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RESEARCH ARTICLE

STUDY THE EFFECT OF THICKNESS ON THE OPTICAL PROPERTIES OF $ZNFe_2O_4$ FILMS PREPARED BY CHEMICAL SPRAY PYROLYSIS METHOD

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ABSTRACT

Zinc Ferrite ($ZnFe_2O_4$) thin films have been deposited by chemical spray pyrolysis method on glass substrates at temperature of (400 ºC) using Zinc Nitrate and Ferric Nitrate as Zinc and Iron sources respectively. The effect of thickness change (200, 300, 400 and 500) nm on the optical properties for all prepared films was studied. The optical properties for all the films were studied by recording the transmittance and absorbance spectrum in the range of (300-900) nm. The results showed that the energy band gap for allowed direct electronic transition varies from 3.10 to 2.60 eV with the increasing of films thickness. The optical constants (absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constant and optical conductivity) as a function of photon energy, for all prepared films were calculated.

INTRODUCTION

The spinel ferrite thin films are used for various applications such as in magnetic sensors, reading heads for magnetic recording media, microwave devices, switch mode power supplies, deflection yoke rings and spintronics devices. These wide applications of spinel ferrites are due to their high permeability, large resistivity, relatively high magnetization and low coercivity. They can also absorb electromagnetic radiation the microwave bands (Gupta *et al.,* 2007) and can be used as a photocatalyst under visible light irradiation (Jang *et al.,* 2009). The spinel type oxide is a cubic structure and consists of tetrahedral A oxygen sites and octahedral B oxygen sites in which metal cation distribution occurs. This spinel type oxide growth process involves the so-called Wagner's cation counter diffusion mechanism Among all spinel ferrite materials, $ZnFe_2O_4$ (Franklinite) has better potential application with its normal spinel structure. There are many techniques available for the synthesis of $ZnFe_2O_4$ thin films such as chemical vapor deposition, spin coating, thermal evaporation, spin spray ferrite plating, sputtering, Laser ablation techniques and spray pyrolysis (Affreen *et al.,* 2012). The technique of spray pyrolysis is simple and inexpensive for the preparation of homogeneous $ZnFe_2O_4$ thin films with a large surface area. In this study, spray deposited Zinc Ferrite thin films are prepared with different thicknesses and their correlation with optical properties is investigated.

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MATERIALS AND METHODS

Zinc Ferrite $ZnFe_2O_4$ thin films with different thicknesses (200, 300, 400 and 500) nm were grown on glass substrates by using the chemical spray pyrolysis technique. These films were prepared by mixing (0.02M) aqueous solution of Zinc Nitrate and (0.04M) aqueous solution of Ferric Nitrate. The prepared solution was sprayed on glass substrates kept at a temperature of (400 ºC) Other deposition conditions such as spray nozzle substrate distance (30 cm), spray time (10 s), spray interval (2 min) and pressure of the carrier gas (1.5 bar) were kept constant for each thickness of the prepared films. Optical transmittance and absorbance spectra in the wavelength of (300-900) nm were recorded by using UV-VIS-NIR spectroscopy (Shimadzu, UV-1800).

RESULTS AND DISCUSSION

The transmission spectra of the $ZnFe_2O_4$ films with different thicknesses are shown in Figure (1). It can be seen that the transmittance of the films varies from 80 to 29 % with increase in the film thickness. This is due to the phenomena that, as the thickness increases the scattering of light increases, so that the coherence between the primary light beam and the beam reflected between the film boundaries is lost resulting in disappearance of the interference with decrease in transmittance (Affreen *et al.,* 2012).

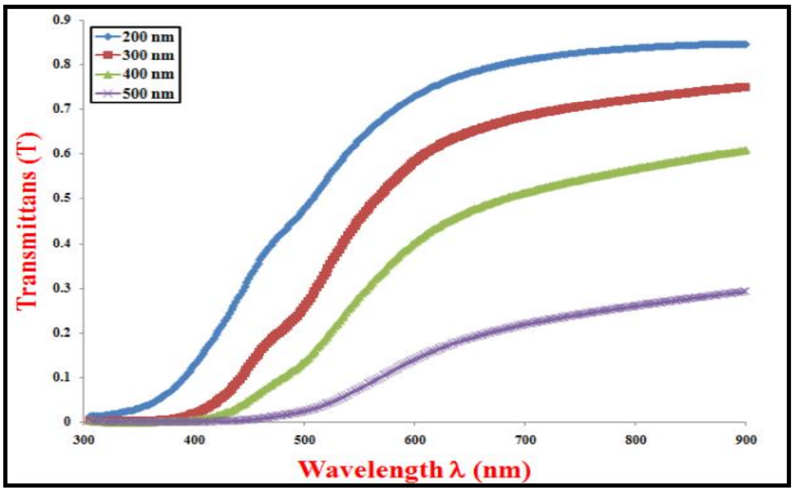

Fig. 1. Transmission spectra of the $ZnFe_2O_4$ films with different thicknesses

The absorbance spectra of the $ZnFe_2O_4$ films with different thicknesses are shown in Figure (2). It is clear that the absorbance increases with increase in the film thickness because, in thicker films more atoms are present so more states will be available for the photons to be absorbed (Affreen *et al.,* 2012).

Figure (3) shows the reflectance as a function of the wavelength of the $ZnFe_2O_4$ films with different thicknesses.

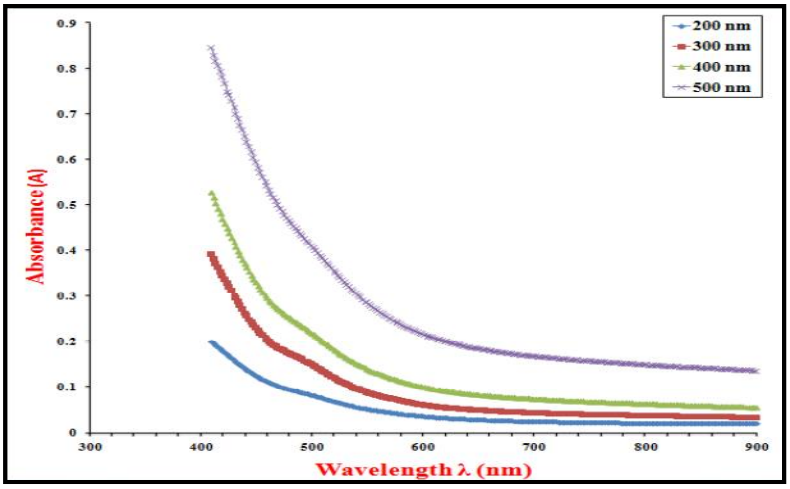

Fig. 2. Absorption spectra of the $ZnFe_2O_4$ films with different thicknesses

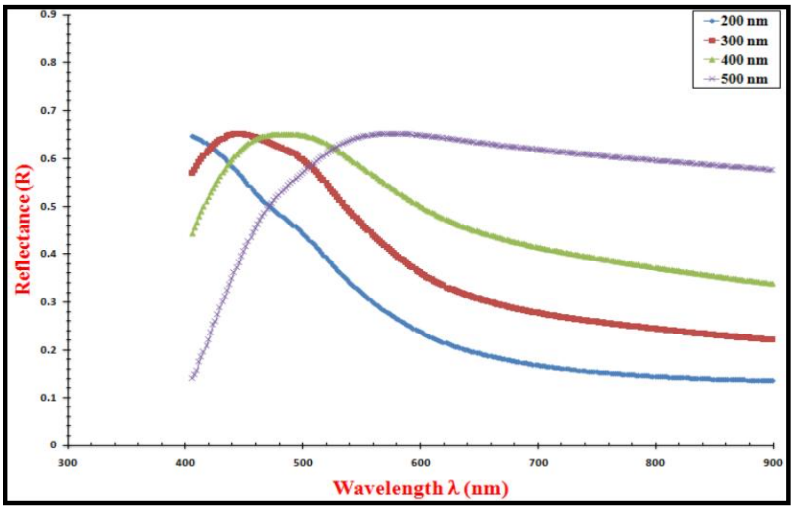

Fig. 3. Reflection spectra of the $ZnFe_2O_4$ films with different thicknesses

The following relation can be used for calculating the absorption coefficient (α) (Khan *et al.,* 2012):

$\alpha = 2.303\ A / t$ ……………. (1)

Where (A) is the absorbance and (t) is the film thickness.

From Figure (4) it can be observed that the absorption coefficient of the $ZnFe_2O_4$ films increases with increase in the film thickness. It is clear also that at high photon energies, absorption coefficient has higher values ($\alpha > 10^4\ cm^{-1}$) which may lead to the conclusion that direct transition of electrons occurs.

Table 1. Values of optical energy gap of $ZnFe_2O_4$ films with different thicknesses

Thickness (nm)	E_g(eV)
200	3.10
300	2.85
400	2.80
500	2.60

The width of the localized states available in the optical energy gap of the films affects the optical band gap structure and optical transitions and it is called Urbach tail, which is related directly to a similar exponential tail for the density of states of either one of the two band edges. The Urbach tail of the films can be determined by the following relation (Ilican *et al.,* 2009):

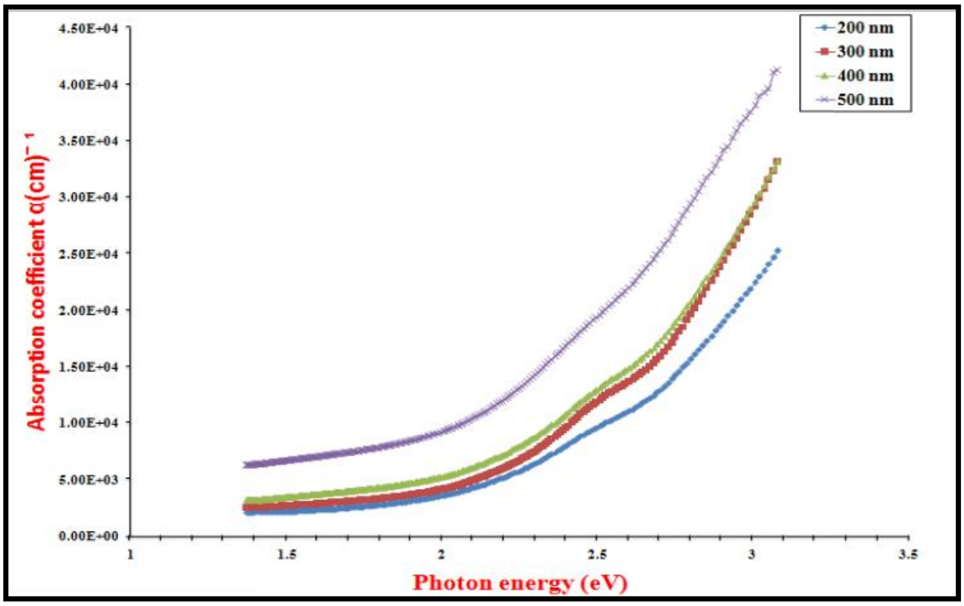

Fig. 4. Absorption coefficient of the $ZnFe_2O_4$ films with different thicknesses

The optical energy gap (E_g) is given by the classical relation (Tauc, 1974):

$\alpha h\nu = B(h\nu - E_g)^r$ …………….(2)

Where (E_g) is the optical energy gap of the films, (B) is a constant and ($h\nu$) is the incident photon energy.

The optical energy gap can be estimated by plotting $(\alpha h\nu)^2$ versus ($h\nu$), then extrapolating the straight line from the upper part of the plot to the photon energy axis at the value ($(\alpha h\nu)^2 = 0$) gives the optical energy gap for the film. The variation of optical energy gap as a function of thickness of $ZnFe_2O_4$ films is shown in Figure (5). The optical energy gap of the films varies from 3.10 to 2. 60 eV as film thickness increases (Wu *et al.,* 2001; Zhou *et al.,* 2002). This is due to the formation of new localized levels which are capable to receive electrons and generate localized energy tails inside the optical energy gap which work on the absorption of low energy photons (deviation of the absorption edge towards the low energies) and this in turn leads to a decrease of the energy gap. The values of optical energy gap are listed in Table (1).

$\alpha = \alpha_o \exp(E / E_U)$ .... (3)

Where (E) is the photon energy, (α_o) is constant and (E_u) is the Urbach energy which refers to the width of the exponential absorption edge.

This behavior corresponds primarily to optical transitions between occupied states in the valance band tail to unoccupied states at the conduction band edge. The (E_U) value was calculated from the slope of Figure (6) using relationship:

$$E_U = \left(\frac{d(\ln \alpha)}{d(h\nu)} \right)^{-1}$$ ………………(4)

Figure (6) shows the variation of (lnα) versus photon energy of $ZnFe_2O_4$ films with different thicknesses. It is clear that Urbach energy increases with increase in film thickness. The values of Urbach energy are listed in Table (2).

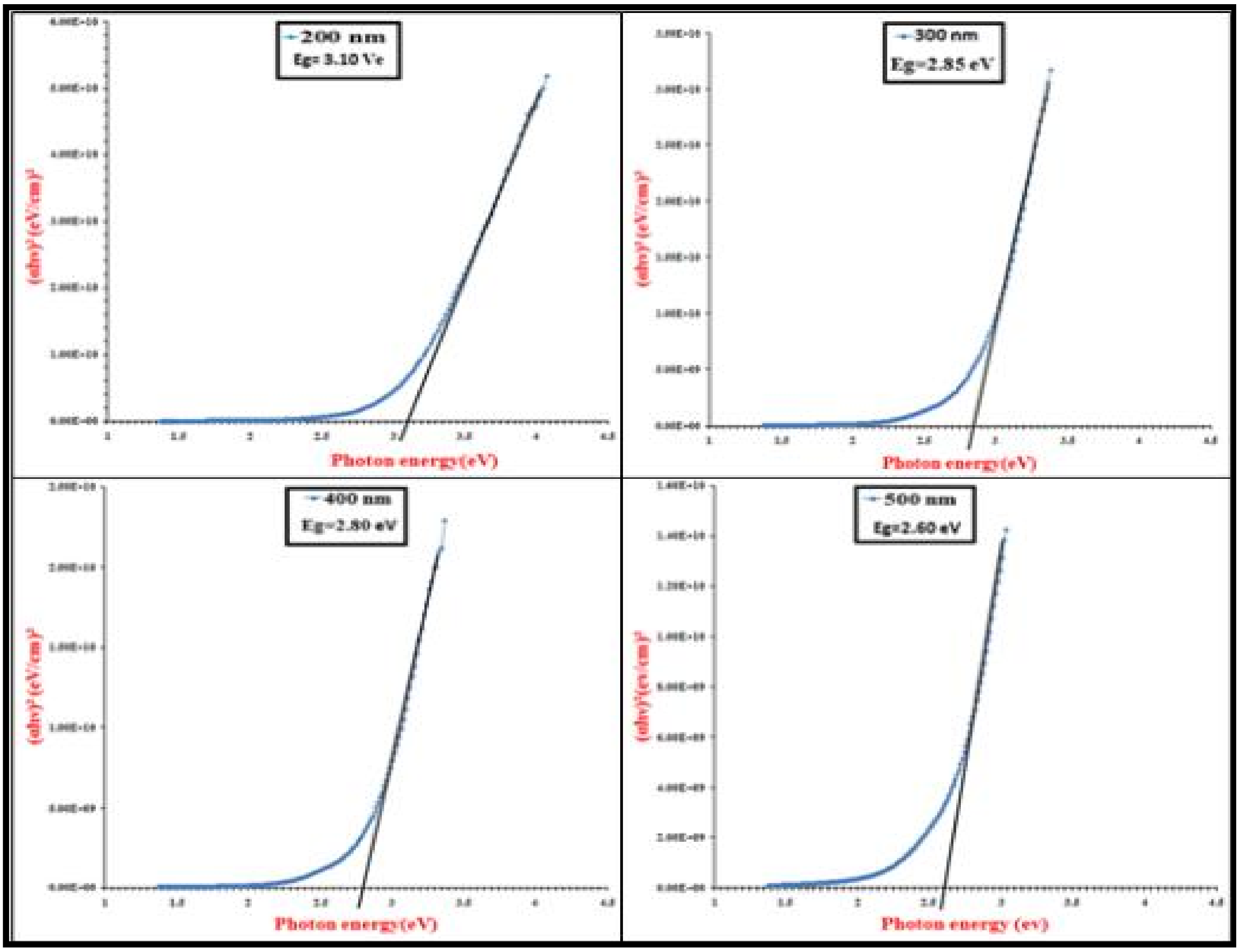

Fig. 5. Energy gap of $ZnFe_2O_4$ films with different thicknesses

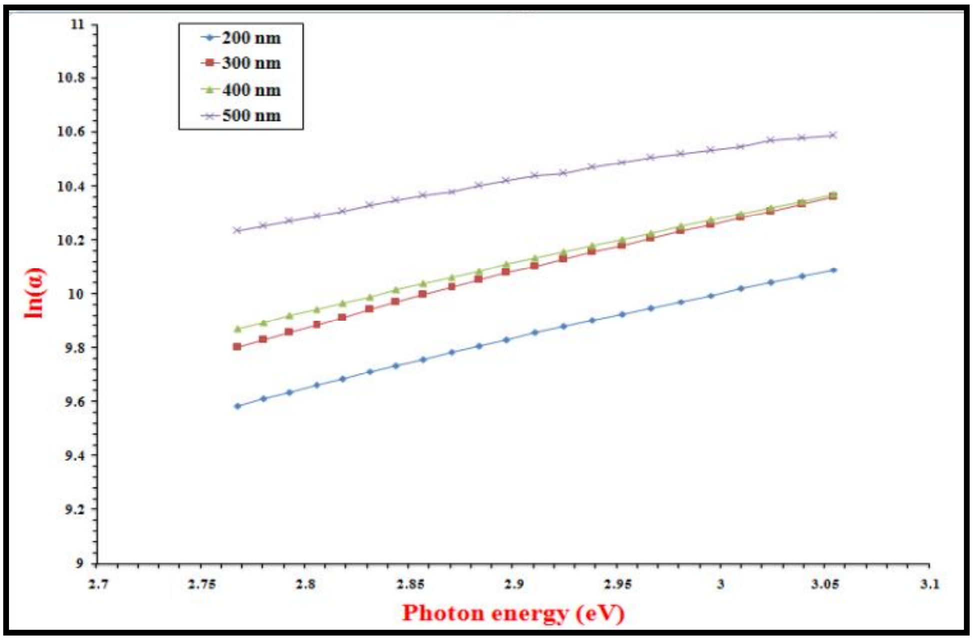

Fig. 6. Urbach energy of $ZnFe_2O_4$ films with different thicknesses

Table 2. Values of Urbach energy of $ZnFe_2O_4$ films with different thicknesses

Thickness (nm)	E_u(meV)
200	571
300	613
400	666
500	704

The refractive index (n_o) can be determined from the reflectance (R) by using the relation (Ezekoye and Okeke, 2006):

$$n_o = \left[\left(\frac{1+R}{1-R}\right)^2 - \left(K_o^2+1\right)\right]^{1/2} + \frac{1+R}{1-R} \quad \text{.................(5)}$$

Figure (7) shows the variation of the refractive index with the photon energy of the $ZnFe_2O_4$ films with different thicknesses. It is clear from this figure that the films are influenced by the film thickness. The refractive index of these films slightly increases with the increase in the films thickness. The refractive index measurements can have a correlation with the electrical properties of the prepared films.

The extinction coefficient (k_o) can be determined by using the relation (Xue *et al.,* 2008):

$$k_o = \alpha\lambda/4\pi \quad \text{........................(6)}$$

Where (λ) is the wavelength of the incident photon

Figure (8) shows the variation in extinction coefficient as a function of the photon energy of the $ZnFe_2O_4$ films with different thicknesses. It can be noticed that the extinction coefficient increases as the films thickness increase.

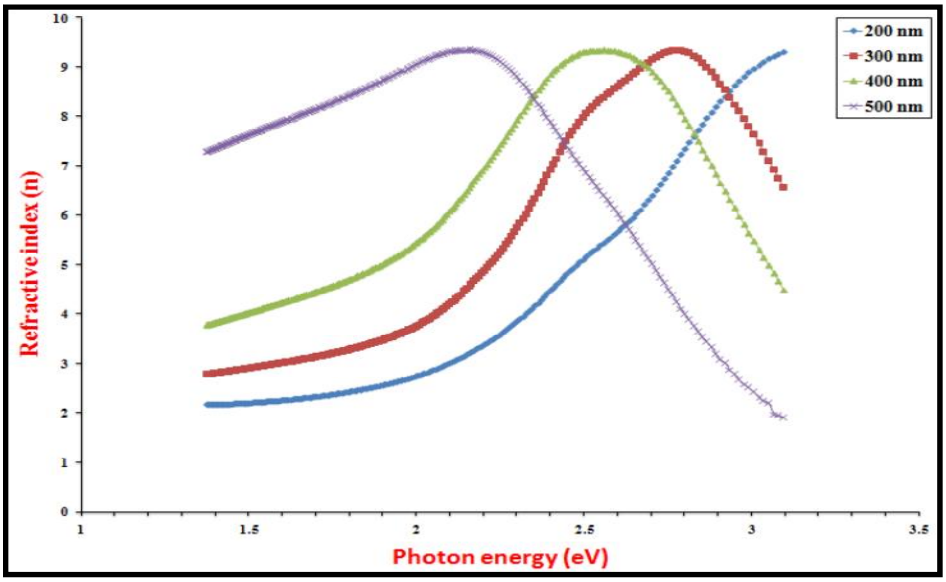

Fig. 7. Refractive index of $ZnFe_2O_4$ films with different thicknesses

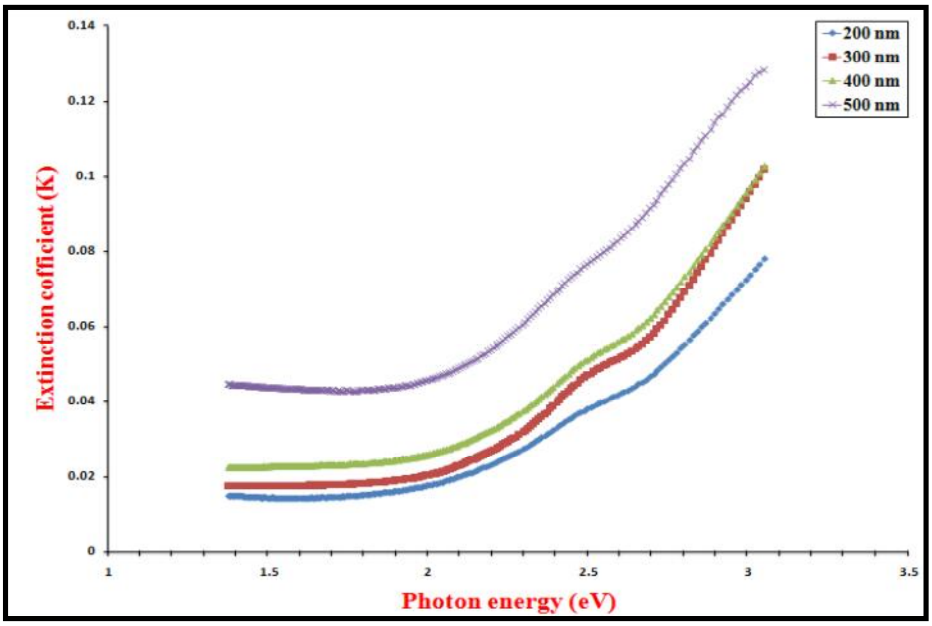

Fig. 8. Extinction coefficient of $ZnFe_2O_4$ films with different thicknesses

This is attributed to the increase in absorption coefficient as the film thickness increases.

The variation of the real (ε_1) and imaginary (ε_2) parts of dielectric constant values versus photon energy of $ZnFe_2O_4$ films with different thickness films are shown in Figures (9) and (10) respectively. The behavior of real part of dielectric constant is similar to that of refractive index because of the smaller value of (k_o^2) compared with (n_o^2) (Baker and Dyer, 1993):

$$\varepsilon_1 = n_o^2 - k_o^2 \quad \text{.............(7)}$$

However, the imaginary part of dielectric constant is mainly depends on the extinction coefficient, which is related to the variation of absorption coefficient (Bhattacharyya *et al.,* 2009):

$$\varepsilon_2 = 2 n_o k_o \quad \text{...........(8)}$$

It is found that the real and imaginary parts of dielectric constant increase with increasing of the films thickness (14).

Conclusion

The transmission spectra of the $ZnFe_2O_4$ films vary from 80 to 29% with increase in the film thickness. The results showed that the optical energy gap for allowed direct electronic transition varies from 3.10 to 2.60 eV as a film thickness increases, and the detailed study the effect of thickness on the optical properties has shown that all the optical properties such as absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant have been affected by increasing the thickness.

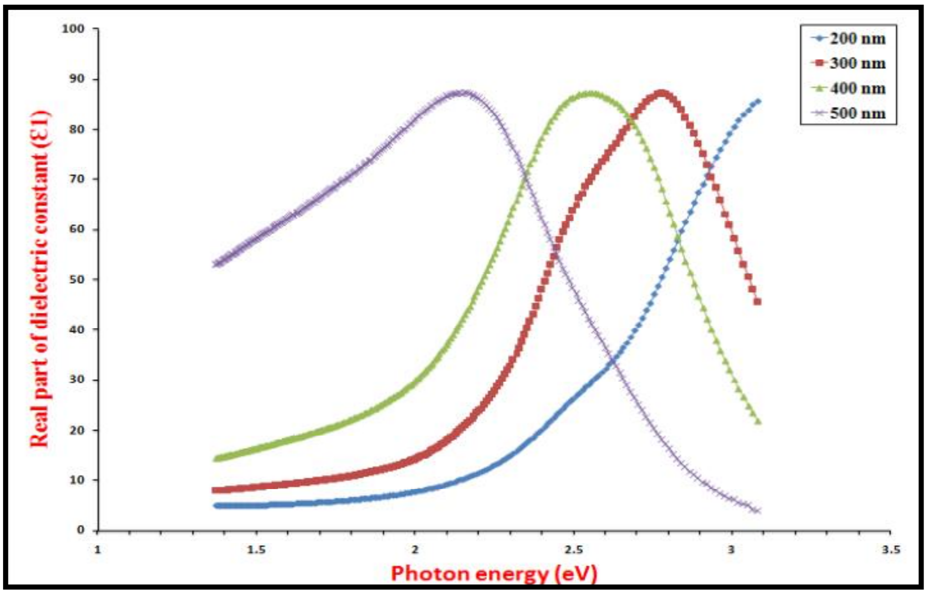

Fig. 9. Real part of the dielectric constant of $ZnFe_2O_4$ films with different thicknesses

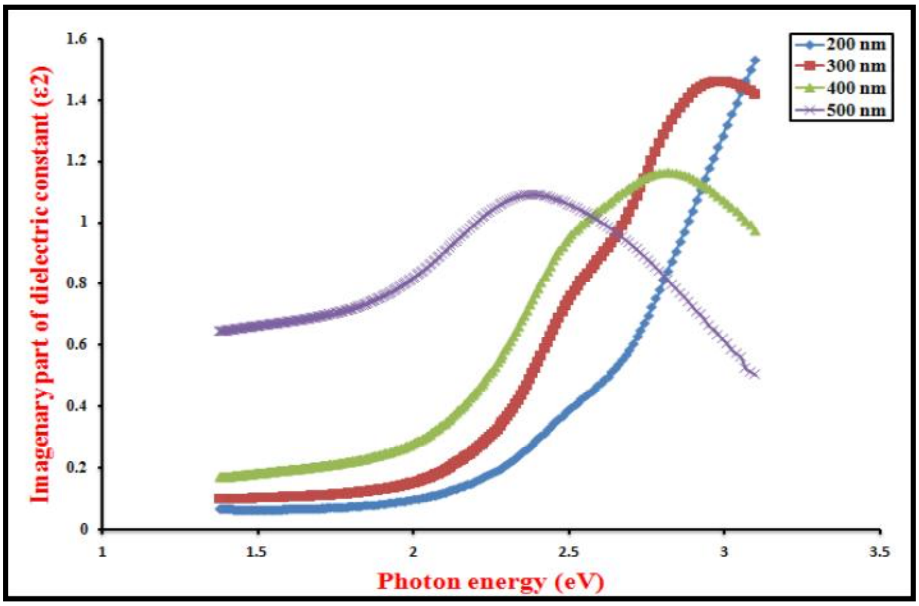

Fig. 10. Imaginary part of the dielectric constant of $ZnFe_2O_4$ films with different thicknesses

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