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Effect of High-Temperature Annealing on Optical Characteristics of Fe_2O_3 Thin Films Prepared by Spray Pyrolysis

Iron oxide (Fe_2O_3) has attracted plenty of interest for usage as photo-electrodes due to its low cost, in addition to its exceptionally stable in water solutions it also has a band gap of approximately 2.1 eV. Chemical pyrolysis through spraying was employed to produce thin films of it on glass surfaces, which were subsequently heated to 500 and 600 degrees for annealing utilizing a UV-visible spectrophotometer, the transmission of light and absorption in the range of wavelengths of (300-900 nm) have been verified in order to investigate the impact of annealing on certain physical characteristics. The optical band gap for thin films has been found to of Fe_2O_3 decreased from 2.86 eV before annealing to 2.78 eV at 500 ºC. Thus, it is feasible for this substance to be utilized in a wide range of technological applications, including photocatalysts and solar filters.

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1. Introduction

Due to its low cost, the 2.1 eV band gap, which is very modest, and the superior solution's aqueous stability, iron oxide (Fe_2O_3) has attracted much interest in its photo-electrode usage. However, the observed effectiveness of the photocurrent quantum of Fe_2O_3 is quite low. Additionally, Low conductivities and ineffective Fe_2O_3 photocurrent efficiencies were considered to be driven on by the recombination of holes and electrons resulting from limited hole motion and the capture of the electrons by the oxygen-deficient iron locations [1,2].

Considering its scientific applications as a catalyst, drug delivery vehicle, photocatalyst, solar filter, spin valve, recording medium, lithium-ion battery, electrochromic device, and photo-electrochemical system for hydrogen generation [3–12], the hematite Fe_2O_3 was chosen as an initial prototype. However, hematite produced by spray pyrolysis has been found to have the highest level of excellence in light response [13,14]. Amorphous oxides are used in electrochromic devices; however, crystalline oxides are important in sensors and catalysts [15-18].

This is owing to the possibility that even little variations to the chemical composition and crystalline structure of metal oxides could affect their physical characteristics. The present investigation intends to evaluate how annealing temperature degrees (500°C and 600°C) affect the optical properties of Fe_2O_3 thin films.

2. Experimental Part

An experimental glass atomizer with a 1 mm output nozzle was used for the spray pyrolysis. The films were applied to preheated glass substrates at 420°C (because this temperature produced the most homogeneous films), and the chemical solution was made by adding 4.0402 g of $Fe(NO_3)_3.9H_2O$ and 0.1 mol/L to 100 ml of deionized water. A magnetic stirrer has been utilized to ensure that the mixture is homogeneous. The optimal circumstances were as follows: average deposition is 10 cm^3/min, spray time is 15 s, pressure of 10^5 N/m^2 has been maintained for the carrier gas, which is filtered compressed air, and it has been kept 30 cm away from the substrate.

The transmittance is the ratio of the intensity of light transmitted (I) through the sample to the intensity of the incident light (I_o) and is given by the following equation [18]:

$$T = I / I_o \quad (1)$$

Equation (2) is used to estimate the absorbance (A) as [19]:

$$A = - Log\ (T) \quad (2)$$

According to the following formula, the reflectance (R) is determined [20]:

$$R + A + T = 1 \quad (3)$$

The sample thickness (t) determines the absorption coefficient (α) of the sample, that represents the reduction in the intensity of the incident ray at a particular distance towards wave propagation through a medium. The values of the absorption coefficient can be obtained from the following equation [21]:

$$\alpha = \frac{2.303A}{t} \quad (4)$$

Also, using the following equation, the energy gap (E_g) can be determined [20]:

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^r \quad (5)$$

where $h\upsilon$ is the photon energy, and r is a constant depending on the dynamics (type) of the optical transition

The quantity describing how far the energy is absorbed by a film is known as the extinction coefficient (K_0). It is also referred to as electromagnetic wave inertia inside the material. It is calculated using the following formula [21,22]:

$$K_0 = \frac{\alpha\lambda}{4\pi} \quad (6)$$

Here, λ stands for the wavelength of the absorbed photons

As a result, refractive index can be characterized as the ratio between the light velocity in vacuum to the light velocity within a material. This ratio can be calculated using the following equation [20]:

$$n_0 = \left[\frac{(1+R)^2}{(1-R)^2} - (K_0^2 + 1)\right]^{1/2} + \frac{(1+R)}{(1-R)} \quad (7)$$

Light interacts with the electrical charges in the medium owing to the polarization of these charges resulting from energy absorption. The challenging electro-static insulation constant (ε) of the medium typically describes this polarization and may be calculated as follows [20]:

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \quad (8)$$

$$\varepsilon_1 = n_0^2 - k_0^2 \quad (9)$$

$$\varepsilon_2 = 2n_0k_0 \quad (10)$$

3. Results and Discussion

Figures (1) to (7) generally indicate that at the high annealing temperature of 600°C, there was an obvious changes in the optical properties of the material, such as absorbance, extinction coefficient, absorption coefficient, and refractive index, due to some changes in the crystalline structure, which may explain the occurrence of transformations. Changes in the crystalline structure accompany phase transitions in iron oxide. Iron oxide undergoes reductions as a result of this annealing, particularly Fe_2O_3 and Fe_3O_4. As a result, phase changes and reduction at the annealing temperature of 600°C can have an impact on the material's structural characteristics and the visibility of some crystalline flaws. In turn, this alters how the shape reacts to an annealing temperature of 500°C [23-25].

Regarding the 500°C annealing temperature, it has been noticed that the absorbance increases after the annealing process and that the absorption spectra in Fig. (1) experience an immediate and rapid reduction at the wavelength of 380 nm. Concerning the absorption coefficient and extinction coefficient depicted in figures (2) and (3), it ought to be observed that both coefficients increase gradually with photon energy up to 2.3 eV; however, that they suddenly increase above that level.

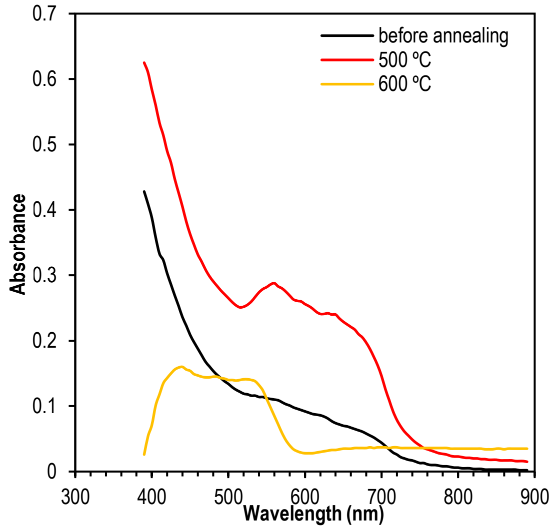

Fig. (1) Absorption spectra of Fe_2O_3 thin films before and after annealing

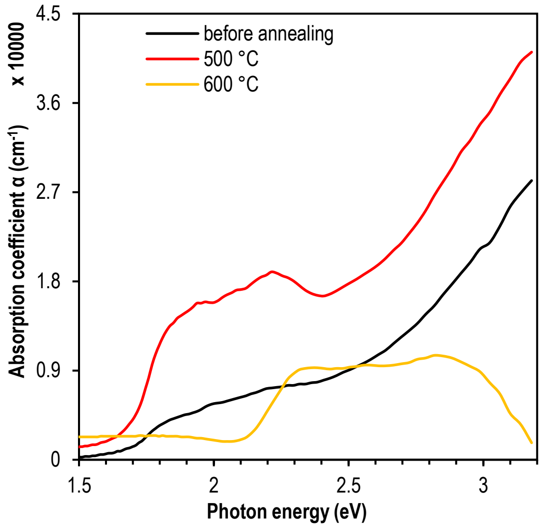

Fig. (2) Absorption coefficient as a function of photon energy of Fe_2O_3 thin films before and after annealing

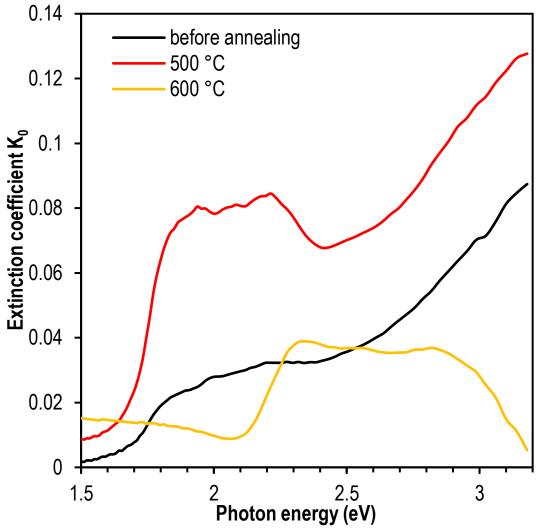

Fig. (3) Extinction coefficient as a function of photon energy for Fe_2O_3 thin films before and after annealing

The fact that the absorption and extinction coefficients increased after the annealing process indicates there were some electronic transfers between the valence and conduction bands, resulting in an obvious rise in the absorption and extinction coefficients to reach the highest value at the annealing temperature of 500°C. The same holds true for the real and imaginary dielectric constants, which are depicted in figures (4), (5), and (6), as well as the refractive index. Additionally, we see that they have grown from their pre-annealing state [27-29].

Figure (7) illustrates how the values of direct optical band gap (E_g) of Fe_2O_3 thin films were calculated by plotting the $(\alpha h\nu)^2$ versus $h\nu$ curves and extrapolating the intercept with the $h\nu$ axis. These data demonstrate that the optical band gap for Fe_2O_3 thin films decreased from 2.86 eV prior to annealing to 2.78 eV after annealing at 500°C temperature. This indicates that an increase in the annealing temperature resulted in a displacement of the absorption edge towards the lower energy [30-32].

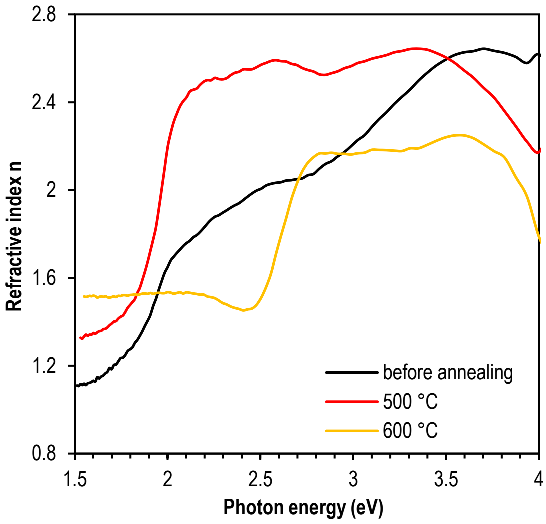

Fig. (4) Refractive index as a function of photon energy for Fe_2O_3 thin films before and after annealing

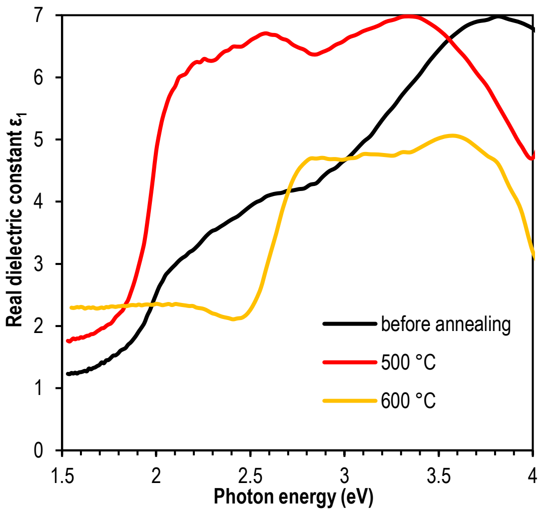

Fig. (5) Real dielectric constant as a function of photon energy for Fe_2O_3 thin films before and after annealing

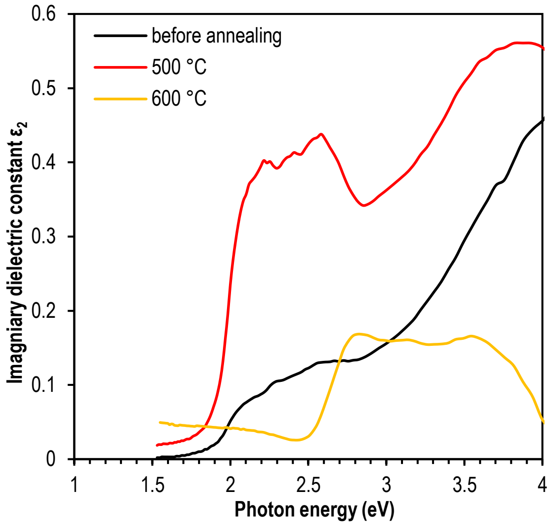

Fig. (6) Imaginary dielectric constant as a function of photon energy for Fe_2O_3 thin films before and after annealing

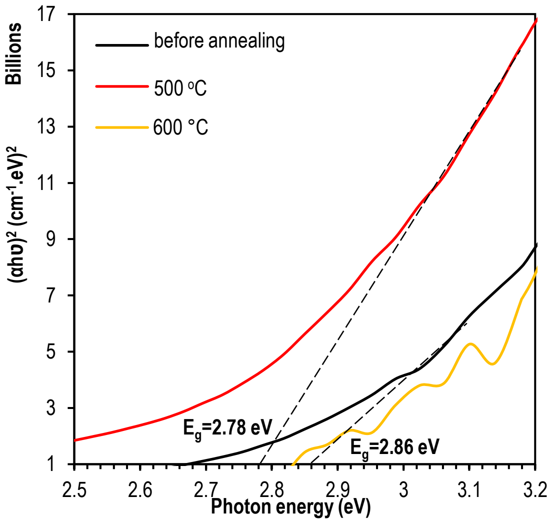

Fig. (7) Variation of $(\alpha h\upsilon)^2$ with photon energy for Fe_2O_3 thin films before and after annealing

4. Conclusions

Chemical spray pyrolysis has been utilized for preparing Fe_2O_3 thin films and the impact of annealing on their optical characteristics was investigated. It was observed that the appearance of various modifications in the crystalline structure of the iron oxide films causes the behavior of the optical properties curve to behave differently at the high annealing temperature of 600°C than it does at the low annealing temperature of 500°C. During annealing at 500°C, we see that the optical coefficients have increased beyond their initial values. The band gap dropped from 2.86 to 2.78 eV after annealing at 500°C and the optical coefficient significantly increased. As a consequence, this substance is able to be used in a broad range of technological applications, including solar filters, photocatalysts, and other fields.

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