Study the Effect of Substrate Temperature on the Optical Properties of CoFe₂O₄ Films Prepared by Chemical Spray Pyrolysis Method

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Abstract: Cobalt Ferrite CoFe₂O₄ thin films have been deposited by chemical spray pyrolysis method (CSP) on glass substrates at different substrate temperatures (300, 350, 400 and 450°C) with an interval of (50°C) using Cobalt Nitrate and Ferric Nitrate as Cobalt and Iron sources respectively, at thickness (400±20) nm. The effect of substrate temperatures change 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 decreases in transmittance and increases in absorbance with increasing the substrate temperatures. The optical energy gap for allowed direct electronic transition was calculated and it was found that decreases with increasing the substrate temperatures (2.40 -2.22 eV), the Urbach energy increases with increasing the substrate temperatures and it is values range between (634.6-700.5) meV. 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.

1. INTRODUCTION

Ferrites are chemical compounds which are composed of a ceramic material and Iron Oxide as their main component. A ferrimagnetic ceramic compound, ferrites, has a spinel type structure. The magnetic property of the ferrite is due the structure and the distribution arrangement of the ions in the sub lattice. Most of the ferrite have a spine structure with formula (AB₂O₄), where "A" are divalent ions such as Mg²⁺, Co²⁺, Ni²⁺, Mn²⁺, and "B" are the trivalent ions such as Fe³⁺ and Al³⁺. Spinel's structure have an oxygen ion sub-lattice, in cubic close-packed arrangement with captions occupying various combinations of the octahedral (O) and tetrahedral (T) sites. The cubic unit cell contains (8) formula units and containing (32) O and (64) T sites [1].

Among all spinel ferrite materials, Cobalt Ferrite CoFe₂O₄ is categorized in to a hard magnetic due to its high coercivity and moderate magnetization. Due to its high magnetic coercivity value and good physical and chemical stability it has been used for various applications. Cobalt Ferrite (CoFe₂O₄) neither has a spinel or invers spinel structure. It has partially inverse spinel structure [Co²⁺Fe⁺¹-k⁻³⁺] (Co₁-k²⁻Fe¹-k⁻³⁺) O₄ having a coercively value of (1000) one and moderate magnetization of (50 emu/g). Due to its high value, they become a perfect for using in high density magnetic storage materials, ferrofluids, medical diagnosis, magneto-mechanical, and torque sensors [2].

2- EXPERIMENTAL PROCEDURE

The Cobalt Ferrite CoFe₂O₄ thin films with different substrate temperatures (300, 350, 400 and 450°C) at thickness (400±20) nm were grown by using the chemical spray pyrolysis technique. The spray solution was prepared by mixing (0.1M) aqueous solution of Cobalt Nitrate (Co(NO₃)₂.6H₂O) and (0.1M) aqueous solution of Ferric Nitrate (Fe(NO₃)₃.6H₂O) the prepared solution was sprayed on glass substrates at different substrate temperatures (300, 350, 400 and 450°C) with an interval of (50°C). 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
substrate temperatures 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).

3. RESULTS AND DISCUSSION

The transmittance spectra of the CoFe$_2$O$_4$ films with different substrate temperatures are shown in figure (1). It can be seen that the transmittance of the films decreases with increasing the substrate temperatures. The reason for this is the increase in scattering of light due to the increase in surface roughness with increasing the substrate temperature [3].

![Fig. (1): Transmittance spectra of the CoFe$_2$O$_4$ films with different substrate temperatures.](image1)

The absorbance spectra of the CoFe$_2$O$_4$ films with different substrate temperatures are shown in figure (2). It is clear that the absorbance increases with increasing the substrate temperature because, more atoms are present so more states will be available for the photons to be absorbed [4].

![Fig. (2): Absorbance spectra of the CoFe$_2$O$_4$ films with different substrate temperatures.](image2)

The following relation can be used for calculating the reflectance (R) [5]:

\[
R = \frac{1}{T^2} + \frac{S}{A} - 1
\]
A+T+R=1

(1)

Figure (3) shows the reflectance as a function of the photon energy of the CoFe$_2$O$_4$ films with different substrate temperatures.

The following relation can be used for calculating the absorption coefficient ($\alpha$) [6]:

$$\alpha = 2.303 \frac{A}{t}$$  (2)

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

From figure (4) it can be observed that the absorption coefficient of the CoFe$_2$O$_4$ films increases with increasing the substrate temperatures. 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 [7].

The optical energy gap ($E_g$) is given by the classical relation [8]:

$$\alpha h\nu = B(h\nu - E_g)^r$$  (3)
Where \( E_g \) is the optical energy gap of the film, \( B \) is a constant and \( (h\nu)^2 \) 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 substrate temperatures of CoFe\(_2\)O\(_4\) films is shown in figure (5). The optical energy gap of the films varies from 2.40 to 2.22 eV as substrate temperatures increases [9]. 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).

Figure (6) shows the optical energy gap of CoFe\(_2\)O\(_4\) films as a function of substrate temperatures.

Fig. (5): Optical energy gap of CoFe\(_2\)O\(_4\) films with different substrate temperature.
Table (1): Values of optical energy gap of CoFe$_2$O$_4$ films with different substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate temperatures ($^\circ$C)</th>
<th>$E_g$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.40</td>
</tr>
<tr>
<td>350</td>
<td>2.37</td>
</tr>
<tr>
<td>400</td>
<td>2.28</td>
</tr>
<tr>
<td>450</td>
<td>2.22</td>
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Fig.(6): Optical energy gap of CoFe$_2$O$_4$ films as a function of substrate temperatures.

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 [10]:

$$\alpha = \alpha_o \exp\left(\frac{E}{E_u}\right)$$

(4)

Where (E) is the photon energy, ($\alpha_o$) 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 (7) using relationship:

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

(5)

Figure (7) shows the variation of (In$\alpha$) versus photon energy of CoFe$_2$O$_4$ films with different substrate temperatures. It is clear that Urbach energy increases with increasing the substrate temperature. That the increase in Urbach energy indicate that the localized levels in the optical energy gap increased with increasing the substrate temperatures. The values of Urbach energy are listed in table (2).
Figure (8) shows the Urbach energy of CoFe$_2$O$_4$ films as a function of substrate temperatures.

![Figure 8](image)

**Fig. (7):** Urbach energy of CoFe$_2$O$_4$ films with different substrate temperatures.

**Table (2):** Values of Urbach energy of CoFe$_2$O$_4$ films with different substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate temperatures (°C)</th>
<th>Eu (meV)</th>
</tr>
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<tbody>
<tr>
<td>300</td>
<td>634.6</td>
</tr>
<tr>
<td>350</td>
<td>645.9</td>
</tr>
<tr>
<td>400</td>
<td>668.8</td>
</tr>
<tr>
<td>450</td>
<td>700.5</td>
</tr>
</tbody>
</table>

**Fig. (8):** Urbach energy of CoFe$_2$O$_4$ films as a function of substrate temperatures.

The refractive index ($n_o$) can be determined from the reflectance (R) by using the relation [11]:

\[ n_o = \frac{1}{2} \left( \frac{R_{max}}{R_{min}} \right) \]
\[ n_o = \left[ \left( \frac{1+R}{1-R} \right)^2 - (K_o^2 + 1) \right]^{1/2} + \frac{1+R}{1-R} \]  \hspace{1cm} (6)

Figure (9) shows the variation of the refractive index with the photon energy of the CoFe$_2$O$_4$ films with different substrate temperatures. It is clear from this figure that the refractive index of these films slightly increases with increasing the substrate temperatures. The reason is due to the reflectivity and the optical energy gap of the films. The refractive index measurements can have a correlation with the electrical properties of the prepared films.

Fig. (9): Refractive index of CoFe$_2$O$_4$ films with different substrate temperatures.

The extinction coefficient ($k_o$) can be determined by using the relation [12]:

\[ k_o = \alpha \lambda / 4\pi \]  \hspace{1cm} (7)

Where ($\lambda$) is the wavelength of the incident photon.

Figure (10) shows the variation in extinction coefficient as a function of the photo energy of the CoFe$_2$O$_4$ films with different substrate temperatures. It can be noticed that the extinction coefficient increases as the substrate temperatures increasing. This is attributed to the increases in absorption coefficient as the substrate temperatures increasing.
Fig.(10): Extinction coefficient of CoFe$_2$O$_4$ films with different substrate temperatures.

The variation of the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric constant values versus photon energy of CoFe$_2$O$_4$ films with different substrate temperatures are shown in figures (11) and (12) 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 ($n_o^2$) [13]:

$$\varepsilon_1 = n_o^2 - k_o^2$$  \hspace{1cm} (8)

However, the imaginary part of dielectric constant is mainly depends on the extinction coefficient, which is related to the variation of absorption coefficient [14]:

$$\varepsilon_2 = 2n_0k_o$$ \hspace{1cm} (9)

It is found that the real and imaginary parts of dielectric constant increases with increasing of substrate temperatures.

Fig.(11): Real part of the dielectric constant of CoFe$_2$O$_4$ films with different substrate temperatures.
CONCLUSIONS

The transmittance spectra of the CoFe$_2$O$_4$ films decreases with increasing the substrate temperatures. The results showed that the optical energy gap for allowed direct electronic transition decreases with increasing the substrate temperatures and varies from 2.40 to 2.22 eV, and the detailed study the effect of substrate temperatures 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 substrate temperatures. The Urbach energy increasing the with increasing the substrate temperatures and it is values range between (634.6-700.5 meV).

References


