The Effect of Thickness on Electrical Conductivity and Optical Constant of Fe_2O_3 Thin Films

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Abstract

In this research the electrical conductivity and optical measurements were made on the Iron Oxide (Fe_2O_3) films prepared by chemical spray pyrolysis method as a function of thickness (250, 350, 450, and 550) ± 20 nm.

The measurements of electrical conductivity (σ), activation energies (Ea_1, Ea_2),and optical constant such as absorption coefficient, refractive index, extinction coefficient and the dielectric constants for the wavelengths in the range (300-900) nm have been investigated on (Fe_2O_3) thin films as a function of thickness. All films contain two types of transport mechanisms, and the electrical conductivity (σ) increases whereas the activation energy (Ea) would decrease as the films thickness increases.

The optical measurement shows that the Fe_2O_3 films have a direct energy gap, and they in general increase with the increase of thickness.

Key words: - Iron Oxide, Electrical Conductivity, Optical Constant, chemical spray pyrolysis

Introduction

One of the most important metal oxide is Iron Oxides because these materials are useful for many applications such as important sensors, catalysts, resistive heaters, electrochemical and photocells [1,2],the performance of materials depends on their properties which are affected by preparation condition. Iron Oxide (Fe_2O_3) is a low-cost semiconductor having hexagonal structure, a relatively low band gap of (2-2.2) eV, therefore it can absorb most of the visible light [3] and can be used for potential application as photo anodes in photo electrochemical solar cells [4,5]as well as are widely employed for semi-reflective glasses, not only because of their energy saving effect but also because of their good durability as a glazing of building. [6]

Electrical and magnetic properties of Fe_2O_3 are strongly dependent on the chemical composition, and method of preparation[1], several methods of deposition techniques have been used by different workers to prepare Fe_2O_3 films such as chemical vapor deposition[4,7], spray pyrolysis[8,9], pulsed laser deposition[10,11], electro chemical deposition[12,13], electro spray technique[14] ,rapid combustion[15], ect.

In this research the chemical spray pyrolysis technique was used to prepare Fe_2O_3 thin films, the electrical conductivity behavior and optical constants are studied as a function of thickness.

Experiment

Iron Oxide (Fe_2O_3) thin films are prepared by chemical spray pyrolysis method at different thickness (250, 350, 450, and 550) nm by spraying the solution of $Fe(No_3)_3.9H_2O$ on preheated glass substrates at about (663) K which measured by using thermocouple type NiCr , these glass substrates are placed on the hot plate for about (25 min) before the spraying process, each spraying period lasts for about (15 sec) followed by (2.5 min) waiting period to a void excessive cooling of the hot substrate due to the spraying process. The distance between sprayer nozzle and substrate of (30) cm, spray rate of (12 ml/min).

The solution was prepared in molarity (0.1) by diluted (4.0402) gm of $Fe\ (No_3)_3.9H_2O$ in (100) ml water accordance with the following equation: [16]

$$M = (W_t / M_{wt}).(1000 / V) \quad \text{……………………… (1)}$$

Where M = molarity, W_t = weight of sample, M_{wt} = molecular weight, V = water volume.

The obtained solution is used to preparation (Fe_2O_3) based on the reaction:-

$$4Fe(NO_3)_3 \xrightarrow{heat} 2Fe_2O_3 \downarrow +12NO_2 \downarrow +3O_2 \downarrow \quad \text{…………… (2)}$$

The films were clear, red-brown colored and having good adhesive properties.

For D.C. measurement films deposited on the glass substrate with Al electrode Keithly models 616 have been used to measure the variation of electric resistance (R) as a function of temperature with range (298- 473) K, then calculated the resistivity (ρ) by the formula: - [17]

$$\rho = \frac{R \cdot b \cdot t}{L} \quad \text{……………………………………… (3)}$$

Where t is film thickness, b is electrodes width; L is distance between two Al electrodes.

The conductivity (σ) of the films was determined by using the relation:-

$$\sigma_{d.c} = \frac{1}{\rho} \quad \text{………………………………………… (4)}$$

For optical parameters measurement of the prepared thin film, we measured the transmission and the absorption spectrum in the range (200-900) nm by using a double beam spectrophotometer (UV).

The incident photon energy (E=hν) was calculated as a function of wavelength (λ) according to equation:

$$E\ (eV) = (1240 / \lambda) \quad \text{.....................} (5)$$

The energy dependence of absorption coefficient (α) near the band edge for band to band and exciton transition could be described by Tauc formulas: [18]

$$(\alpha h\nu) = B`\ (h\nu - Eg^{opt})^{r} \quad \text{...................} (6)$$

Where B` is a constant inversely proportional to amorphousity, (Eg^{opt}) is the optical energy gap ,r is constant depending on the material and the type of the optical transition and may take values 2,3 for allowed and in allowed direct transitions respectively whereas take values 1/2,3/2 for allowed and in allowed indirect transitions respectively.

The variation of absorption coefficient for each wavelength was calculated from equation: [19]

$$\alpha = 2.303\ (A / t) \quad \text{...................} (7)$$

Where A = absorbance.

Also transmittance (T) and absorbance (A) spectrum used to determine the optical constants which including refractive index (n), extinction coefficient (k), and dielectric constant (ε) for each wavelength in the range (200-900) nm.

The refractive index value can be calculated from the formula: [17]

$$n = \{[4R / (R-1)]-k^2\}^{1/2} - [(R+1) / (R-1)] \quad \text{....................} (8)$$

Where R is the reflectance which is calculated by using equation:

$$R = 1-T-A \quad \text{...............................} (9)$$

The absorption coefficient (α) is related to extinction coefficient (k) by: [17]

$$\alpha = 4\pi k / \lambda \quad \text{...........................} (10)$$

The complex dielectric constant can be introduced by: [17]

$$\varepsilon = \varepsilon_1 - i\,\varepsilon_2 \quad \text{.............................} (11)$$

Where $$\varepsilon_1 = n^2-k^2 \quad \text{.............................} (12)$$

$$\varepsilon_2 = 2nk \quad \text{.............................} (13)$$

Where ε_1= real part of dielectric constant, ε_2 = imaginary part of dielectric constant.

The thickness of the sprayed samples (250, 350, 450, and 550) nm was measured by using the weighing method according to the following relation: [20]

$$t = (m / à\ .\rho) \quad \text{.........................} (14)$$

Where t= thickness of film, m= mass of film, ρ= density of films, à= area of film. Using a sensitive balance whose sensitivity is of the order (10^{-4}) gm.

Results and Discussion

Fig (1) shows the plots of lnσ versus $10^3/T$ at different thickness for (Fe_2O_3) films, It is observed that the electrical conductivity (σ) increases from ($3.01*10^{-7}$) $ohm^{-1}.cm^{-1}$ to ($9.09*10^{-7}$) $ohm^{-1}.cm^{-1}$ with the increase of (t). The increase trend in σ upon increasing thickness can be attributed to the increases number of carriers available for transport due to improvement in the films structure with the increase of (t) it yields more packing density, reducing dangling bonds, the trapping centers of charge carriers, and defects like vacancy sites. This figure also shows two mechanisms for electrical conductivity at lower and higher temperature with two values of activation energy (Ea_1, Ea_2) for all films. The effect of the film thickness on the activation energies (Ea_1, Ea_2) of (Fe_2O_3) films are shown in Fig (2), it is clear from this figure that both Ea_1 and Ea_2 decrease with the increase of thickness (t), this behavior can be attributed for the same reasons as we mentioned before. Table (1) shows the values of the electrical conductivity and the activation energies of deposited films.

The influence of different thickness on the optical properties of Fe_2O_3 thin films grown on glass substrates are studied deeply. The variation of the absorption coefficient (α) of (Fe_2O_3) films as a function of photon energy at various thicknesses (250, 350, 450, and 550) nm is shown in Figure (3), where a decrease in absorption coefficient with the increase of thickness (t) within all the range of the spectrum; we deduce that the absorption is not attributed to the free carriers only, but to impurities or localized electronic states. It could be recognize that all the films exhibits high values of absorption coefficient ($\alpha > 10^5$ cm^{-1}) which means that there is a large probability of the allowed direct transition.

Fig (4) and table (2) show the optical energy gap as a function of thickness (t).The optical energy gap (Eg^{opt}) values were calculated from Tauc equation (6) by plotting the relation $(\alpha h\nu)^2$ versus photon energy (hν) and select the optimum linear part, which describes the allowed direct transition, then we determined Eg^{opt} by the extrapolation of the portion at (α =0) as shown in fig (5). It is clear that the Eg^{opt} increased from (2.34 eV) to (2.42 eV) when the thickness increased. This increase in energy gap value leads to shift in the band gap to shorter wavelength. This may be due to the fact that the decrease of the density of localize states in the Eg which caused the energy gap seems large. Other factors, such as the reduction in the number of defects in films and the increases in stoichiometric composition, might also lead to the increase in the optical band gap.

The variation of the refractive index values (n) versus photon energy (hν), at different thickness (250, 350, 450, and 550) nm as given in Fig (6), it is obvious from result that the refractive index values increase with the increase of thickness, this behavior may be due to improvement in the films structure ,reducing of dangling bonds and defects like vacancy sites, it yields more packing density. The values of the refractive index of these films range from (2.45 to 2.74) at λ = 450 nm.

Extinction coefficient (k) versus photon energy as a function of thickness is shown in Fig (7), the decrease in extinction coefficient values could be recognized with the increase of thickness, this behavior of the extinction coefficient values similar for all the range of the wavelength spectrum to that of the absorption coefficients for the same reasons as we mentioned before.

Fig (8 a, b) shows the effect of different thickness on the values of the real (ε_1) and imaginary (ε_2) parts of the dielectric constant. From this figure we can notice that the real part of the dielectric constant (ε_1) increase with the increase of thickness in all the range of the spectrum while the imaginary part of the dielectric constant (ε_2) showed an opposite trend because the variation of (ε_1) mainly depend on the value of the refractive index while the (ε_2) value mainly depend on the extinction coefficient values which are related to the variation of absorption coefficient.

Conclusion

In conclusion, we studied in detail the influence of film thickness on the electrical conductivity and optical constant of (Fe_2O_3) films. Throughout our research we showed that:-

1. The electrical conductivity are strongly dependent on the film thickness, it shows as increasing behavior with the increase of thickness, whereas the activation energies showed an opposite trend. We should mention that the behavior of the electrical conductivity as a function of thickness is a result of the community between two mechanism of transport, hopping charge transport between localized gap states near Fermi level and charge transport to extended state beyond the mobility gap.
2. All films prepared have high values of absorption coefficient ($\alpha > 10^5$ cm^{-1}) .We can use (Fe_2O_3) films as a window for wavelength ($\lambda > 450$ nm) and as Filter for wavelength ($\lambda < 450$ nm).
3. The optical energy gap values increase when films thickness increases
4. The variation in films thickness resulted increase values of refractive index and real part of the dielectric constant while decrease the values of the absorption coefficient, extinction coefficient, and the imaginary part of the dielectric constant when films thickness increases.

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Table No. (1) :The electrical conductivity and activation energies of (Fe_2O_3) films at different thickness

Films thickness (nm)	σ x 10^{-7} at R.T $(\Omega.cm)^{-1}$	Ea_1 (eV)	Tem. rang (K)	Ea_2 (eV)	Tem. rang (K)
250	3.01	0.894	298-393	0.192	403-473
350	4.96	0.802	298-393	0.173	403-473
450	6.611	0.722	298-393	0.144	403-473
550	9.09	0.621	298-393	0.125	403-473

Table No. (2):The optical constant of (Fe_2O_3) films at different thickness.

Films thickness (nm)	Eg^{opt} (eV)	Optical constant at λ =450 nm				
		α x 10^5 cm^{-1}	n	k	ε_1	ε_2
250	2.34	0.871	2.453	0.195	2.41	0.613
350	2.37	0.827	2.5	0.188	2.533	0.602
450	2.4	0.8	2.615	0.174	2.73	0.581
550	2.42	0.77	2.74	0.163	2.966	0.564

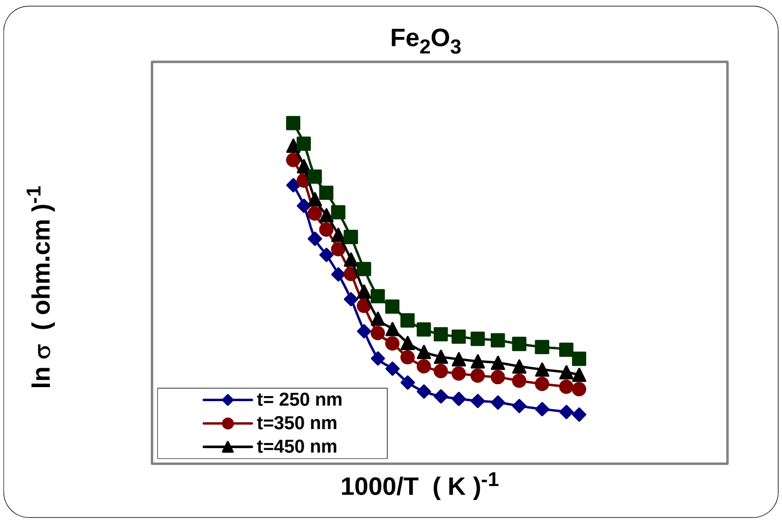


Figure No.(1): Variation lnσ versus 10^3/T as a function of thickness for (Fe_2O_3) films

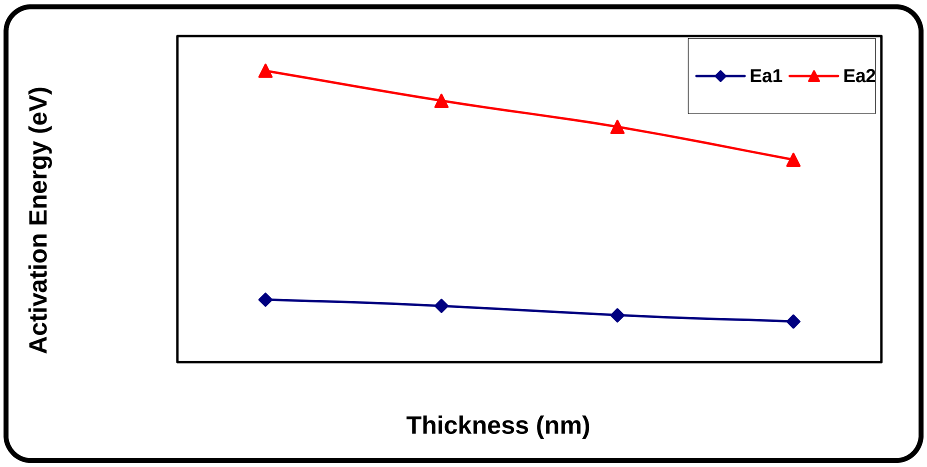


Figure No.(2): Variation activation energies as a function of thickness for (Fe_2O_3) films

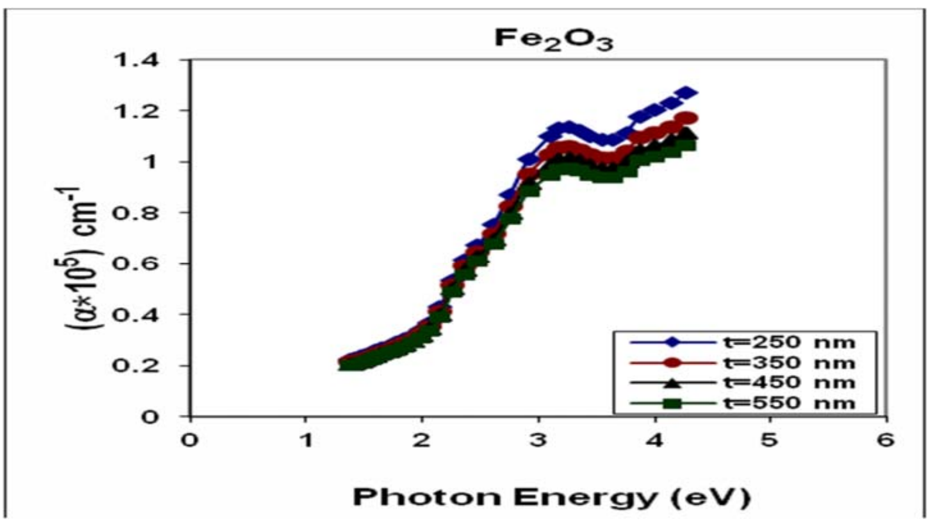


Figure No.(3): Absorption coefficient behavior as a function of photon energy for (Fe_2O_3) thin films deposited at different thickness

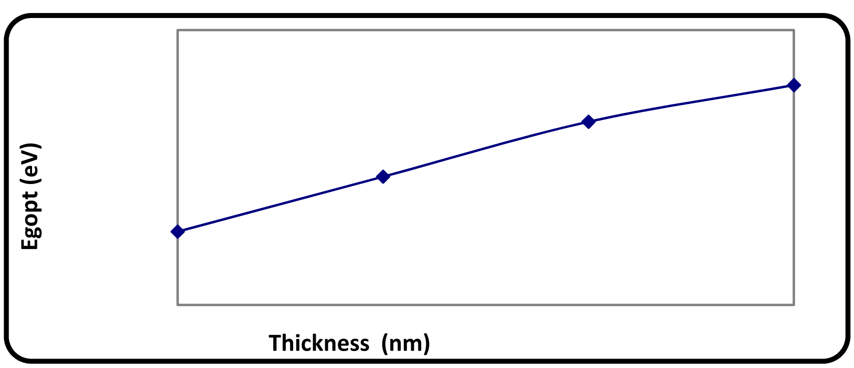


Figure No.(4): Variation optical energy gap as a function of thickness for (Fe_2O_3) films

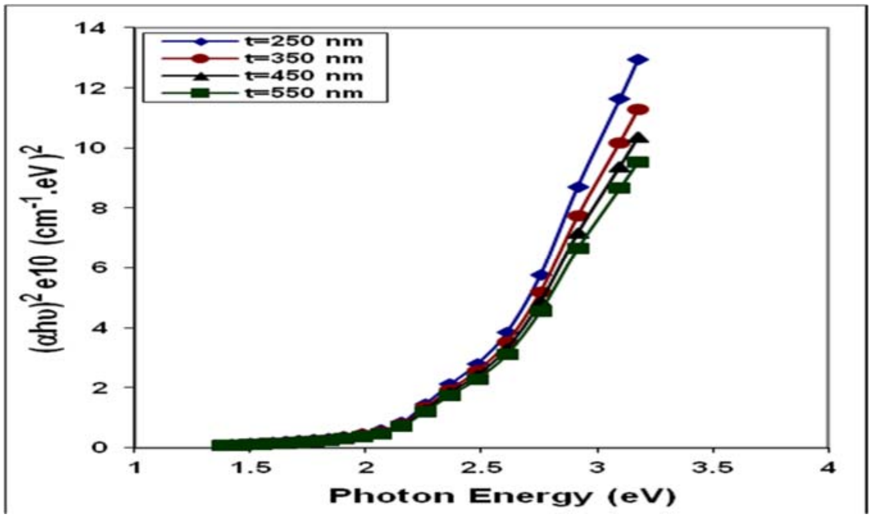


Figure No.(5): Variation $(\alpha h\nu)^2$ & photon energy as a function of thickness for (Fe_2O_3) films

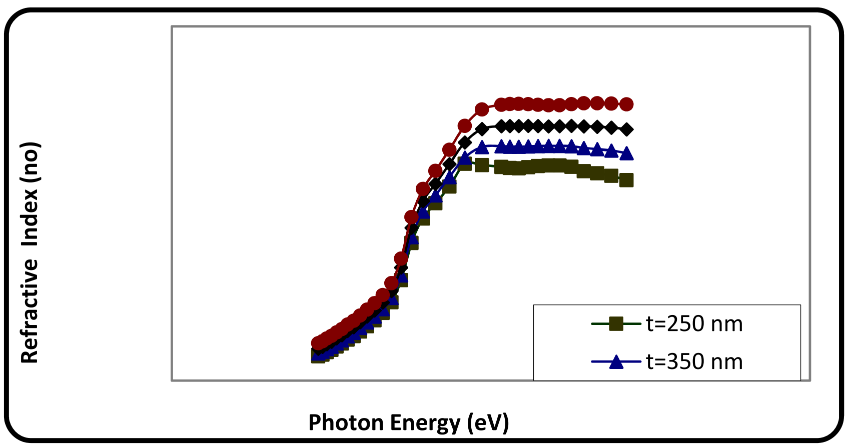


Figure No.(6): Variation refractive index & photon Energy as a function of thickness for (Fe_2O_3) films

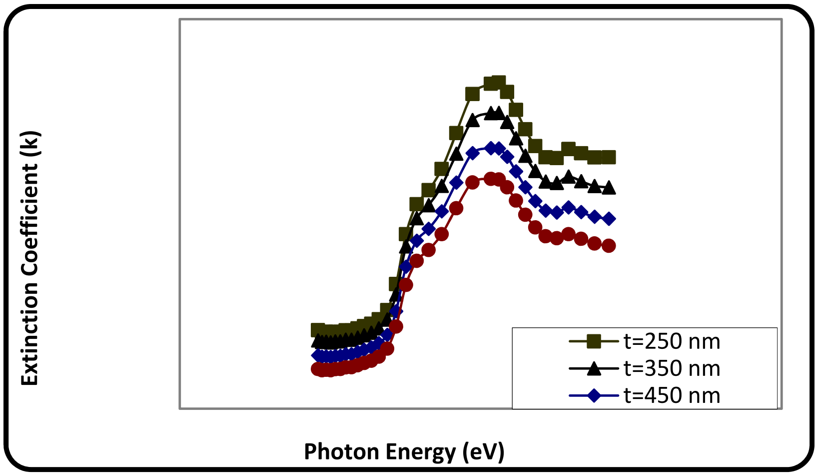
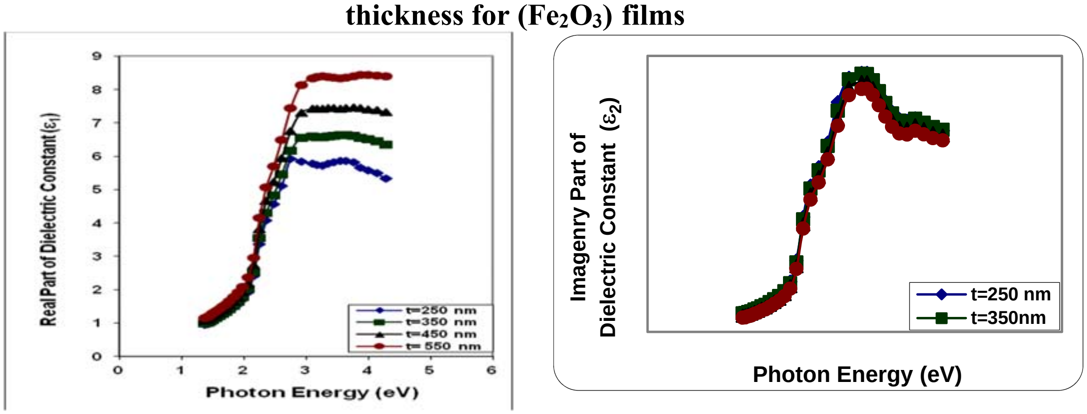


Figure No.(7): Variation extinction coefficient & photon Energy as a function of thickness for (Fe_2O_3) films



(a) **(b)**

Figure No.(8): dielectric constant of (Fe_2O_3) thin films & photon energy:-

(a) Real part at different thickness. (b) Imaginary part at different thickness.

تأثير السمك على التوصيلية الكهربائية والثوابت البصرية لأغشية Fe_2O_3 الرقيقة

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الخلاصة

في هذا البحث أجريت القياسات البصرية والتوصيلية الكهربائية لاغشية أوكسيد الحديد (Fe_2O_3) المحضرة بطريقة الرش الكيميائي الحراري دالة لتغير السمك (250, 350, 450, and 550) ± 20 nm. ولقد حسبت التوصيلية الكهربائية (σ), وطاقات التنشيط (Ea_1, Ea_2), والثوابت البصرية مثل معامل الامتصاص ومعامل الخمود وثابت العزل الكهربائي ضمن مدى الاطوال الموجية nm (300-900) لاغشية (Fe_2O_3) دالة لتغير السمك , وقد أظهرت كل الاغشية آليتين للانتقال الالكتروني ولوحظ زيادة التوصيلية الكهربائية مع نقصان طاقات التنشيط بزيادة سمك الاغشية المحضرة. وبينت القياسات البصرية ان لاغشية (Fe_2O_3) فجوة طاقة مباشرة وتزداد قيمتها بصورة عامة بزيادة السمك.

الكلمات المفتاحية :- أوكسيد الحديد ، الثوابت البصرية، التوصيلية الكهربائية ، الرش الكيميائي الحراري .