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Influence of Post- Annealing on The Properties of Cu_xS: Al, Fe Films Deposited By C B D

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Abstract

Thin films of copper sulfide (Cu_xS) were deposited at room temperature on glass substrates from solution containing copper (II) chloride, triethanolamine, and thiourea at appropriate pH (10-11). Two types of doping salts were used ($AlCl_3$ & $FeCl_3$) in four different weights (1, 1.5, 2, and 2.5) mg. The effect of introducing impurities and post-annealing was studied .The as-deposited films were found to be amorphous, while the post annealed were polycrystalline. The changes in optical and electrical properties of doped films were also studied. The electrical conductivity was found to be highly dependent on annealing conditions, the resistivity of doped films was between (0.022-8.75) Ω cm. Optical band gaps of doped films determined from absorption spectra were found to have values within the range of (2.17-2.33) eV.

Keywords: Chemical bath deposition, Optical properties, Electrical properties, Post-annealing

تأثيرالمعالجة الحرارية على خصائص أغشية كبرتيد النحاس المشوبة بالحديد والالمنيوم والمرسبة بطريقة الترسيب بالحمام الكيمياوي

الخلاصة

في هذا البحث رسبت أغشية رقيقة من مادة كبرتيد النحاس على قواعد زجاجية بدرجة حرارة الغرفة بأستخدام كلوريد النحاس ، تراي ايثانول امين و الثايوريا وبدالة حامضية ملائمة (10-11). أستخدام نوعين من املاح الاشائبة هما كلوريد الحديد وكلوريد الالمنيوم ($FeCl_3$ & $AlCl_3$) بأربعة أوزان مختلفة هي (1،1.5،2 و2) ملغم.درس تأثير كل من أضافة الشوائب والمعالجة الحرارية. من خلال دراسة حيود الاشعة السينية تبين ان الاغشية المرسبة من غير معالجة حرارية تكون عشوائية بينما تلك المعالجة حراريا كانت متعددة البلورات. درس التغير في الخصائص البصرية و الكهربا ئية للأغشية المشابة . ظهر قياس التوصيلية الكهربا ئية انها تعتمد كثيرا على شروط المعالجة الحرارية. المقاومية الكهربائية للاغشية المشابة كانت بين (0.022 -8.75) Ωcm . حددت فجو ة الطاقة البصرية للاغشية المشوبة من طيف الامتصاصية وتتراوحت (2.17-2.33) eV .

Introduction

Copper sulfide being an important semiconductor material has received a great deal of attention due to its unique physical and chemical properties [1-7] and notable application include solar radiation [8], catalyst [9], coating on the polymer surface to increase its conductivity [10] etc. These films exhibit low IR transmittance and

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higher IR reflectance coupled with low visible reflectance and visible transmittance [11] .The energy band gap of Cu_xS, ranging from (1.2 to found to exist in two forms at room temperature as "copper-rich" and "copper- poor". Copper-rich phase exists as chalcocite, djurleite and anilite. Copper-poor phase exists as covellite [13] .The superiority of a chemical bath deposition (CBD) lies in the advantages of having variety of substrates (insulators, semiconductors, and metals) for deposition, a large surface area, simplicity, and lower cost [14]. Applications of (CBD) films include photovoltaic, laminated sheet glass for transport, safety, and security, as well as being a precursor compound in layered and mixed semiconductors structures [15].

The aim of our work is to study the effect of post- annealing on the structural and electrical properties of the films obtained by chemical bath deposition (C B D).The structural, electrical and optical properties can be tailored by changing the post-annealing conditions.

Experimental

Cu_xS films were deposited using a chemical bath. By several trails the following preparative parameters were optimized. The total volume of the deposition was 50 ml made from 10 ml of flowing constituents: 0.5 mol / l of $CuCl_2$.$2H_2O$, 9.4 mol / l of triethanolamine (TEA), 30 % NH_3, 1 mol /1 of $SC(NH_2)_2$, and distilled water. Substrates used for deposition Cu_xS films are microscope glass slides washed in distilled water to remove the impurities and residuals from substrate, followed by rinsing in chromic acid (1mg of CrO_3 in 20ml of 2.35) eV and has p-type conduction is attributed to free holes from accepter levels of copper vacancies [12]. The copper sulfide was distilled water) for one day to introduce functional group called nucleation or epitaxal centers, which formed the basis for the thin films growth and finally washed again with distilled water. Glass substrates were immersed vertically into the above beaker for 2 hr at room temperature (23-25) ºC. The as deposited film of Cu_xS at optimized preparative parameters had thickness (160nm,246nm,278nm and 320nm for one, two, three and four dipping) .Certain samples were deposited by keeping deposition time fixed and changing the dipping number. All samples deposited at room light illumination and other under darkness. After deposition, the substrates were taken out, washed with distilled water. Dopant salts ($AlCl_3$ & $FeCl_3$) were used in four different weights for each material (1, 1.5, 2, and 2.5) mg, these salts were add to the bath solution before immersing the substrate. post-annealing was carried out at different time and temperatures.

Measurements

X-ray diffraction system (Lab X –XRD-6000 / Shimadzu) has the following characteristics: Source: radiation of CuKα with 1.54Å wavelength, Scanning speed: (5degree/min). Incidence angle: 10-60 degree. For optical measurements the deposited film from one slide was removed carefully using HCL solution. Optical measurements included transmittance and absorption spectra using phoenix-2000UV-VIS

spectrophotometer in the range of Thickness measurement was made by optical method using He-Ne laser with incident angle 45°. The film thickness (d) is calculated using the following formula [16]:-

$$d = \frac{\Delta x}{x} \cdot \frac{l}{2} \quad \ldots\ldots(1)$$

Where x is the fringe width, Δx is the distance between two fringes and λ is the wavelength of laser light.

The value of absorption coefficient (α) has been calculated by using the following relation [17, 18]:-

$$a = 2.303 \frac{A}{d} \quad \ldots..(2)$$

Where :A is absorptance and d is the thickness of the thin film.

The absorption coefficient (α) and optical band gap (Eg) are related by [19]:-

$$ahn = A(hn - Eg)^{n} \quad (3)$$

Where : A is constant depending on transition, h is plank's constant, υ is the frequency of the incident photon, Eg is the optical bandgap of the material and n has different values depending on the nature of the absorption process, and equal 1/2 , 3/2 , 2 , and 3 for allowed, forbidden of direct and indirect transition respectively. The plot of $(\alpha h\nu)^2$ versus $(h\nu)$ gives the best result. By extrapolating the liner part down to ($h\nu = 0$) the value of E_g could be determined.

For the electrical measurements aluminum electrodes in a coplanar configuration, were evaporated in vacuum on the surface of the Cu_xS films. The electrical resistivity of the deposited films was determined using the equation [20]:-

$$R = r \frac{L}{A} \quad \ldots\ldots(4)$$

Where ρ, is the electrical resistivity of the films, L the distance between electrodes and A the area of the ohmic contacts.

400-900.

Results and discussion

The X-ray diffraction spectra recording for Cu_xS thin films shows the nature of the deposited films under different conditions as shown in figure (1 a- d). The main features of all films were amorphous, and such results were already mentioned by others [3, 21]. The non crystalline nature in the films could be attributed to many parameters among those the wide band gap, low temperature used during deposition and glass substrate. Increasing the dipping number shows certain small peaks which are attributed to the increasing in the films thickness and this result confirmed some earlier studies [22]. Doped films show also the amorphous nature as shown in figure (2 a, b).

Annealing of the as-deposited films shows some degree in crystallinity as shown in figure (3a,b). Table (1) shows the peaks as well as a comparison with the results of Bagul et al. [23]. Form table(1) one can notice also that increasing annealing time with lower temperature, no plans belonging to the Cu_xS phase appear and this is probably due to phase change, while at low annealing time no such phenomena takes place .

Figure (4a,b) shows the optical transmittance of films prepared under illumination and dark conditions. It is clear from figure (4. b) that transmittance decreases as the number of dipping increase for a specific wavelength. Increasing dipping number means an increase in film thickness, hence increasing absorption. Figure (5a,b) shows the

increasing of doping weight. The decreasing of the transmittance with decreasing could be attributed to contribution of absorption by impurities. The doping process leads to the formation of structure defects and tails in the edge of the energy bands.

Figure (6a,b) shows the optical transmittance of annealed films under different conditions. Annealing process of the as-deposited films increase the optical transmittance, this decreasing could be attributed to the decreasing in the defects. In additional the annealing leads to transformation of amorphous material to polycrystalline .By comparing the influence of the two parameters (doping and post annealing), the increasing in transmittance with annealing temperature in the NIR range in comparison with transmittance before annealing is so clear.

Figure (7a,b) shows the effect of the doping process on the absorption coefficient, the absorption coefficient increases as the doping weight increases and this could be attributed to absorption by impurity levels. The effect of doping on the optical energy gap is shown in figures (8a, b) where the experimental values of $(\alpha h\upsilon)^2$ against $h\upsilon$ is plotted. The variation of $(\alpha h\upsilon)^2$ with $h\upsilon$ is linear after the absorption edge which suggest that the direct transition is present. Extrapolation the straight line portion of the plot to energy axis for zero absorption coefficient give optical band gap energy of the film. It is clear from these figures that the band gap decreases with doping which is due to the additional defects and tails in the region between the valance band and conduction band within the energy gap. Tables (2) show the results of the optical energy gap of doped films. It is clear from table (2), increasing Al and Fe weights decreases the band gap value and this is due to the increase in the splitting in the shallow levels companied doping.

The electrical measurements (I-V curves) of the films are registered in the dark and shown in figure (9) .All curves shows a linear relationship of resistivity calculated form the current-voltage curve.

Also the effect of the doping process on the electrical properties is shown in the figure (9) .The dark current of samples doped with Al increases as the doping weight increase and this is attributed to the doping process which leads to increase in the charge carriers' density. On the other hand, the Fe doping causes decreasing in the dark current. The decreasing in the dark current values with Fe doping could attributed to the composition effect, since the starting materials used in preparing the bath solution are not highly pure, so doping with Fe will compensate the originally exist impurities .The doping with Al and Fe reflected clearly in the variation of resistivity with doping weight as shown in the figure (10). In the case of Al, three different regions exist, the first one is ($w < 1.5$) mg where the weight has no high influence, and for ($1.5 < w < 2$) mg a sharper decrease in the resistivity takes place and for ($w > 2$) mg again the value of ρ does not change with weight Table (3) summarize the results of the electrical properties as a function of dopent impurity and weight.

Conclusions

In this investigation, the Cu_xS thin films were grown on the glass substrate by CBD, and the effects of doing process on optical and electrical

properties were studied. Major findings as following

1- Increasing doping weight causes decreasing in the transmittance fore alldoped films**.**

2- both doping salts causes a decrease in the values of optical energy gap , and the decrease with Fe bigger (2.33-2.15eV) than that with Al (2.33-2.15eV) .

3- Increasing the electrical resistivity with Fe shows that Fe will compensate the dopant aleady exisits in solution , will Al decreases the electrical resistivity which indicate that Al giving the same conductivity .

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Table (1) shows the obtained results from the XRD

Annealing		2θ (degree)	Plane	Copper sulfide	Bagul results	
Time (min)	Temperature (°C)				2θ (degree)	Plane
30	300	28	6 6 2	$Cu_{1.76}S$	28.12	6 6 2
		29.4	1 0 2	CuS	29.375	1 0 2
		32	8 6 0	$Cu_{1.76}S$	32.5	8 6 0
		34.1	0 4 4	Cu_2S	34.75	0 4 4
240	200	29.7	1 0 2	CuS	29.375	1 0 2
		31.8	8 6 0	$Cu_{1.76}S$	32.312	8 6 0

Table (2): The result of optical band gap at different deposition conditions.

Doping weight (mg)	Optical band gap Eg (eV)
1.0 of Al	2.29
1.5 of Al	2.25
2.0 of Al	2.21
2.5 of Al	2.18
1.0 of Fe	2.33
1.5 of Fe	2.24
2.0 of Fe	2.22
2.5 of Fe	2.17

Deposition condition	Number of dipping	Optical band gap Eg (eV)
illumination	1	2.40
Dark	1	2.47
illumination	2	2.43
illumination	3	2.41
illumination	4	2.44

Annealing temperature (°C)	Annealing time (min)	Optical band gap Eg (eV)
100	30	2.37
150	30	2.41
200	30	2.48
250	30	2.5
300	30	2.56
200	15	2.4
200	60	2.44
200	90	2.45
200	120	2.45
200	240	2.48

Table (3): The result of electrical at different doping weight.

Doping weight (mg)	Dark resistivity ρ (Ω cm)
1.0 of Al	0.2
1.5 of Al	0.179
2.0 of Al	0.035
2.5 of Al	0.022
1.0 of Fe	1.811
1.5 of Fe	3.104
2.0 of Fe	5.821
2.5 of Fe	8.75

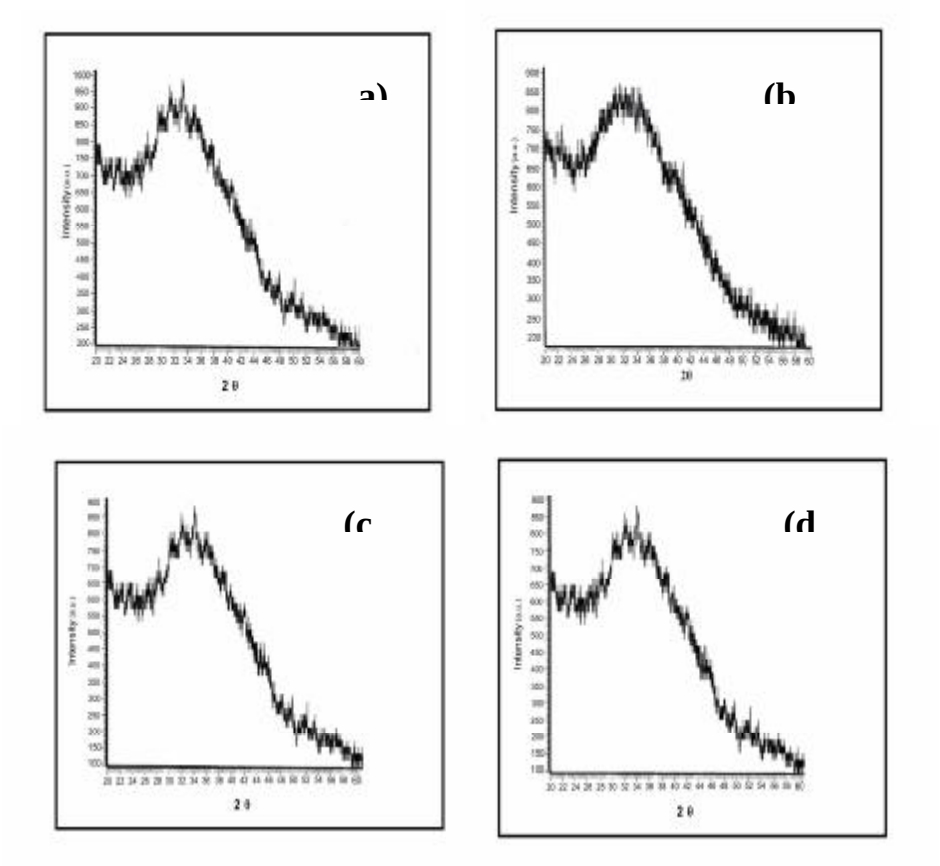


Figure (1) Shows the XRD of the Cu_xS for different depostion .(a,b) For the depostion film the illumintion and dark .(c,d) For the number of the dipping .

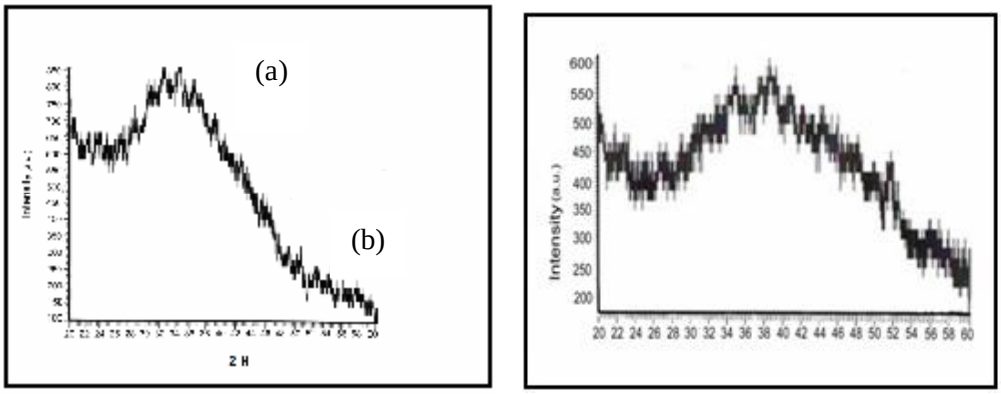


Figure (2): Shows the XRD of the doped samples. (a) Al. (b) Fe.

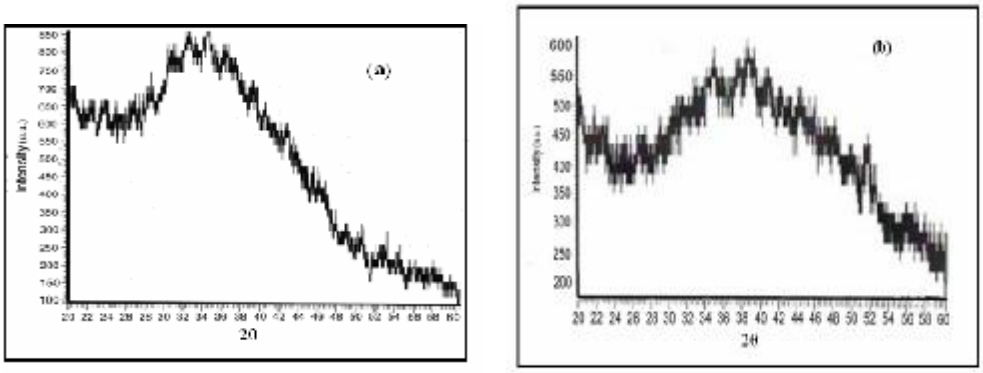


Figure (3 a,b): Shows XRD of the annealed films. (a) At 30 min and 300 ºC. (b)At 240 min and 200 ºC .

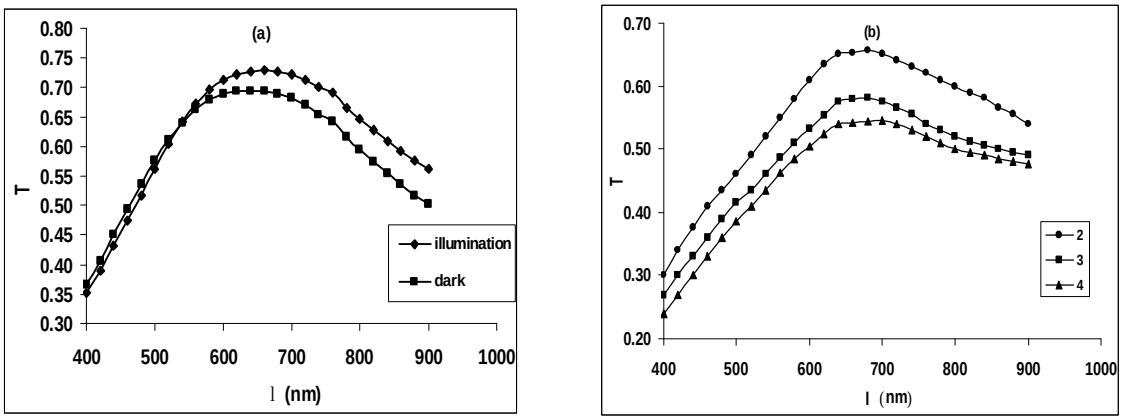


Figure (4a,b): the optical transmittance spectra of Cu_xS films for various preparations parameters. (a) For films in the illumination and the dark. (b) For number of the dipping.

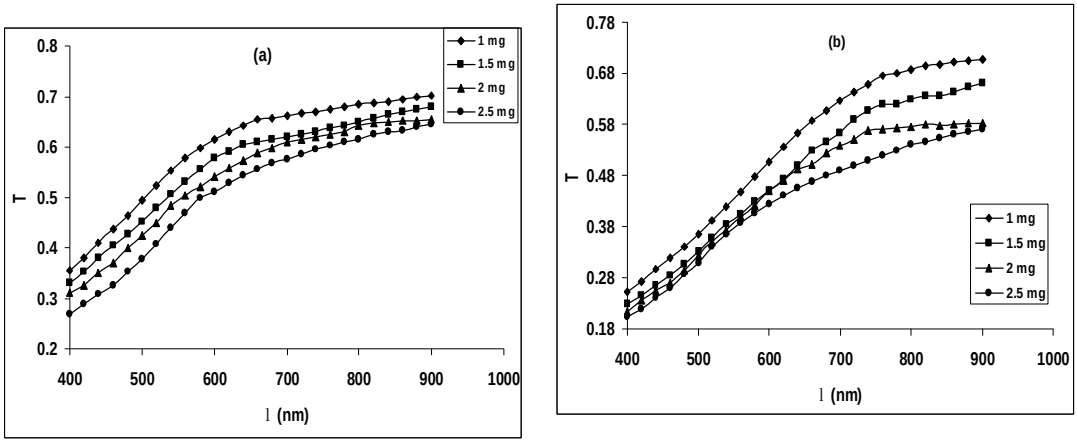


Figure (5a,b): the optical transmittance spectra for doped samples. (a) Al . (b) Fe .

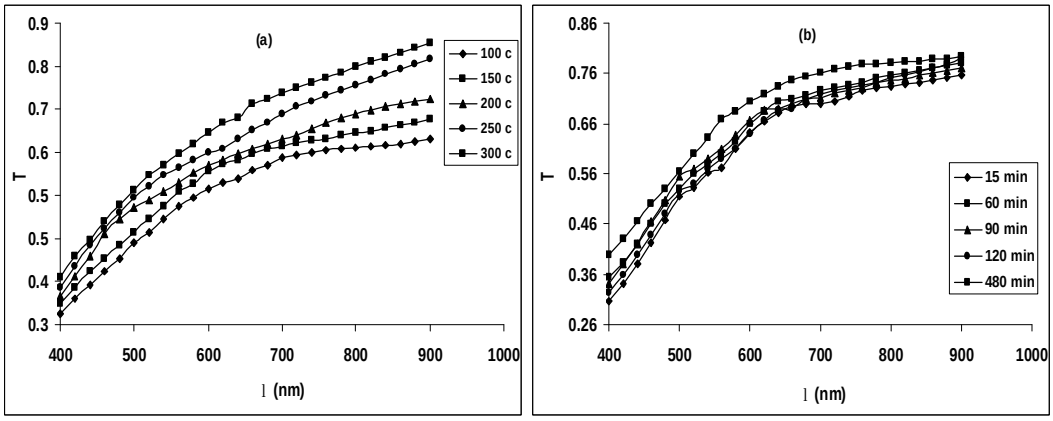


Figure (6a,b): the optical transmittance spectra of Cu_xS films at different
Figure (6a,b): the optical **temperatures and times. (a) For different temperatures and constant time is 30 min. (b) For different times and constant temperature is 200 °C**

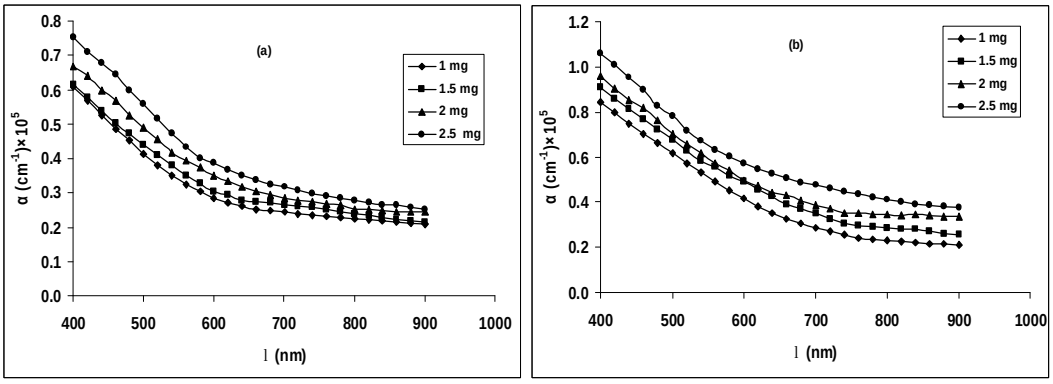


Figure (7a,b): The absorption coefficient for doped samples. (a) Al. (b) Fe.

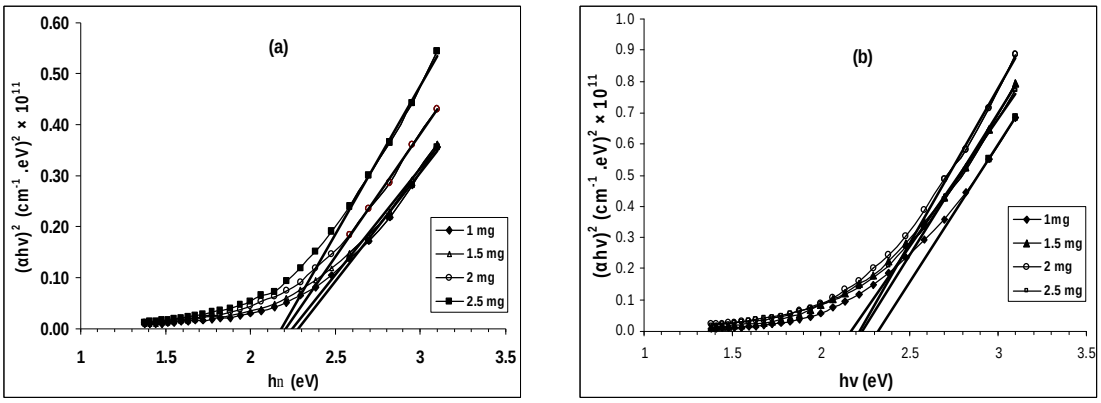


Figure (8a,b) The direct optical energy gap for doped samples. (a) Al. (b) Fe .

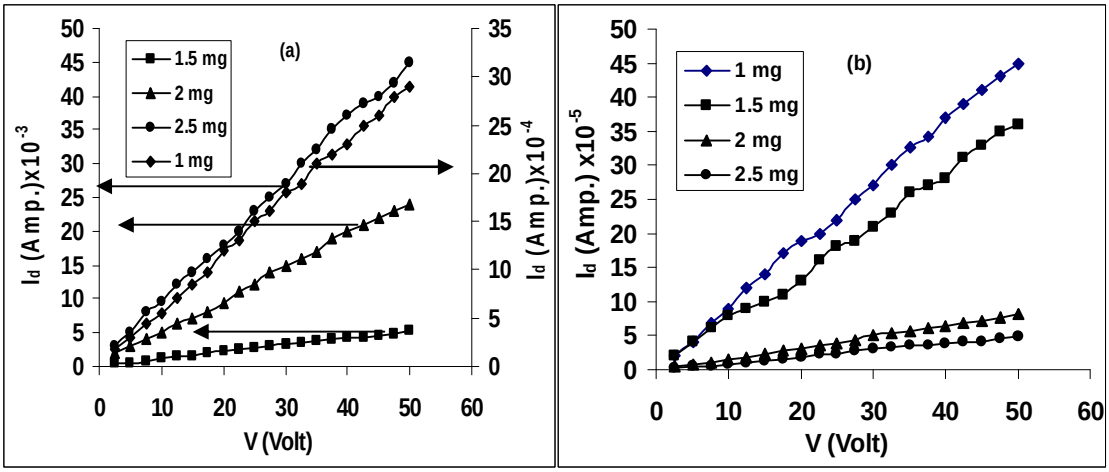
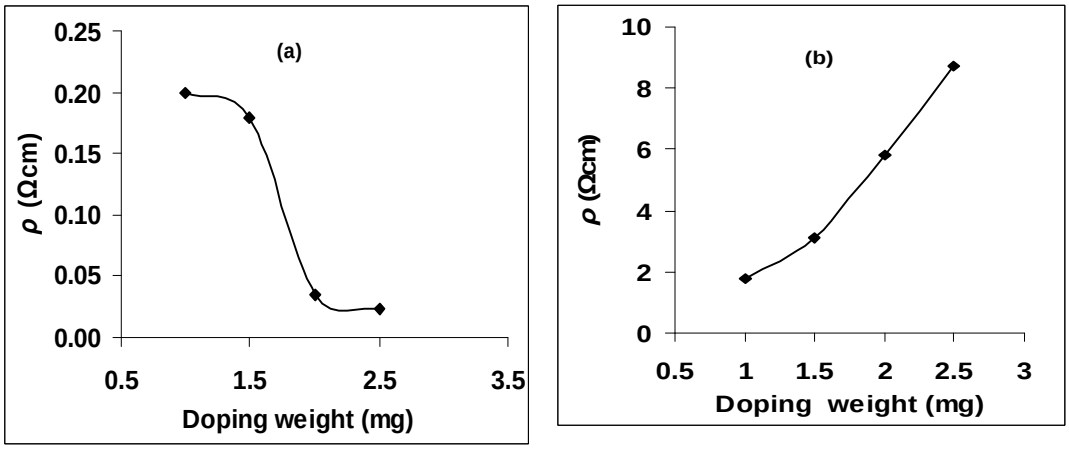


Figure (9) I-V characterization for doped samples. (a) Al. (b) Fe.



Figure(10) The relation between the resistivity and doping weight. (a) Al. (b) Fe