Effect OF Film Thickness And Annealing Time On Structural And Optical Propertieis Of The Oxides (Fe_2O_3), (Co_3O_4) And Their Mixtures

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Abstract

Thin film technology is one of the most important technologies that have contributed to the development of semiconductors and their applications in several industrial fields. The Iron Oxides (Fe_2O_3) and (Co_3O_4) thin films and their applications are of importance, in that these two materials are considered as important industrial materials , and used in spectrally selective coating, temperature sensors, resistive heaters, and photo cells.

Thin films of Iron Oxide (Fe_2O_3), Cobalt Oxide (Co_3O_4) and their mixtures in different ratios (75:25, 50:50, 25:75) were prepared by the method of chemical spray pyrolysis deposition at different thicknesses ($77< t <200$) nm on cover-glass substrates: thickness of (1) mm at temperature (653)°K, and at temperature (753)°K for (one, and two) hour. The nature of the thin-films' surfaces are examined by optical microscopy, while the crystallinity of the compounds is examined by X-ray diffraction (XRD).

The results of (XRD) have shown that the films of (Fe_2O_3) and (Co_3O_4) and their mixtures are of amorphous structure. Annealing operations led to transition of the films' structure from the amorphous to polycrystalline state. These obtained results were found in agreement with the American Standard for Testing Materials (ASTM). Film thickness, and annealing time were investigated, the results show the crystallite size increases with the increase of the thickness of the thin film. .

The increase in the annealing time for more than one hour resulted in the appearance of some peaks in diffraction spectrum of the prepared films. This verifies that it is polycrystalline, and this increases the time to organize itself in the crystalline lattice and decreases the crystalline defect. This research also included the study of the optical properties of the prepared samples by recording the absorption and transmission spectrum over the spectral range (200-900) nm, the optical energy gap for the allowed direct transition was evaluated. In general, the optical energy gap decreases with increase of the film thickness percentage of (Co_3O_4) in the sample, and it increases after annealing.

The optical parameters are investigated and calculated such as optical absorption coefficient, photon energy, and the width of localized states too. It is found that the values of absorption coefficient the increases with increasing percentage of (Co_3O_4).

Key word: Spray deposition, Thickness, Iron, Cobalt.

Introduction

Thin film science and technology have gone through a thorough development which results in numerous new devices (e.g. Light Emitting Diodes (LED), fuel cells and solar cells) and new materials with fundamentally new properties. Thin film research shares the knowledge from multi-disciplines (e.g. materials science, chemistry, solid state physics, mechanics,...etc.). It has also given a clear picture of its physical properties and crystal structure. Several methods were used in the preparation of the thin films (1).

The processes that occur at the surfaces and in thin films, are based on teaching and research over a number of years. Many of the experimental techniques used to produce clean surfaces, and to study the structure and composition of solid surfaces, have been around for about a generation. Over the same period, we have also seen unprecedented advances in our ability to study materials in general, and on a microscopic scale in particular, largely due to the development and availability of many new types of powerful microscope (2).

The major industries which are related to surface and thin film science are the micro – electronics, opto-electronics and magnetic industries, and the chemistry – based industries, especially those involving catalysis and the emerging field of sensors. These industries form society's immediate need for investment and progress in this area, but longer term goals include basic understanding, and new techniques based on this understanding; there are few areas in which the interaction of science and technology is more clearly expressed (3).

The high performance of modern optical instruments depends upon the quality of components such as lenses, prisms and mirrors. All of these reflecting or partially reflecting surfaces, and their performance would be limited by the natural reflect ivies of the materials of which they are made, were not for the possibility of altering the reflectivity by the deposition of a thin transparent film. This technique allows, for instance, the control of losses due to reflection in lenses, and makes possible the construction of mirrors with unique properties. The method is even more useful in equipment designed to utilize infra-red radiation, since reflection losses are much greater in the infra-red than in visible part of the spectrum (4).

The examination of surface chemistry by Auger and photoelectron spectroscopy can trace its roots back to cloud chambers in the 1920 and even to Einstein's 1905 paper on the photo – electric effect. But the real credit arguably belongs to e many scientists in the 1950 and 1960 who harnessed the new ultra – high vacuum (UHV) technologies for the study of clean surfaces and surface reactions with adsorbents ,and the production of thin films under well – controlled conditions; In the past 30 years, the field has expanded and the 'scientific generation' was quite short; different sub – fields were developed often based on the expertise of groups who have started literally a generation ago(5).

Iron compounds are the most common coloring agents in ceramics , iron exhibits so many forms with different kiln atmospheres, temperatures, and firing cycles, and with different glaze chemistries that places it among the most exciting of all materials. Chemically, iron is amphitricha like alumina. (Fe_2O_3) generally behaves as a refractory anti-flux material in a glaze melt, combining with alkalis. Oxidation iron-red glazes, for example, can have very low alumina contents yet do not run off because the iron acts like alumina to stabilize and stiffen the melt. However these glazes will likely have reduced durability. Likely, in glazes low in flux, it can behave as an alkali, combining with silica.

(Fe_2O_3) is greatly affected by a reducing atmosphere where it can act as a flux in both bodies and glazes at high temperatures. Its fluxing action in reduction is quite remarkable and can be demonstrated by using a line blend in a clear glaze. Higher amounts of iron exhibit dramatically the increased fluidity. (Fe_2O_3) is the most natural state of iron oxide where it is combined with the maximum amount of oxygen. In oxidation firing, it remains in this form to typically produce amber to yellow up to 4% in glazes (especially with lead and calico), turns tan around 6%, and browns in greater amounts. In the 20% range, matte ness is typical (6).

Thin film technology is one of the most important technologies that have contributed to the development of semiconductors and their applications in several industrial fields. The Iron Oxide (Fe_2O_3) and Cobalt Oxide (Co_3O_4) thin films and their applications are of importance, in that these two materials are considered as important industrial materials , and used in spectrally selective coating, temperature sensors, resistive heaters, and photo cells(7).

In this research, thermal chemical spray technique was used. This method provides advantage over known methods in that it is economical in view of the low cost of preparing the films in addition to the lack of need for complex instrumentation. The method is fast and can provide large areas with the increasing scientific and technological development.

Experimental : Procedures, and Observations

Iron Oxide (Fe_2O_3), Cobalt Oxide (Co_3O_4) thin films and a mixture of both compounds in molarity (0.1) at different ratios (75:25 , 50:50 , 25:75) were prepared by the method of chemical spray pyrolysis deposition heated at (653) °K. Pre-cleaned glass of (3.8 x 2.6) cm^2 in area, and thickness (1) mm were used as substrate. A diluted (4.0402) gm of $Fe(NO_3)_3.9H_2O$ in (100) ml water as molarity (0.1) was used. Also a diluted (2.9104) gm of $Co(NO_3)_2.6H_2O$ in (100) ml water as molarity (0.1) was used in accordance with the following equation [1] (8):

$$M = (W_t / M_{wt}).(1000/V_1)$$
.... [1]

where M = molarity , W_t = weight of sample , M_{wt} = molecular weight, V_1 = water volume.

For amixture compound, then (ρ) is stated in the relation[2] below:(9)

$$\rho_{mix} = (\rho(Fe_2O_3).percentage\, in\, mix + \rho(Co_3O_4).percentage\, in\, mix) \quad [2]$$

$(x)Fe_2O_3$	100	75	50	25	0
$(100-x)Co_3O_4$	0	25	50	57	100

(Percentage of all prepared films)

The solutions for the preparation of Iron Oxide (Fe_2O_3) were in accordance with equation [3], while for Cobalt Oxide (Co_3O_4) preparation ,they were used in accordance with equation [4] .

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

$$3Co(NO_3)_2 \xrightarrow{heat} Co_3O_4 \downarrow + 6NO \uparrow + 4O_2 \uparrow \quad [4]$$

The prepared solutions of (Fe_2O_3) and (Co_3O_4), were both homogeneous on the glass substrates . As a result of substrate heating, several gases are liberated to leave thin films of (Fe_2O_3) and (Co_3O_4). The thickness of the prepared thin films $(77 < t < 200)$ nm was measured by using the weighing method previously employed [10-12] for (Fe_2O_3) and (Co_3O_4) thin film according to the following relation:

$$t = \frac{m}{A.\rho} \quad [5]$$

t = thickness of film, m= mass of film , ρ= density of film , A = area of film

Using a sensitive balance whose sensitivity is of the order (10^{-4}) gm (Metter HK-160), in addition tothe method as asimple computer program for measuring the thickness of all samples.

Thin films structure of Iron Oxide (Fe_2O_3), Cobalt Oxide (Co_3O_4), and a mixture of both compounds in different ratios (75:25 , 50:50 , 25:75) before and after annealing at degree (753) for (one and two) hour, were examined by using X-ray apparatus (XRA) (554811/ 554812) Leybold Didactic Gm H, 1988 (Germany) to determine the location of Bragg reflection peaks, and for determining the lattice plane spacing of various crystals.

As to the optical measurements of the prepared thin film, a double beam spectrophotometer (UV) /Visible Recording Spectrophotometer, UV210) (Shimadzu Company) (Japan) was used to measure the absorbance and transmittance of the thin films over the spectral range (200-900) nm, for calculating the absorption coefficient (α) from the relation [6]:(13,14)

$$\alpha = 2.303\ (\frac{A}{t}) \ldots\ldots [6]$$

Where $A =$ absorption (see table 2)

From the measurement of absorbance as a function of spectral range (200-900) nm , we calculated the optical energy gap from the calculation of the variable absorption coefficient (α) for each wavelength from equation (6). Also incident photon energy ($E = h\upsilon$) was calculated as a function of wavelength according to equation [7], (see table 1):

$$E(eV) = (1240/\lambda) \ldots\ldots [7]$$

Results and Discussion

The structure of the prepared thin films of Iron Oxide (Fe_2O_3), Cobalt Oxide (Co_3O_4), and their mixture before and after annealing at 753°K was investigated by X – ray diffraction. The results have shown that these films are of amorphous structure before annealing, while after annealing the operation led to transition in these films from the amorphous to polycrystalline state. Film thickness (77< t < 200)nm, temperature of annealing at (753°K), and annealing time (one and two) hour were investigated see Figs(1-3).

The results show that the crystallite size increases as the thickness of the film increases, this means high probability of appearance of direct transition of electronic occurrence (ASTM) [15] .When we increase temperature more than (653)°K, this operation does not show any obvious difference at this temperature (as general properties of film), it means that the films were in the stability state at this temperature.

On the other hand, the increase in the temperature of annealing resulted in an increase in a sequence of grains, then mixing with each other, would lead to the increase in the size. The increase in the time of annealing, for more than one hour, resulted in the appearance of some peaks in the diffraction spectra of the prepared films and increase in its figures. This confirms that it is polycrystalline, and this increase in the time gave the material atoms enough energy to re-organize itself in the crystallized lattice and decrease crystalline defect. Thus the annealing operation results in the decrease of the absorption coefficient value with the increase of the annealing temperature. From the values of (α), it is apparent that these values increase immediately with the increase of the percentage of (Co_3O_4) in the films.

The relation between absorption coefficient and photon energy was realized that the width of the localized states inside the forbidden gap increases with the increase of the percentage of (Co_3O_4) in the sample, and it decreases after annealing .

Conclusion

From above, it is shown that the accuracy of using the chemical spray method plays a main role in identifying the nature of thin films prepared by this method. Throughout our research we conclude the following:

1. All prepared films were of amorphous structure prior to annealing.
2. Annealing operations led to transition of the films structure from amorphous to polycrystalline state.
3. The crystallite size increases with the increase of the thickness of thin film.
4. The increase in the annealing time resulted in the appearance of some peaks in the diffraction spectrum of the prepared films .
5. Annealing operations resulted in reducing the absorption coefficient (α) with increasing annealing temperature.
6. The doping operation does not show any obvious difference on the crystalline structure.
7. The optical energy gap (E_g^{opt}) decreases with the increase of the thickness of thin film, and also with the increase of the percentage of(Co_3O_4) in film before annealing, and the increase after annealing.
8. Absorption coefficient values increase immediately with the increase of the percentage of(Co_3O_4) in the film.

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Table (1): Experimental conditions and thickness of the spray-deposited thin films, and their mixtures and energy gap

Film	Composition of the spray solution (M) $Fe_2O_3 : Co_3O_4$	Spray temperature (°C)	Film thickness (nm)	(E_g^{opt}) before annealing (eV)	(E_g^{opt}) after annealing (eV)
A	100 : 0	380	78	2.73	2.82
B	100 : 0	380	138	2.71	2.79
C	100 : 0	380	198	2.72	2.76
D	75 : 25	380	78	2.68	2.70
E	75 : 25	380	138	2.61	2.67
F	75 : 25	380	198	2.57	2.66
G	50 : 50	380	78	2.54	2.58
H	50 : 50	380	138	2.49	2.53
I	50 : 50	380	198	2.48	2.55
J	25 : 75	380	78	2.35	2.18
K	25 : 75	380	138	2.30	2.41
L	25 : 75	380	198	2.28	2.30
M	0 : 100	380	78	1.93	1.95
N	0 : 100	380	138	1.90	1.93
O	0 : 100	380	198	1.88	1.90

Table (2): Maximum values of energy gap (α) before and after annealing

Fe_2O_3 %	Co_3O_4 %	Max(α) before annealing (cm^{-1})	Max(α) after annealing (cm^{-1})
100	0	1.253×10^5	1.131×10^5
75	25	1.514×10^5	1.463×10^5
50	50	1.821×10^5	1.742×10^5
25	75	2.140×10^5	2.031×10^5
0	100	2.321×10^5	2.121×10^5

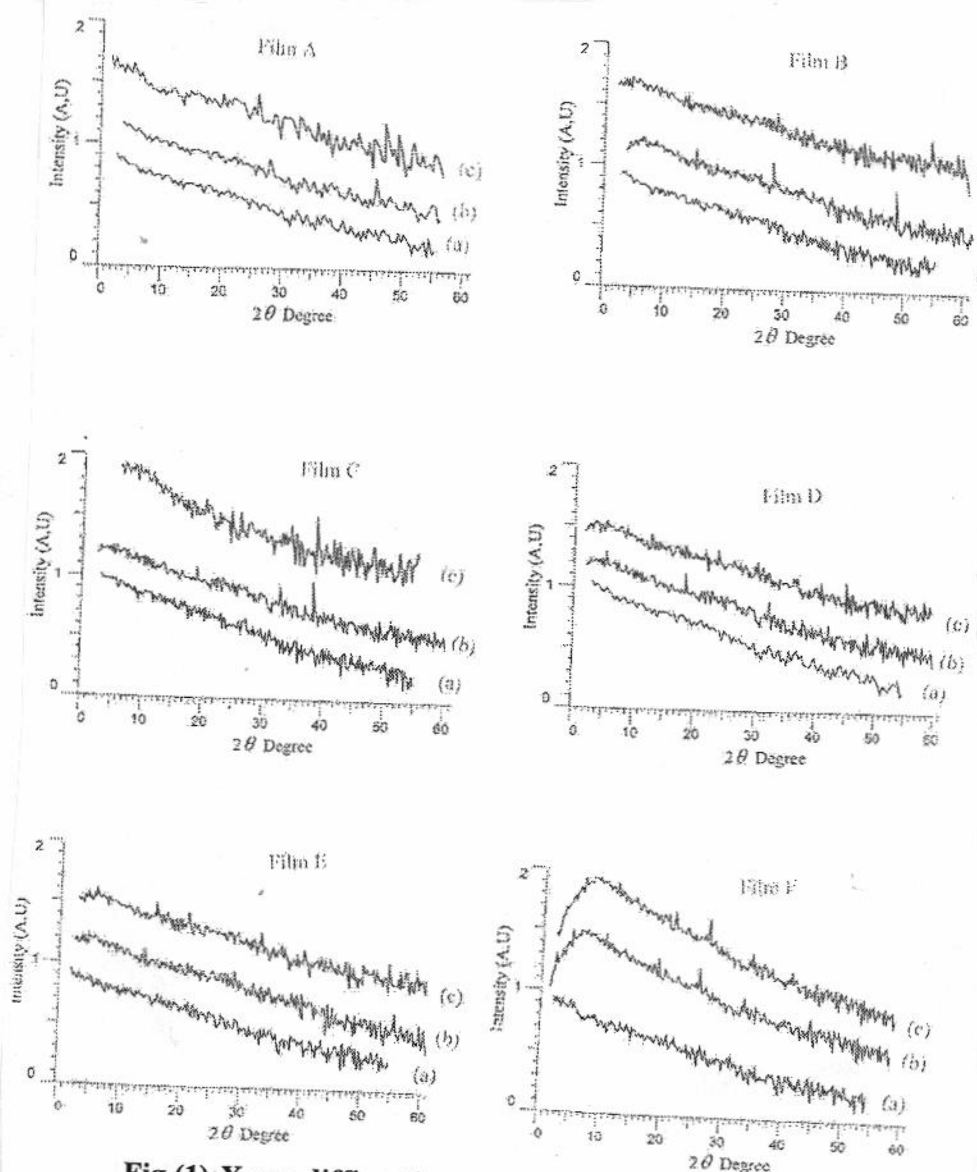

Fig.(1):X ray diffiraction patterns for films (A-F)
(a) before annealing (b) after one hour annealing
(c) after two hour annealing

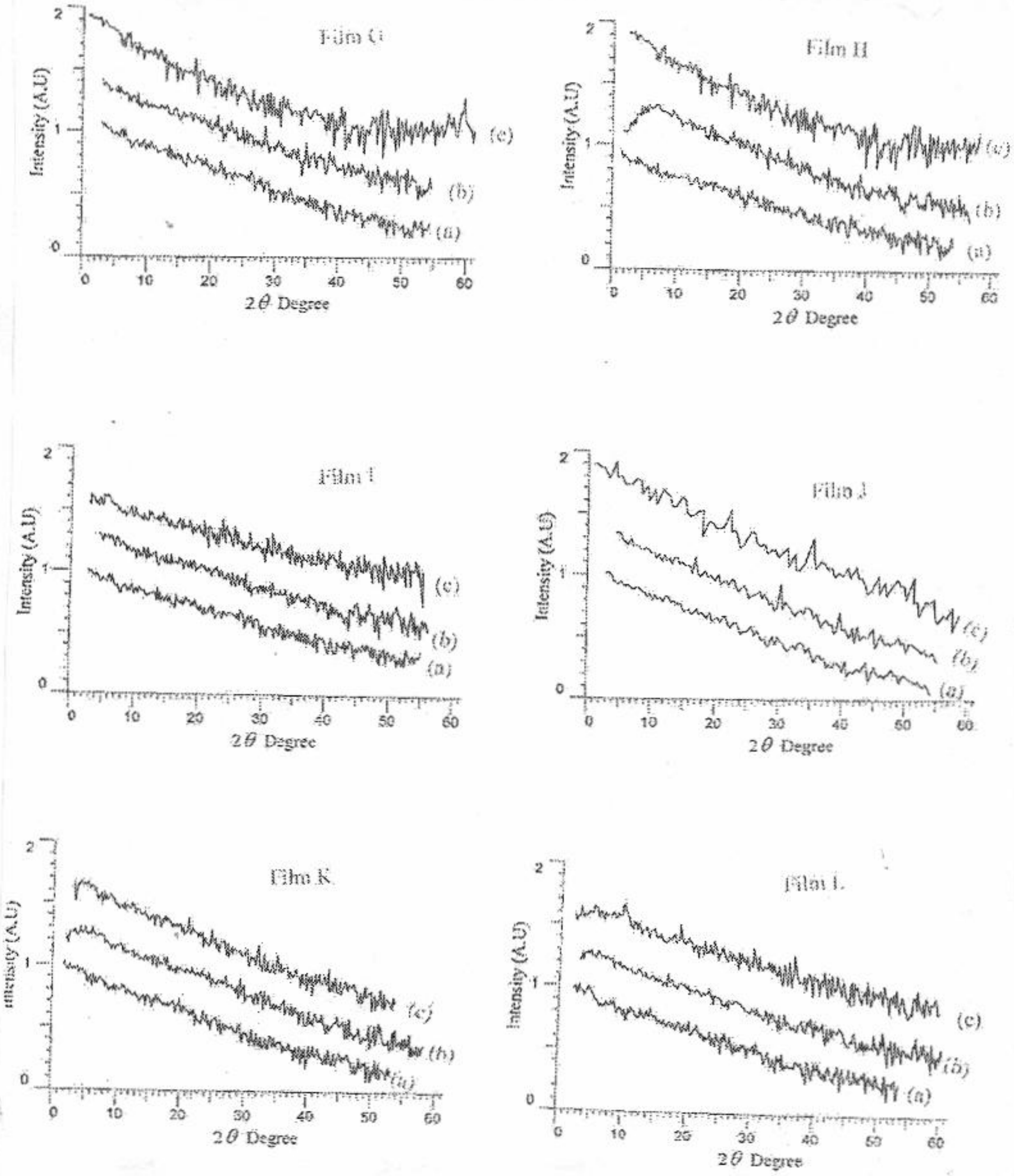

Fig.(2): X ray diffiraction patterns for films (G-L)
(a) before annealing(b) after one hour annealing
(c) after two hour annealing

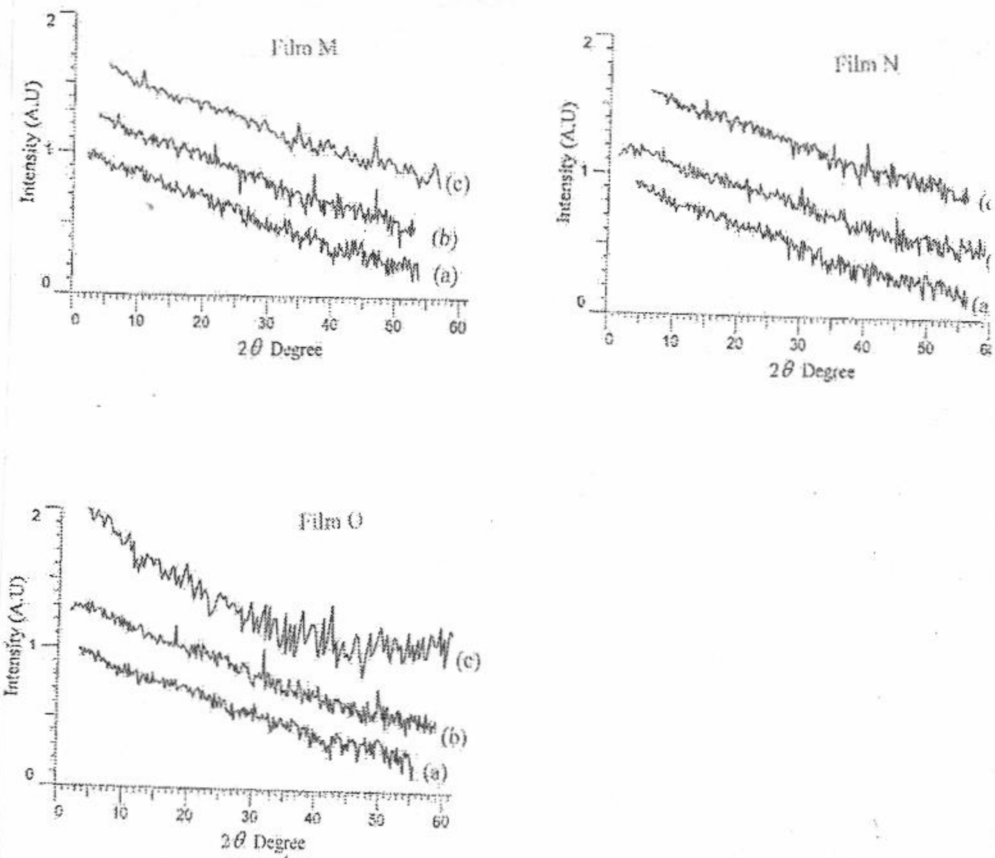

Fig.(3):X ray diffiraction patterns for films (M-O)
(a) before annealing (b) after one hour annealing
(c) after two hour annealing

تأثير سُمْكِ الغشاء وزمن التلدين على الخصائص التركيبية والبصرية لأغشية أوكسيدي (Fe_2O_3) و (Co_3O_4) ومزيجهما

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الخلاصة

تعد تقنية الاغشية الرقيقة واحدة من أهم التقنيات التي ســاهمت فــي تطــوير أشــباه الموصلات وتطبيقاتها في مجالات صناعية عديدة . أن لأغشية أوكــسيد الحديــد(Fe_2O_3) وأوكسيد الكوبلت (Co_3O_4) الرقيقة وتطبيقاتهما أهمية من حيث كونهما يعتبــران مــادتين مهمتين وتستخدمان في طلاء السطوح الانتقائية بأطياف مختلفة وفــي متحســسات الحــرارة والسخانات عالية المقاومة وفي الخلايا الضوئية .

لقد تم تحضير أغشية رقيقة مــن أوكــسيد الحديــد وأوكــسيد الكوبلــت ومزيجهما بنسب مختلفة(75:25, 50:50, 25:75)بطريقة الرش الكيميائي الحراري وبسُمك مختلف nm (77< t < 200) على قواعد من الزجاج سُمكها mm (1) وبدرجة حرارة (653 ^{o}K) . ثم أجريت عملية التلدين بدرجة حرارة ^{o}K(753) لساعة وساعتين و تــم فحــص طبيعة سطوح الأغشية الرقيقة بالمجهر الضوئي بينما تم فحص تركيبها البلوري بحيود أشعة أكس .

أظهرت نتائج حيود ألاشعة السينية أن أغشية أوكسيدي الحديد والكوبلت ومزيجهما ذات طبيعة عشوائية بينما أدت عمليات التلدين إلى تحول تركيب الأغشية من الحالة العشوائية إلى متعدد البلورات . وقد جاءت هذه النتائج متطابقة مع ما ورد في بطاقة المؤسسة الأمريكية

لفحص المواد(ASTM) .تم بحث تأثير سمك الغشاء وزمن التلدين على الخصائص التركيبية والبصرية للاغشية المحضرة وأظهرت النتائج أن حجم التبلور يزداد بزيادة سمك الغشاء الرقيق .

لقد أدت زيادة زمن التلدين لأكثر من ساعة إلى ظهور بعض القمم في طيف حيود الأغشية المحضرة .وذلك يؤكد إنها متعدد البلورات وهذا يزيد زمن تنظيم نفسها في الشبيكة البلورية ويقلل من العيوب البلورية. كما تضمن البحث دراسة الخصائص البصرية للنماذج المحضرة بواسطة تسجيل طيف الامتصاص والنفاذية $nm(900-200)$ وتم حساب طاقة الفجوة البصرية للانتقال المباشر المسموح. وجدنا بشكل عام أن طاقة الفجوة البصرية تتناقص مع زيادة سُمك الغشاء وكذلك مع تزايد نسبة أوكسيد الكوبلت في النموذج وتزداد بعد التلدين .

تم أيضا بحث الخواص البصرية الأخرى وحسابها مثل معامل الامتصاص وطاقة الفوتون وسعة الحالات الموضعية ووجدنا أن قيم معامل الامتصاص تزداد تدريجيا بزيادة نسبة (Co_3O_4) في الغشاء.

كلمات مفتاحية: الترسيب بالرش ، السُمك ، الحديد ، الكوبلت .