PHYSICAL PROPERTIES OF Mn DOPPED $CuAlS_2$ PYROLYTIC THIN FILMS

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Abstract:

$CuAlS_2$:Mn thin films were prepared by spray pyrolysis technique. The prepared films were deposited on the glass substrate temperature T_s of 613^{o}K. The optical properties were studied as a function of Mn doping concentration. The estimated direct energy gaps are in the range (3.29-2.92)eV for Mn concentration range (0.1-5) wt%.

The DC electrical conductivity of pyrolytic-sprayed $CuAlS_2$ thin films doped with Mn is measured in the temperature range (300-400^{o}K). The doping concentration ranges from 0% to 5% by weight. In the lower temperature region, the conductivity and the activation energy are functions of doping concentration for less than 0.7%. However they are nearly constant for concentration more than 0.7%. In contrast for what is expected, the overall conductivity decreases with a doping concentration. Under the band model, the behavior of the electric conductivity is attributed to the existence of donor's levels and the effect of replacement of Mn in the Al site as a favorable one.

INTRODUCTION

The $CuAlS_2$ semiconductor is one of the members of $A^1B^3C_2^6$ type chalcopyrite compounds that have been investigated for the possibility of using it as a light-emitting device. It has a wide energy gap (3.1-3.5eV) [1-9]. The compound emits in the blue to ultra-violet region of the spectrum. To achieve a shift towards the red end of the spectrum; many workers have investigated this type of semiconductor doped with different transition elements [1-16]. A $CuAlS_2$ monocrystal doped with Mn was found to answer this requirement [7].

As promising material easy to make thin film electroluminescence displays, $CuAlS_2$:Mn thin films obtained by spray pyrolysis technique are subjected to investigation in this work. The investigations are X-ray diffraction analysis, optical absorption analysis, and DC electrical conductivity measurements. This was applied to undoped and up to 5%doped thin films. The DC electrical conductivity was carried out in the temperature range from (300-370^{o}K). The results obtained are discussed with the help of band theory.

EXPERIMENTAL

The thin films under investigation are prepared using spray pyrolysis technique [17]. The spray set up and the experimental details follow closely previous investigation [18]. Briefly; three 0.05M solutions of the compounds $Cu(NO_3)_2$, $Al(NO_3)_3$ and thiourea ($SC(NH_2)_2$) are added together to form the spaying solution. The net ratio of Cu:Al:S in such a solution is 1:1:2. The Mn doped films are prepared by adding different specific weights percentage (0.1-5)% of Mn as $MnCl_2$ solution. The compound solutions are then sprayed onto heated glass substrates using air as the carrier gas. The spraying rate in our investigation is about 3ml/min. The substrate temperature (T_s) is uniformly controlled at the required temperature. The thickness of the prepared samples is estimated to be in the range of (0.16-0.20) μm. The films are clear and greenish in color. A Philips X-ray diffractometer type Pw

1140/00 is used for X-ray studies. Absorption optical measurements are carried out using Pie-Unicom SP-800 UV/VIS Double beam spectrophotometer. It covers the range from 200-900 nm. The DC electrical conductivity is measured using Van der Pauw method [19]. Ohmic contacts are achieved by evaporating Aluminum electrodes. The measurements are carried out in the temperature range (300-370 ^{o}K).

RESULTS AND DISCUSSION

X-ray diffraction analysis were carried out on thin films prepared for different substrate temperature in the range (420-670^{o}K). The optimum temperature was found to be 610^{o}K at which the film shows the characteristic peaks of monocrystal X-ray diffraction reported before [20]. This is shown in Fig.(1). It appears that {112} plane of the chalcopyrite structure is the preferable face for crystallinity. The same behavior was also found for single crystals [20]. The lattice parameters [a,c] found in this study together with those available in the literature are listed in Table (1).

Table-1 Lattice parameters a and c together with available literature data.

a (nm)	c (nm)	references
0.5297	1.0503	Present work
0.5333	1.0435	[14]
0.5338	1.0441	[21]

The same procedure was carried out for Mn-doped samples but apparently we could not get the same features. It appears that the introduction of Mn into the film enhances disorder. The same behavior was again found for monocrystal [7].

As for the optical measurements: the absorption spectra with different concentrations for Mn ions, as well as in the undoped samples are featureless beyond the absorption edge. The A and B bands related to the presence of Fe^{+3} contamination [7,22,23] did not appear in our spectra. The optical edge shifts towards lower energies as the concentration of Mn increases.

Under the assumption that the transition probability becomes constant near the absorption edge; the variation of the absorption coefficient (α) with the incident photon energy ($h\nu$) was taken to be related via the relation [24-26]

$$\alpha = \alpha_o (h\nu - E_g)^{1/2} / h\nu \qquad \text{----------} \qquad (1)$$

where α_o is a constant independent on the photon energy. E_g is the direct band to band transition and is determined by plotting $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) as shown in Fig (2). Extrapolating of the straight line to $(\alpha h\nu)^2=0$ gives the allowed band gap transitions. As can be seen from the figure, the energy gap varies from 3.34eV for the undoped sample to the asymptotic value 2.92 for 5wt% of Mn.

To summarize the DC electric conductivity measurements; the conductivity (σ) for undoped and Mn doped sample under various measurements temperature are shown in Fig.(3a). On the other hand, Fig.(3b) shows the variation of Log(σ) versus the reciprocal of the temperature for the same sample.

The straight lines in Fig.(3b) fit the equation:

$$\sigma = \sigma_o \exp [-(E_a)/KT] \qquad \text{----------} \qquad (2)$$

where E_a is the activation energy, K is the Boltzman constant, and σ_o is a constant.

In general there is an increase in the conductivity value with the increase of temperature for either undoped or doped samples. Initially the conductivity decreases with increasing the

Mn wt%. At about 0.7wt% of Mn the conductivity suffers a drastic drop in its value to a more or less leveled value depending on the temperature.

The activation energy varies from the value of 20meV for the undoped up to the leveled-up value of 60meV for a doped concentration over 0.7wt%. Fig. (4) shows the variation of the variation of the activation energy $E_a(c)$ as calculated from the slopes of Fig. (3). Also, the optical direct (E^d_g) variation with Mn concentration. As seen from Fig. (3a), we have two regions. The two regions mentioned above are separated by an abrupt change in the conductivity values. Also, as shown in Fig. (4), this border marks the abrupt change in the activation energy, and direct optical gaps.

From the values of $E_a(c)$ obtained and the experimental result that the pure sample has n-type conduction, one has to conclude that the conductivity is due to donor's *electrons.* In accordance with the curve of the undoped thin film in Fig. (3), one has to assume the existence of impurities in the original undoped solution. Thus, DC electrical conductivity in our case is due to electrons from impurities-donors. For temperature less than $370^{\circ}K$, the number of electrons in the conductivity band increases, and so the conductivity increases the temperature. As the donor's electrons go to the conduction band, they are free to move. They would suffer from scattering with the host lattice and recombination with either a donor ion or hole (due to accepter impurities) if they have a sufficient energy. So, by acquiring the specified energy at $T\sim370^{\circ}K$, the recombination process takes its toll. Such electrons will not contribute to the electrical conductivity, both processes (scattering and recombination) increase with the increase of the temperature. The sequence is a decrease in conductivity. Such a process is a reversible one.

In the case of $CuAlS_2$:Mn thin films, Mn may well be expected to replace either Cu and/or Al sites in the host lattice [7]. To satisfy charge neutrality requirement, the $[Mn]_{Cu}$ (Mn occupying the Cu site) form a donor level, while the $[Mn]_{Al}$ (Mn occupying the Al site) form an acceptor level. Both the donor and the acceptor must be ionized to contribute to the DC electrical conductivity [27]. Such a replacement is accompanied, in principle, by change in the optical direct gap as shown in Fig. (4) especially for the concentration less than 0.7% by wt. The absorption edge shifts toward lower energies as the concentration of Mn increases [7].

Let us now take the case of $[Mn]_{Al}$ together with the presence of impurities in the undoped sample. One expects additional acceptor levels to the ones due to the original impurities. Also, one has to assume that Mn can interact initially with the impurities' donors forming an ionic bond. So, this results in a decrease in the impurities-donors-concentration. In other words, there would be a decreased in the electrical conductivity. This process is irreversible and depends on the concentration of the dopant and the impurities. It will terminate by the depletion of the impurities. Hence, the presence of the dopant can compensate the effect of the impurities presence; in other words, it can deplete the number of the electrons in the donor levels. This depletion is a function of Mn concentration. Again; in other words, this explains the decrease of the conductivity with doping. The end of this depletion is the end of the donor impurities present in the intrinsic material. In our case we find that the concentration of the original impurities is about $1.3x10^{19}$ atoms per gm. For concentration above 0.7wt%, the residual donor levels due to other non-interactive impurities takes over the conductivity job.

CONCLUSION

In this study, the optical and the DC electrical properties and the crystal structure of $CuAlS_2$ film doped with Mn have been investigated. The DC electrical conductivity of $CuAlS_2$:Mn thin films was found to decrease with increasing Mn doping concentration, and goes through a maximum on increasing the temperature. The conductivity is a function of the dopant concentration up to 0.7% by wt. This unexpected behavior is explained as follows:

In doping with Mn of $CuAlS_2$ thin films, the Mn ions appear to favor the $[Mn]_{Al}$ sites. In doing so; they create accepter levels. Also it will compensate any donor levels present. The change in the situation accompanying this replacement would result in a decrease in the optical direct and indirect band gap. In nullification the existing donor levels, it will have the unexpected results of decreasing the DC electrical conduction. This effect is limited to specify

limits of concentration according to the sample used. In applications, one has to compensate between the optical and electric properties.

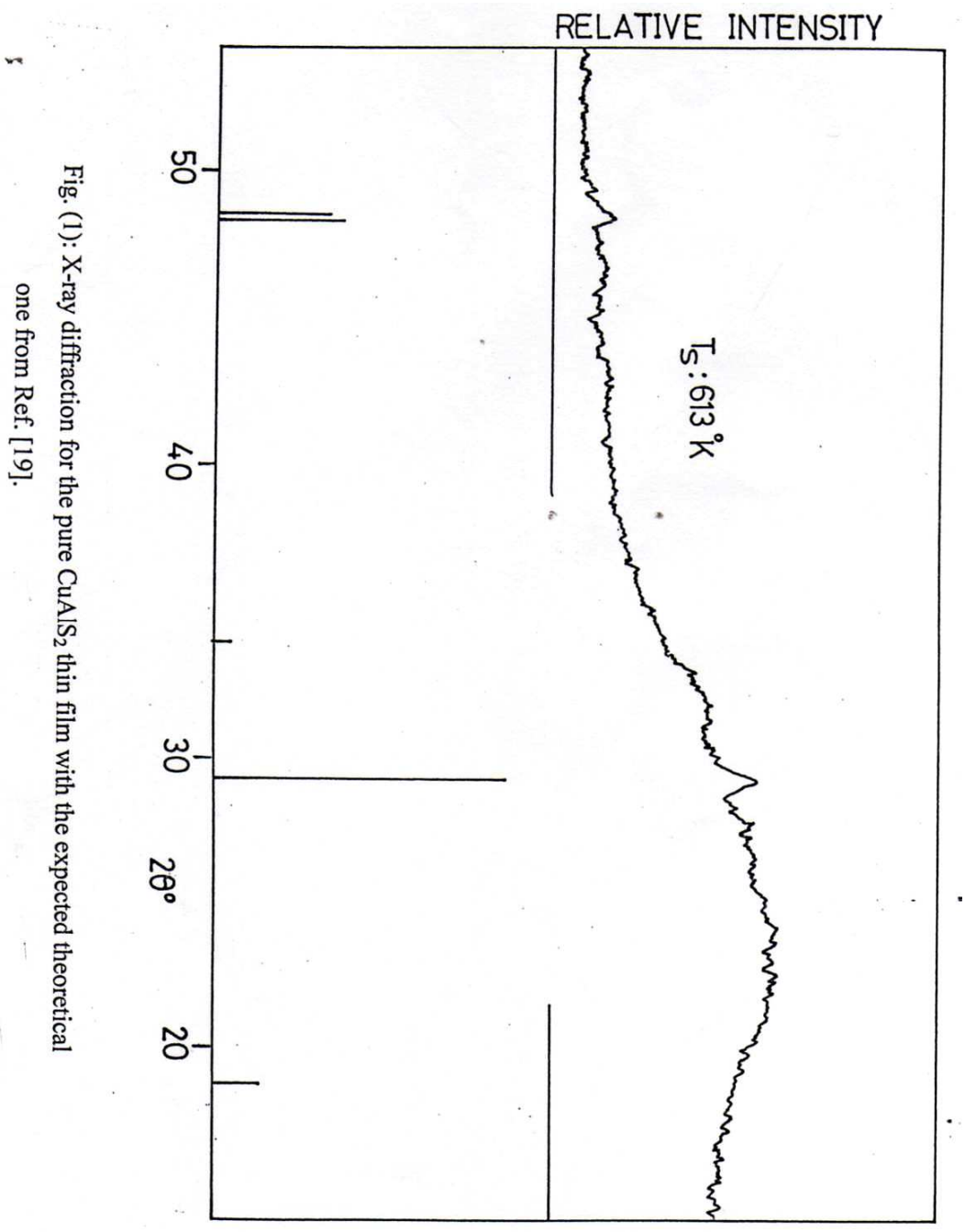

Fig. (1): X-ray diffraction for the pure $CuAlS_2$ thin film with the expected theoretical one from Ref. [19].

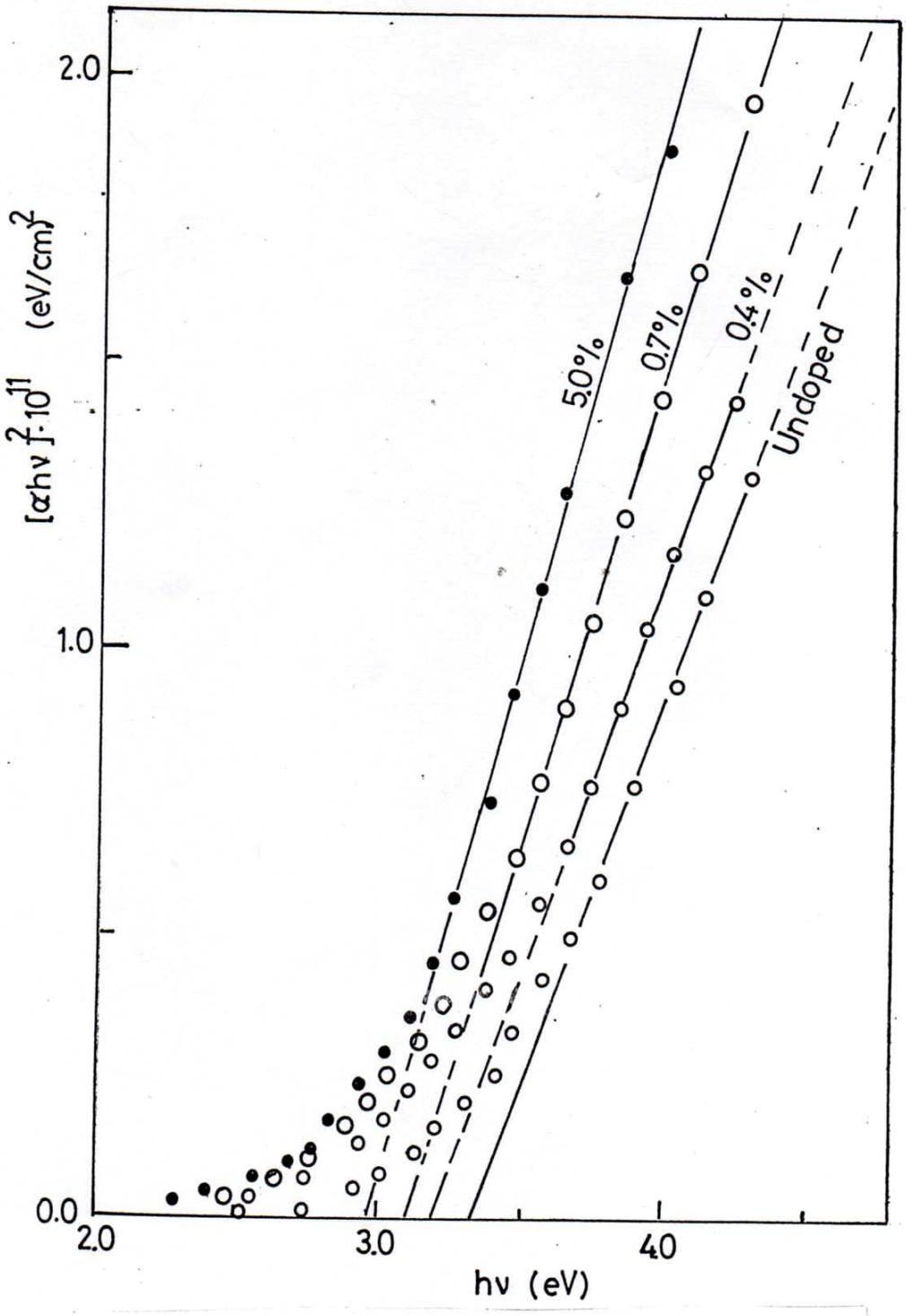

Fig . (2): $(\alpha h\nu)^2$ versus $(h\nu)$ for films doped with different Mn wt%.

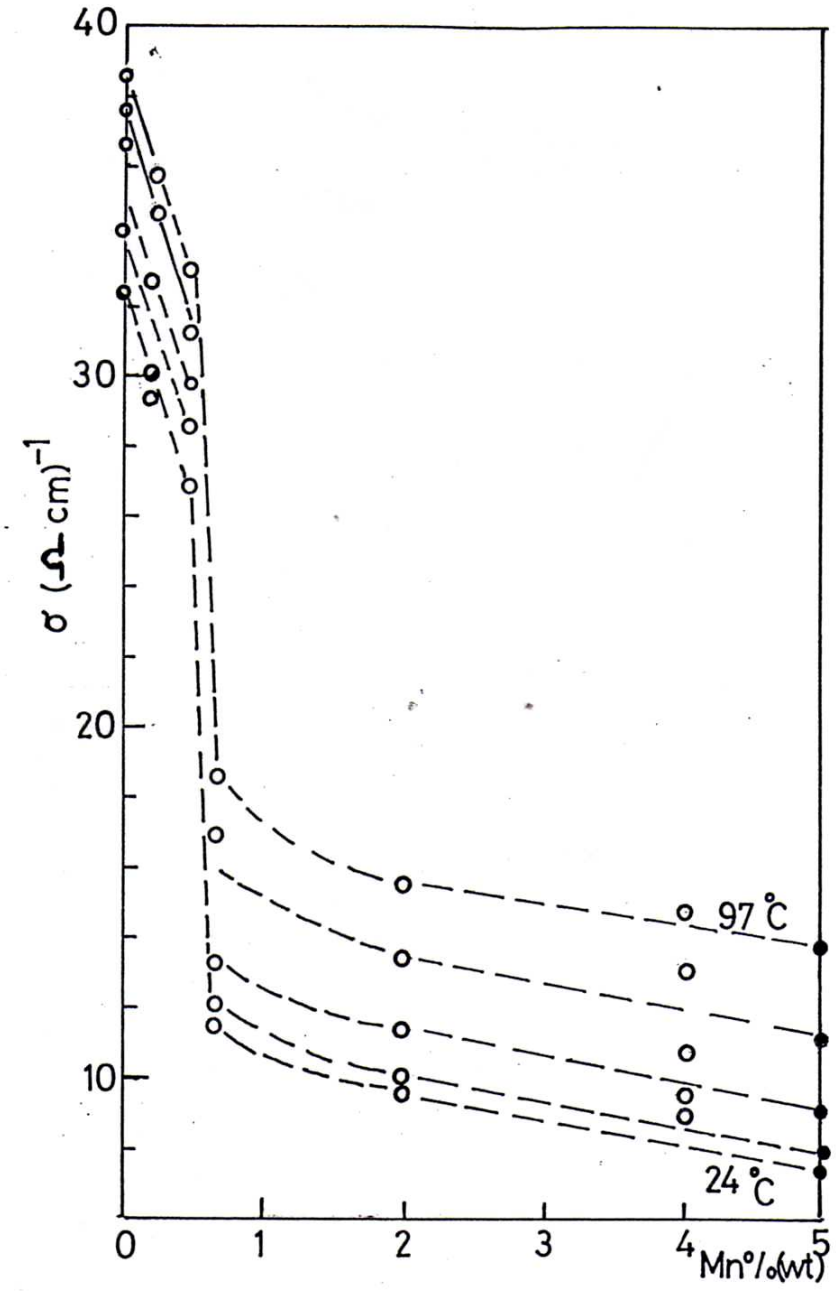

Fig. (3a): σ versus T for undoped and different Mn wt%doping concentrations

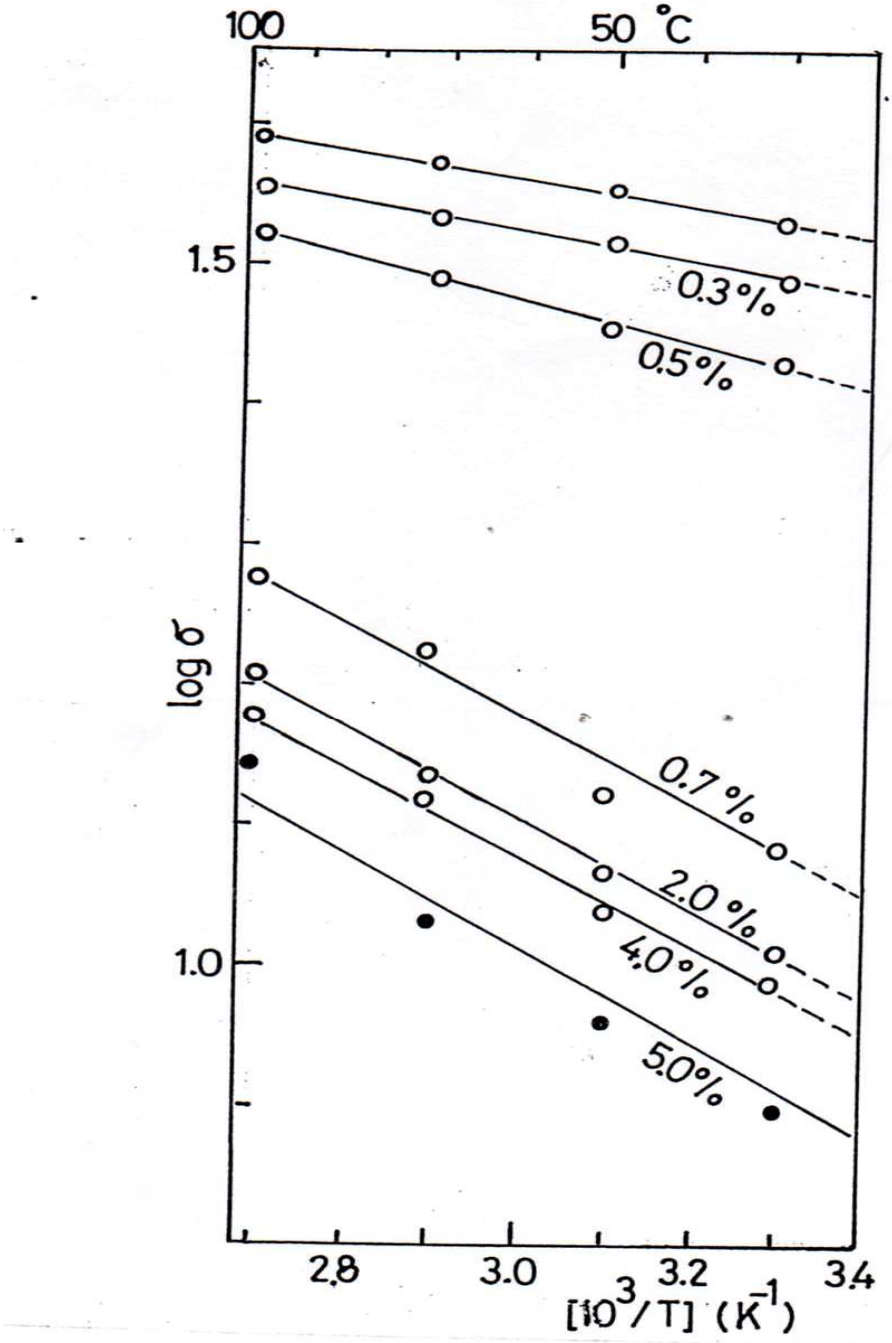

Fig. (3b): log σ versus 1/T for different Mn wt%doping concentrations.

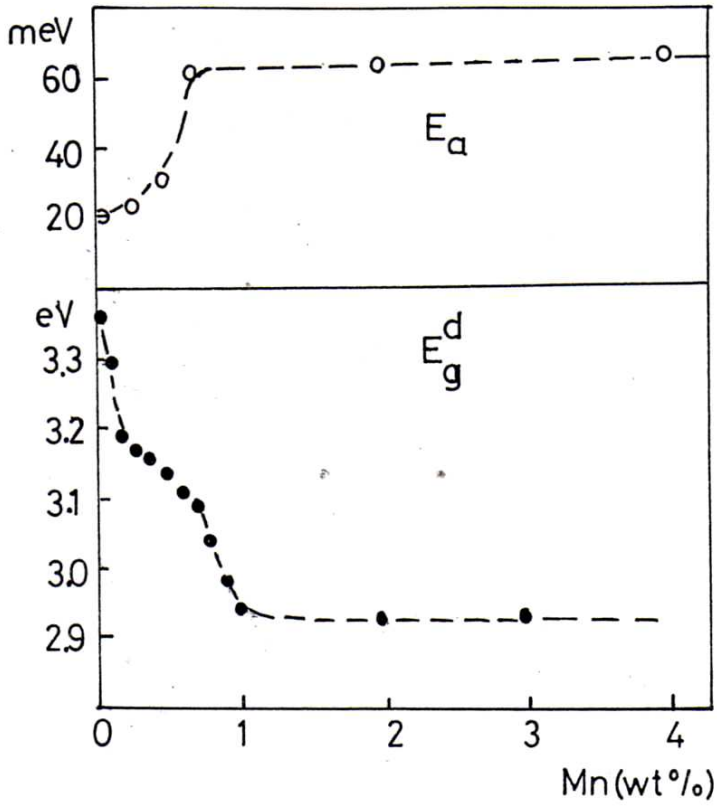

Fig. (4a): Activation energy E_a versus Mn wt% **4a above**

Fig. (4b): Optical direct energy gap E^d_g versus Mn wt% **4b below**

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المستخلص

تم في هذا البحث تحضيراغشيه $CuAlS_2$ المشوبة بعنصر Mn بطريقه الرش الكيميائي الحراري . درجه حراره التحضير (613) كلفن وعلى قواعد زجاجيه .
من دراسه الخواص الضوئيه للاغشيه كداله لنسبه التشويب بعنصر Mn تبين ان فجوه الطاقه المباشره تقع ضمن المدى ev (2.92 – 3.29) لنسب التشويب wt% (5 – 0.1) تم حساب التوصيله الكهربائيه المستمره للاغشيه المشوبه وضمن درجه قياس حراريه (400 – 300) كلفن وقد تبين بانه عند الدرجات الحراريه الواطئه تكون كل من التوصيله الكهربائيه وطاقه التنشيط داله الى تركيز الشوائب حتى نسبه0.7% وتقريبا تكون ثابته عند تركيز اكبر من 0.7%