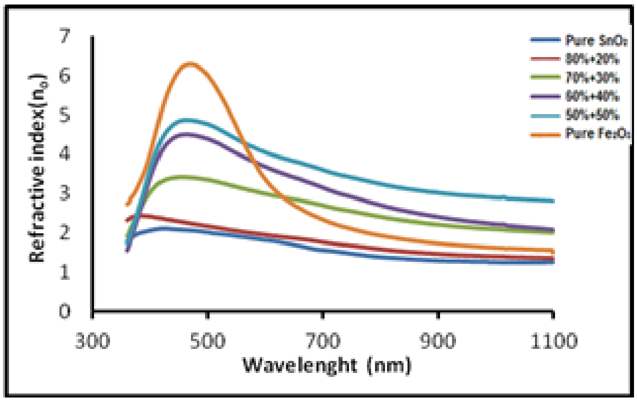


Fig.7.The Refractive index of SnO_2 /Fe_2O_3 nanocomposite.

The extinction coefficient was evaluated using equation[25]:

$$k_o = \frac{\alpha\lambda}{4\pi} \quad (7)$$

Fig.8. shows the variation of extinction coefficient with wavelength for SnO_2/Fe_2O_3 nanocomposite with different Fe_2O_3 concentration. The extinction coefficient decreases as the wavelength increases, and its increases as the Fe_2O_3 concentration increases. The increase of surface roughness with increasing Fe_2O_3 concentration for crystalline film will increase surface optical scattering and optical loss [26].

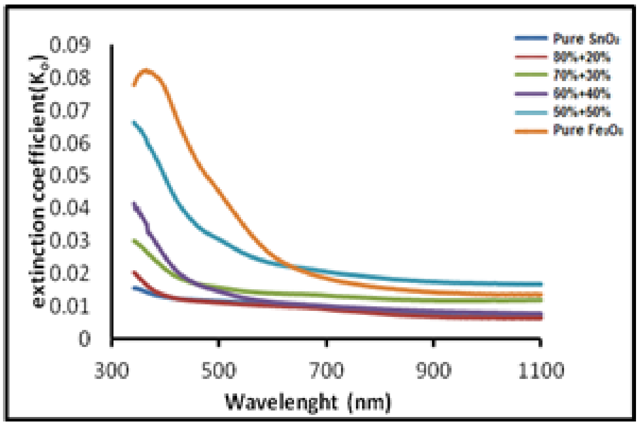


Fig.8. The Extinction Coefficient of SnO_2 /Fe_2O_3 nanocomposite.

represents the real and imaginary parts of complex dielectric constant and given by the following relations [27]:

$\varepsilon_r = n^2 - K^2$ (8)

$\varepsilon_i = 2\, n\, K$ (9)

The real and imaginary part of dielectric constant of the SnO_2/Fe_2O_3 nanocomposite thin films have been investigated using equations (8) and (9) as shown in fig.9.

The variation of (ε_r), (ε_i) with wavelength for SnO_2/Fe_2O_3 nanocomposite with different Fe_2O_3 concentration. The obtained results show that the values of real part of dielectric constant (ε_r) are decreased with increasing of wavelength for SnO_2/Fe_2O_3 thin films, especially, it increased with increasing of Fe_2O_3 concentration .

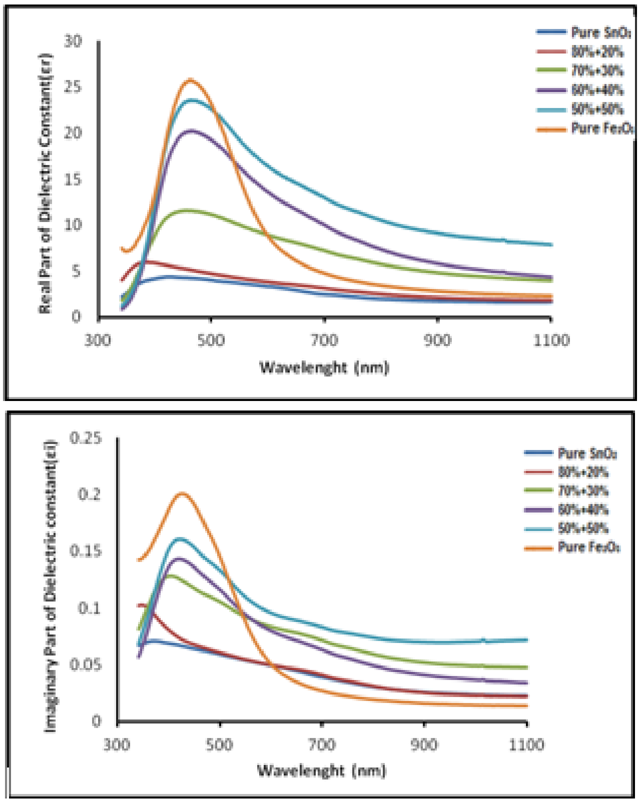


Fig.9. The Real and Imaginary Parts of Dielectric Constant of SnO_2 /Fe_2O_3 nanocomposite.

To calculate the optical conductivity used the following relationship[28]:

$$\sigma_{\text{optical}} = \frac{\alpha n c}{4\pi} \quad (10)$$

Where (σ) is the optical conductance, (c) is the velocity of the radiation in the space, (n) is the refractive index and (α) is the absorption coefficient. The optical conductivity is calculated by using equation (10), fig.10, Shows the variation of optical conductivity as a function of photon energy for different Fe_2O_3 concentration of SnO_2/Fe_2O_3 nanocomposite thin films. From the figure, we can see that the optical conductivity of SnO_2/Fe_2O_3 nanocomposite increases with increasing photon energy. This suggests that the increase in optical conductivity is due to electron exited by photon energy, and the optical conductivity of the films increases with increasing Fe_2O_3 concentration in the films.

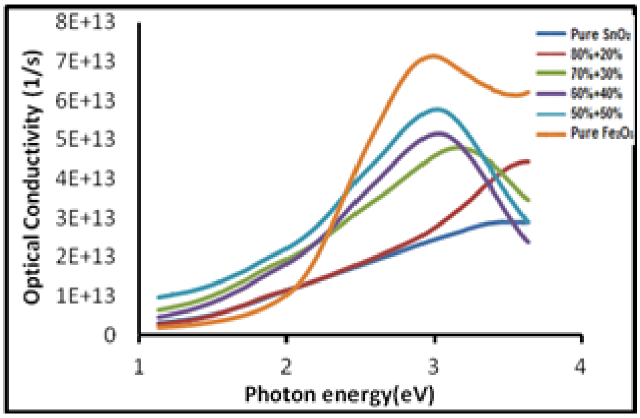


Fig.10.The Optical Conductivity of SnO_2 thin films with different Fe_2O_3 concentration.

Conclusions

The SnO_2/Fe_2O_3 nanocomposite thin films with different Fe_2O_3 concentrations (0,20,30,40,50,100%) prepared by chemical spray pyrolysis method at substrate temperature of (400 ^oC) on glass substrate**.** The optical properties showed that The transmittance for all films increased with the increasing in the wavelength range, and decreases with the increase in the Fe_2O_3 concentration , the pure SnO_2 thin film has a maximum transmittance of 88% in the near-infrared region, and the Fe_2O_3 thin film has a minimum transmittance of 64% in the visible region. The band gap decreases when the Fe_2O_3 concentrations increases and the band gap values range between 3.4eV and 2.62 eV.

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