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Study of the Effect of Annealing on Optical Properties of $ZnFe_2O_4$ Films Prepared by Chemical Spray Pyrolysis Method

*Sabah A. Salman, Nabeel A. Bakr**and Rusul K. Ismail.*

Department of Physics, College of Science, University of Diyala, Diyala, Iraq.

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Abstract: Zinc Ferrite ($ZnFe_2O_4$) thin films have been deposited by chemical spray pyrolysis method with thickness of (500 nm) on glass substrates at temperature of (400 ºC) using Zinc Nitrate and Ferric Nitrate as Zinc and Iron sources respectively. The effect of annealing with different temperatures (450 and 500) ºC for (2h) 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 spectra in the range of (300 - 900) nm. The results showed that the energy band gap for allowed direct electronic transition varies from 2.60 to 2.70 eV with increase in annealing temperature. 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.

Keywords: Spinel ferrites, $ZnFe_2O_4$ thin films, Chemical Spray Pyrolysis, Optical Properties.

1 Introduction

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 [1] and can be used as a photocatalyst under visible light irradiation [2]. 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 applications 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 [3]. 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 and study the effect of annealing and their correlation with optical properties is investigated.

2 Experimental Procedure

Zinc ferrite $ZnFe_2O_4$ thin films were grown on glass substrates by using the chemical spray pyrolysis technique with thickness of (500 nm) and annealing with different temperatures (450 and 500) ºC for (2h). These films were prepared by mixing (0.02 M) aqueous solution of Zinc Nitrate and (0.04 M) 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 all films. Optical transmittance and absorbance spectra in the wavelength of (300 - 900) nm were recorded by using UV-VIS-NIR spectroscopy (Shimadzu, UV-1800).

3 Results and Discussion

The transmission spectra of the $ZnFe_2O_4$ films with different annealing temperatures are shown in figure (1). It can be seen that the transmittance of the films increased with increasing the wavelength to reach the highest value in the visible and near infrared region at the range of wavelengths (600 - 900) nm for all the films. We also note that the annealing process did not show any significant change in the transmittance.

*Corresponding author E-mail: nabeelalibakr@yahoo.com

The absorbance spectra of the $ZnFe_2O_4$ films with different annealing temperatures are shown in figure (2). It is clear that the absorbance decreased with increasing the wavelength for all films; also we noted that the absorbance decreased with increasing the annealing temperature.

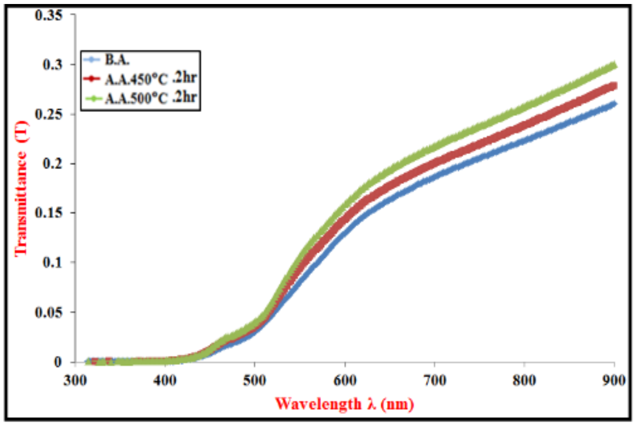

Fig. (1): Transmission spectra of $ZnFe_2O_4$ films before and after annealing.

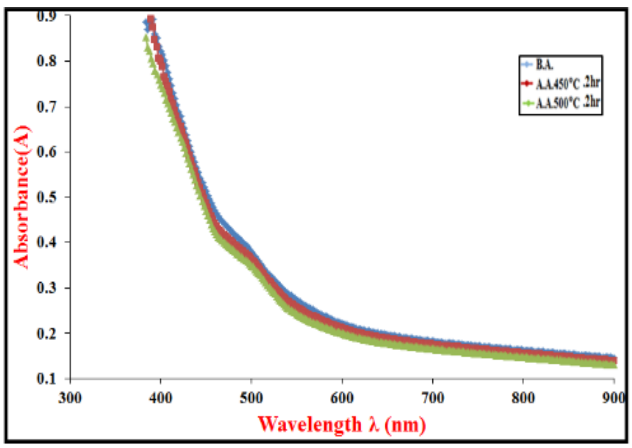

Fig. (2): Absorption spectra of $ZnFe_2O_4$ films before and after annealing.

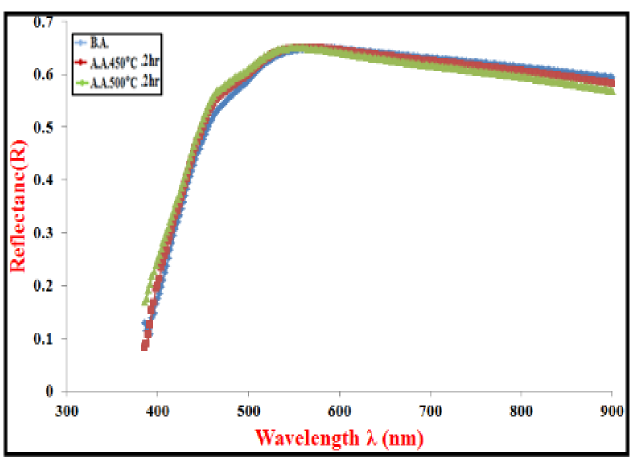

Fig. (3): Reflection spectra of $ZnFe_2O_4$ films before and after annealing.

Figure (3) shows the reflectance as a function of the wavelength of the $ZnFe_2O_4$ films with different annealing temperatures. We note that the reflectance increased with increasing the wavelength for all films and increases with increasing of annealing temperature at short wavelengths, while at long wavelengths, the reflectance decreased with increasing the wavelength for all the films and decreases with increasing the annealing temperature.

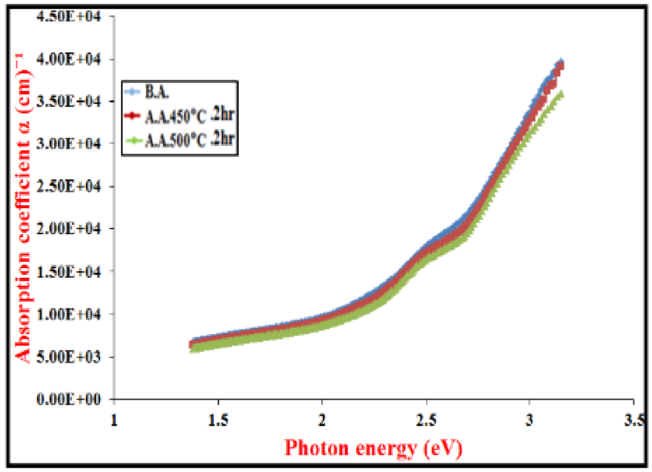

Fig. (4): Absorption coefficient of $ZnFe_2O_4$ films before and after annealing.

The following relation can be used for calculating the absorption coefficient (α) [4]:

$$\alpha = 2.303\ A\ /\ t \tag{1}$$

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

Figure (4) shows the absorption coefficient as a function of the photon energy of $ZnFe_2O_4$ films before and after annealing. The results show that the absorption coefficient increases with increasing the photon energy for all films, also we note that the absorption coefficient values are greater than (104 cm^{-1}) at high photonic energies suggesting the occurrence of direct electronic transition [5]. After annealing process the absorption coefficient values decreases with increasing the annealing temperature because the annealing process helps the atoms to arrange themselves in the right direction, leading to increase in the grain size and thus the improvement in the crystal structure as well as that the annealing process leads to the removal of synthetic defects and works to reduce the dislocations density [6].

The optical energy gap (E_g) is given by the classical relation [7]:

$$\alpha h\nu = B(h\nu - E_g)^r \tag{2}$$

Where (E_g) the optical energy gap of the films, (B) is a constant and (hν) is the incident photon energy.

The optical energy gap can be estimated by plotting $(\alpha\ h\nu)^2$ versus (hν), 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 annealing temperatures of $ZnFe_2O_4$ films is shown in figure (5).

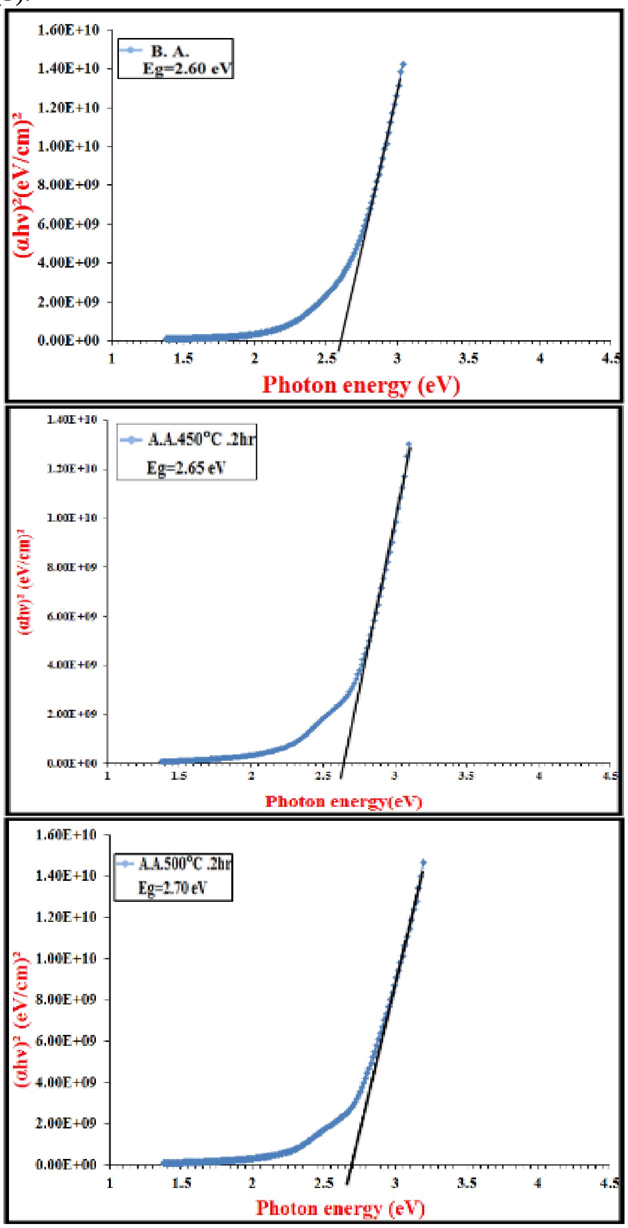

Fig. (5): Energy gap of $ZnFe_2O_4$ films before and after annealing.

Table 1: Optical energy gap of $ZnFe_2O_4$ films before and after annealing.

Thickness (500 nm)	E_g (eV)
B.A.	2.60
A.A.450 °C - 2hr	2.65
A.A.500 °C - 2hr	2.70

The optical energy gap of the films varies from (2.60 to 2.70) eV with increasing the annealing temperature. The increase in the value of the optical energy gap with the annealing temperature is attributed to the increase in the crystallization of the films and reducing the crystalline defects and thus reducing the number of energy levels between the valence band and conduction band. The values of optical energy gap are listed in table (1). 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 [8]:

$$\alpha = \alpha o \exp(h\nu/E_u) \qquad (3)$$

Where ($h\nu$) 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. Figure (6) shows the variation of ($\ln\alpha$) versus photon energy of $ZnFe_2O_4$ films before and after annealing. The E_u values were calculated as the reciprocal of the straight line slopes shown in the figure.

It is clear that Urbach energy values decrease with increasing of annealing temperature, and this means that the behavior of optical energy gap is opposite of behavior of Urbach energy. The values of Urbach energy are listed in table (2).

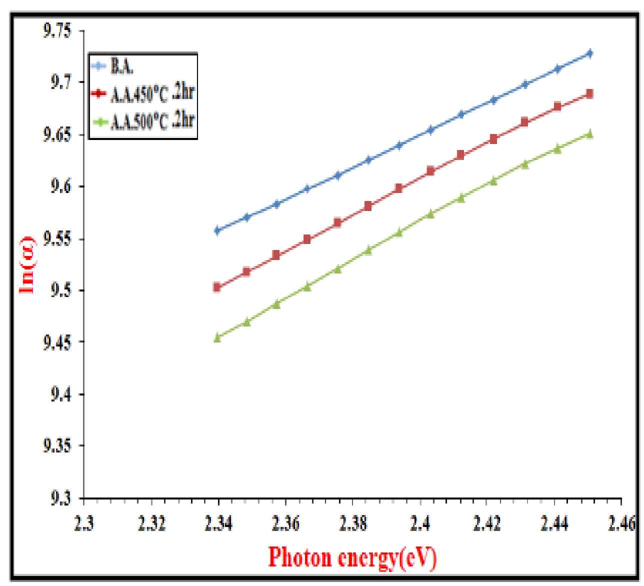

Fig. (6): Urbach energy of $ZnFe_2O_4$ films before and after annealing.

Table 2: Urbach energy of $ZnFe_2O_4$ films before and after annealing.

Thickness (500 nm)	E_u (meV)
B.A.	704
A.A.450 °C - 2hr	666
A.A.500 °C - 2hr	555

The refractive index (n_o) can be determined from the reflectance (R) by using the relation [9]:

$$n_o = \left[\left(\frac{1+R}{1-R} \right)^2 - \left(K_o^2 + 1 \right) \right]^{1/2} + \frac{1+R}{1-R} \qquad (4)$$

Figure (7) shows the variation of the refractive index with photon energy of $ZnFe_2O_4$ films before and after annealing. It is clear from this figure that the refractive index increases with increasing the photon energy and then begins to decrease for all the films; also it is noted that the values of the refractive index decrease with increasing of annealing temperature at low energies and these values increase with the annealing temperature at high energies.

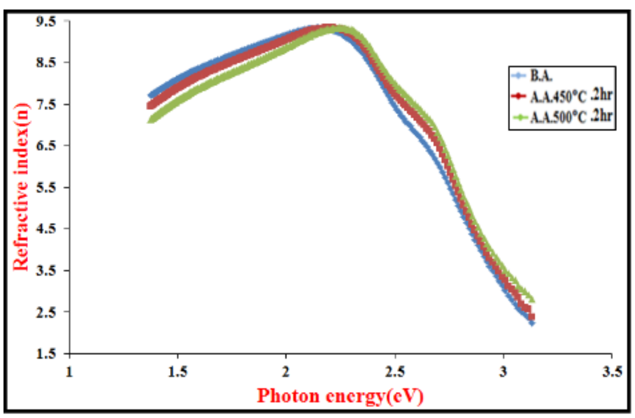

Fig. (7): Refractive index of $ZnFe_2O_4$ films before and after annealing.

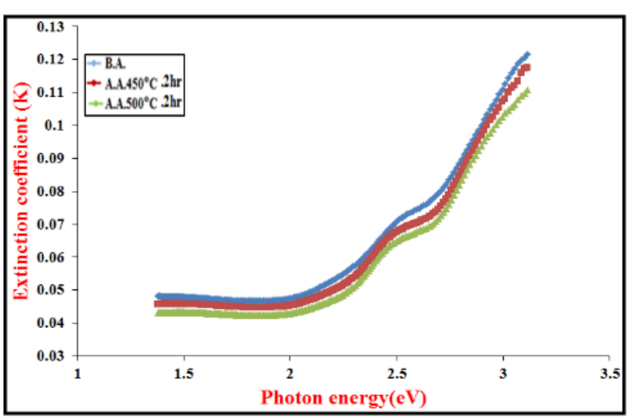

Fig. (8): Extinction coefficient of $ZnFe_2O_4$ films before and after annealing.

The extinction coefficient (k_o) can be determined by using the relation [10]:

$$k_o = \alpha\lambda / 4\pi \qquad (5)$$

Where (λ) is the wavelength of the incident photon.

Figure (8) shows the variation in extinction coefficient as a function of the photo energy of the $ZnFe_2O_4$ films before and after annealing. It can be noted that the extinction coefficient gradually increases with increasing the photon energy and then followed by a rapid increase at high photonic energies for all films, and after annealing process a decreases is noted in the values of extinction coefficient with increasing the annealing temperature. This can be attributed to the decrease in absorption coefficient with the annealing temperature.

The variation of the real (ε_1) and imaginary (ε_2) parts of dielectric constant values versus photon energy of $ZnFe_2O_4$ films before and after annealing 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) [11]:

$$\varepsilon_1 = (n_o^2 - K_o^2) \qquad (6)$$

However, the imaginary part of dielectric constant mainly depends on the extinction coefficient, which is related to the variation of absorption coefficient [12]:

$$\varepsilon_2 = (2\, n_o K_o) \qquad (7)$$

It is found that the real and imaginary parts of dielectric constant decreases with increasing the annealing temperature.

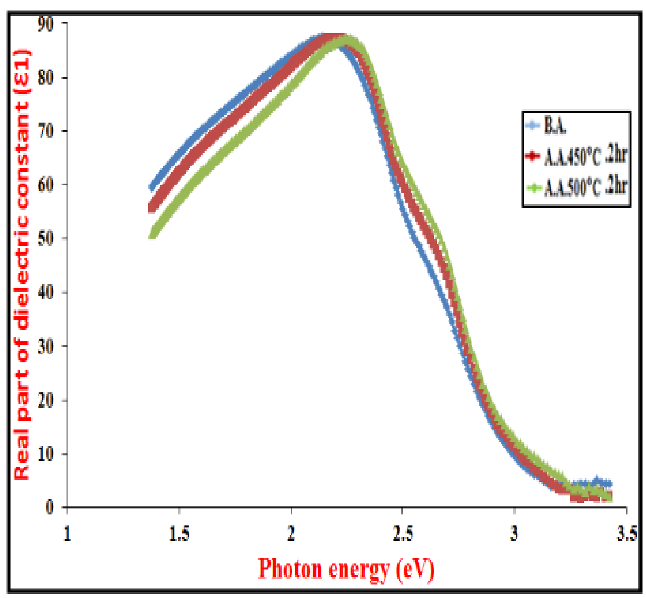

Fig. (9): Real part of dielectric constant of $ZnFe_2O_4$ films before and after annealing.

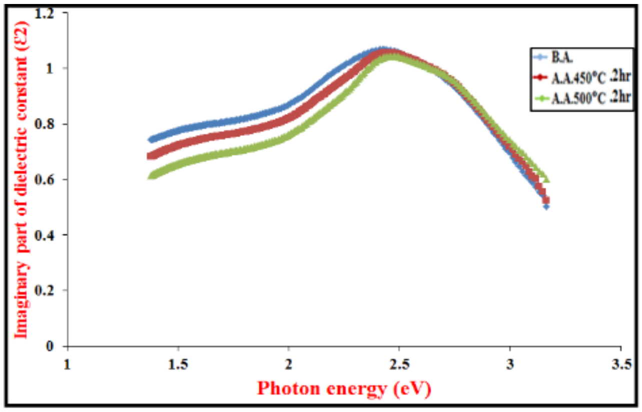

Fig. (10): Imaginary part of dielectric constant of $ZnFe_2O_4$ films before and after annealing.

The Optical conductivity (σ) can be determined by using the relation [13]:

$$\sigma = \alpha n_o c/4\pi \tag{8}$$

Where (c) is the light velocity.

Figure (11) shows the variation of the optical conductivity with the photon energy of the $ZnFe_2O_4$ films with different annealing temperatures. We noted that the optical conductivity decreases with increasing the annealing temperature.

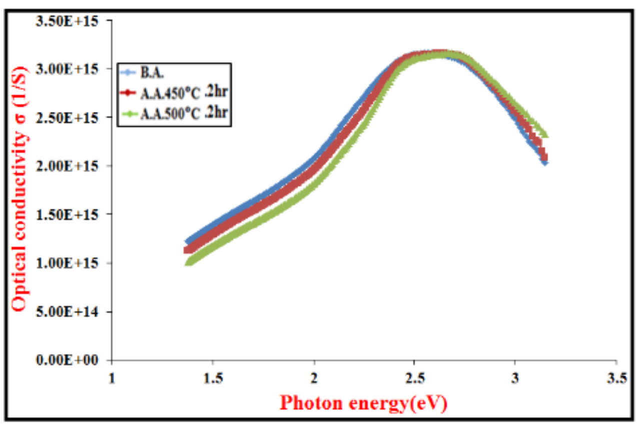

Fig. (11): Optical conductivity of $ZnFe_2O_4$ films before and after annealing.

4 Conclusions

The transmission spectra of $ZnFe_2O_4$ films increased with increasing the wavelength to reach the highest value in the visible and infrared regions at the range of wavelengths (600 - 900) nm and the transmittance increased with increasing the annealing temperature. The results showed that the optical energy gap for allowed direct electronic transition varies from (2.60 to 2.70) eV as the annealing temperature increases, the effect of annealing with different temperatures (450 and 500) ^oC for (2h) on the optical properties has shown that all the optical constants such as absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constant and optical conductivity have been affected by increasing the annealing temperature.

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