Optical and DC Electrical Investigations of $CuFeS_2$ Thin Films Prepared by Spray Pyrolysis Technique

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Abstract

$CuFeS_2$ thin films are prepared using the spray pyrolysis technique. The effect of substrate temperature (473-713 ˚K) on the optical and electrical properties of the thin films is investigated. Both optical spectra (Absorption and Reflectivity) show two electronic transitions: one is around 2.55eV and the other is around 3.65eV. The variation of the DC electrical resistivity of the thin films is discussed in relation with the optical results and structural configuration.

Introduction

The chalcopyrite $CuFeS_2$ is an interesting magnetic semiconductor. However this unusual combination is accompanied by different reports of its optical [1-9], magnetic [5,7,10-24] and electrical [5,7,9,11,25-26] properties.

The optical absorption edge of the compound is thought, at first, to have the value around 0.6eV [1,2,4,6]. This value was unusual in comparison with other analogous compounds: for example $CuAlS_2$ (3.4eV) [27-29] and $CuGaS_2$ (2.5eV) [30]. This was later rectified, by attributing this value to what is called "charge transfer" type transition [2,4,6]. The real "band-to-band" transition was found to be varied between (3.2-3.7)eV [6,8]. On the other hand, other researchers pointed out the possibility of the existence of a gapless case in the presence of magnetic order [16-17].

The magnetic moment value $3.8\mu_B$, evaluated from neutron diffraction experiment [10] does not fit with either the magnetic moment of Fe^{3+} ($5\mu_B$) or Fe^{2+} ($4\mu_B$). The value has to be attributed to the hybridization of d and p orbits, of the trivalent atoms. On the other hand, a magnitude of $1.75\mu_B$ has also been reported [18].

The unit cell of the compound is usually taken in the tetragonal system [10,12-13,31-33] with two $CuFeS_2$ molecules. Also, it has been found that the crystal changes at the critical pressure of 60 Kbar from the tetragonal system to a triclinic system [9]. Some authors have reported the same transfer below 80˚K [19]. The crystalline transformation mentioned above is accompanied by an abrupt change in the electric conductivity: from a semiconductor range to near a semi-metal range [9]. The electric conductivity of the compound has usually a metallic behavior with changing in temperature [5,14].

Synthetic $CuFeS_2$ has been prepared as a single crystal by chemical transport reaction [9], or from the melt by Bridgement method [8]. Thin films are obtained by evaporation of the compound [4-6]. Also, $CuFeS_2$ ultra-fine powder is prepared via solvothermal reaction at (200-250)˚C, [24]. Even nanoparticles of this compound with analogous ones ($CuInS_2$, $CuInSe_2$, $CuGaS_2$, $CuFeS_2$ and $AgInS_2$) are prepared in colloids [34].The present work is undertaken to study the optical and the electrical properties of $CuFeS_2$ thin films prepared by a chemical spray pyrolysis technique. To our knowledge; this technique has not been tried before for such a compound. The effect of structural configuration due to formation temperature (via the substrate temperature T_s) on the optical and electrical properties of the thin films obtain is studied in detail.

Experimental Technique

Three 0.048M solutions of $Cu(NO_3)_2.3H_2O$, $Fe(NO_3)_3.9H_2O$, and thiourea $CS(NH_2)_2$, are prepared in distilled water. These solutions are added together to obtain a solution with Cu:Fe:S proportional to 1:1:2. This final solution is sprayed (at an optimized spray rate of 10cc/min) on a temperature controlled glass substrate. The distance between the nozzle and the substrate is kept fixed at (30cm) throughout the work. The substrate is heated at the required temperature for 20 minutes pervious to the spraying. The spraying is carried out on and off periodically (10 secs on and 20secs off). By this procedure, the substrate is kept at the required temperature. Also, it gives enough time for the solution droplets to evaporate and the compound to settle down. The spray set-up and the preparation technique has been described elsewhere [35]. The thin films obtained are clear, brown-red in color, non-transparent, have good adhesion to the substrate and exhibit smooth surfaces free from pinholes. On viewing by reflection, they exhibit a metallic luster. The thickness of the films is in the range 0.42-1.2 μm.Optical measurements (absorption and reflectivity), are carried out by using Pie-Unicom SP-800 UV/VIS. Double beam spectrophotometer. It covers the range from 200-900 nm. The resistivity is measured using the gap method by evaporating two Aluminum strips as electrodes of length 1cm with 2mm distance in between. All measurements (optical and electrical) are carried out at room temperature.

Results and Discussions

The spectra of the optical absorbance for different substrate temperature ($T_{s)}$ are shown in Fig (1). The value of the optical absorption coefficient α is found to be of the order of $10^4 cm^{-1}$ (i.e. $>10^3 cm^{-1}$), indicating the presence of a direct band-to-band transition [36]. The direct band transition is determined by plotting $(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$) as shown in Fig (2). This is in accordance with the equation [37-38]:

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

where α_o is a constant and E_g is the direct band to band transition. Extrapolating of the straight line to $(\alpha h\upsilon)^2=0$ gives the allowed band gap transitions. As can be seen from the figure, there are two transitions: The first (E_{g1}) is around 2.55eV and the second (E_{g2}) is around 3.65eV. This is shown schematically in the insert of Fig (1).

The reflectivity spectra for different T_s are shown in Fig.(3). The reflection of the air-film interface at normal incidence is related to the optical indices by the equation [39]:

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \qquad \text{---------- (2)}$$

with $k = (\alpha\lambda/4\pi)$, where n, k, λ are the reflective index , extinction coefficient and wavelength, respectively. From equation (2) and Fig (3), the spectral dependence of n and k are calculated and shown in Fig. (4) for a $CuFeS_2$ thin film prepared at substrate temperature of 593˚K. Using the n and k values obtained from Fig. (4), and Kramers-Kroning analysis [40], the real ε_1 and imaginary ε_2 parts of the dielectric constant are calculated using the relations:

$$\varepsilon_1 = n^2 - k^2 \quad \text{and} \quad \varepsilon_2 = 2nk \qquad \text{---------- (3)}$$

The spectral dependence of ε_1 and ε_2 is shown in Fig. (5)

The imaginary part of the dielectric constant is related to the photon energy for direct allowed band-to-band transitions is in the form [41]:

$$(h\nu)^4 \varepsilon_2^{\,2} = \alpha_o (h\nu - E_g) \qquad \text{for } h\nu > E_g \quad \text{------(4)}$$

$$\varepsilon_2 = 0 \qquad \text{for } h\nu < E_g \quad \text{------(5)}$$

The direct allowed energy gaps are determined by plotting $(h\nu)^4 \varepsilon_2^{\,2}$ as a function of $(h\nu)$, as shown in Fig. (6). As one can see from the figure, the curves yield straight lines, which indicates a good fit to the equation. Extrapolation of the straight lines to $(h\nu)^4 \varepsilon_2^{\,2} = 0$ gives

two electronic transition, one is around 2.55eV and the other is around 3.65eV. on the other hand, both absorption and reflectivity methods give the same results.

It appears from the absorption curve for different formation temperature (T_s), Figs. (1,2), that the optical absorption technique is not sensitive enough for structural variations, though the spectrum gives a general picture of the energy scheme. On the other hand, the reflectivity curves are a better manifestation of the different structure configuration. In the range of our measurements, the reflectivity spectra of our specimen are in close resemblance with those obtained for $CuFeS_2$ crystal under pressure [9]. One can see the hump at 2.2eV in our T_s=653˚K and with that of crystalline specimen under 4.2 Kbar [9]. Also, there is a good agreement between our curves for T_s=563, 593˚K with those above 60Kbar of pressure [9].

The DC electric proparties of the deposted films have been mesured. Hot-probe measurements indicate that the prepared $CuFeS_2$ films display p-type conduction. Fig. (7) shows the variation of resistivity (ρ) as a function of the substrate temperature T_s. The figure shows a striking feature. By increasing the substrate temperature, the resistivity begins with the value of ~$8.5x10^{+3}$ Ω.cm at 473˚K, and ends with ~$19.9x10^{+3}$ Ω.cm at 693˚K via a minimum of the value of ~0.07 Ω.cm at 593˚K. Such a behavior is common in chemical spray pyrolysis technique [42]. The minimum value at 593˚K is comparable with the value of ~0.08 Ω.cm obtained for single crystals under normal pressure [43]. On the other hand, our values are very high compared with ~0.003 Ω.cm. Obtained for n-type sintered polycrystalline specimen [5]. Also, the same value of ~0.003 Ω.cm has been achieved by subjecting a $CuFeS_2$ crystal to a pressure over 60 Kbar with a change in the crystalline system from tetragonal to hcp structure. Though the resistivity values mentioned are within the semiconductor realm, it has a metallic behavior.

Apparently, the optical properties do not fulfil the criteria for the investigation of the effect of the temperature of formation T_s. The electrical conductivity is a better test for that. The optical properties are an indication of the molecular structure while the DC electrical conductivity is a bulk property, and hence the difference.

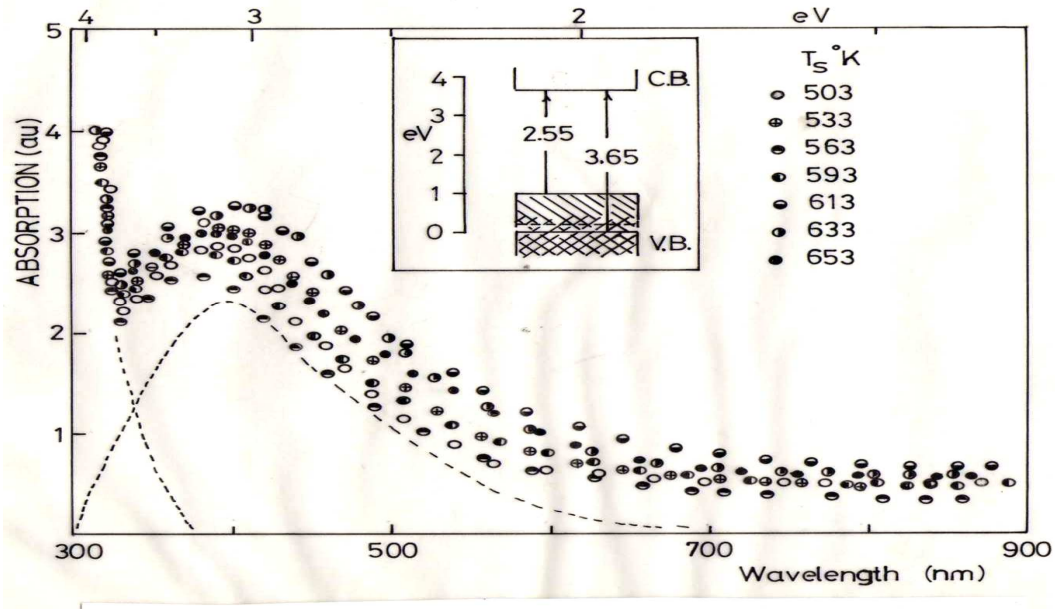

Fig. (1) : Absorption spectra for $CuFeS_2$ thin films prepared at different T_s.

The insert is a proposed energy schematic diagram.

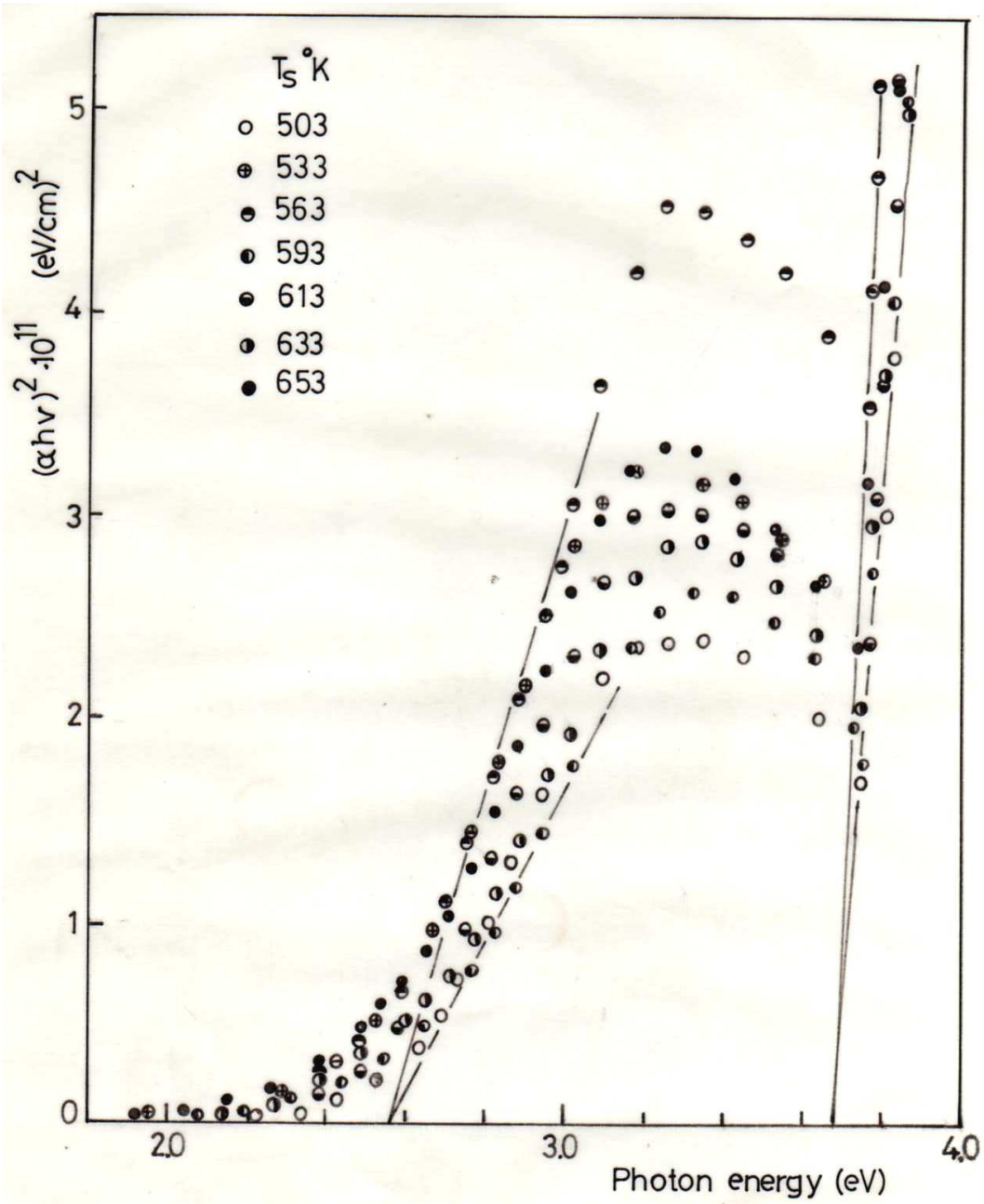

Fig. (2) : The plot of $(\alpha h\nu)^2$ versus $(h\nu)$ for $CuFeS_2$ thin films prepared at different T_s.

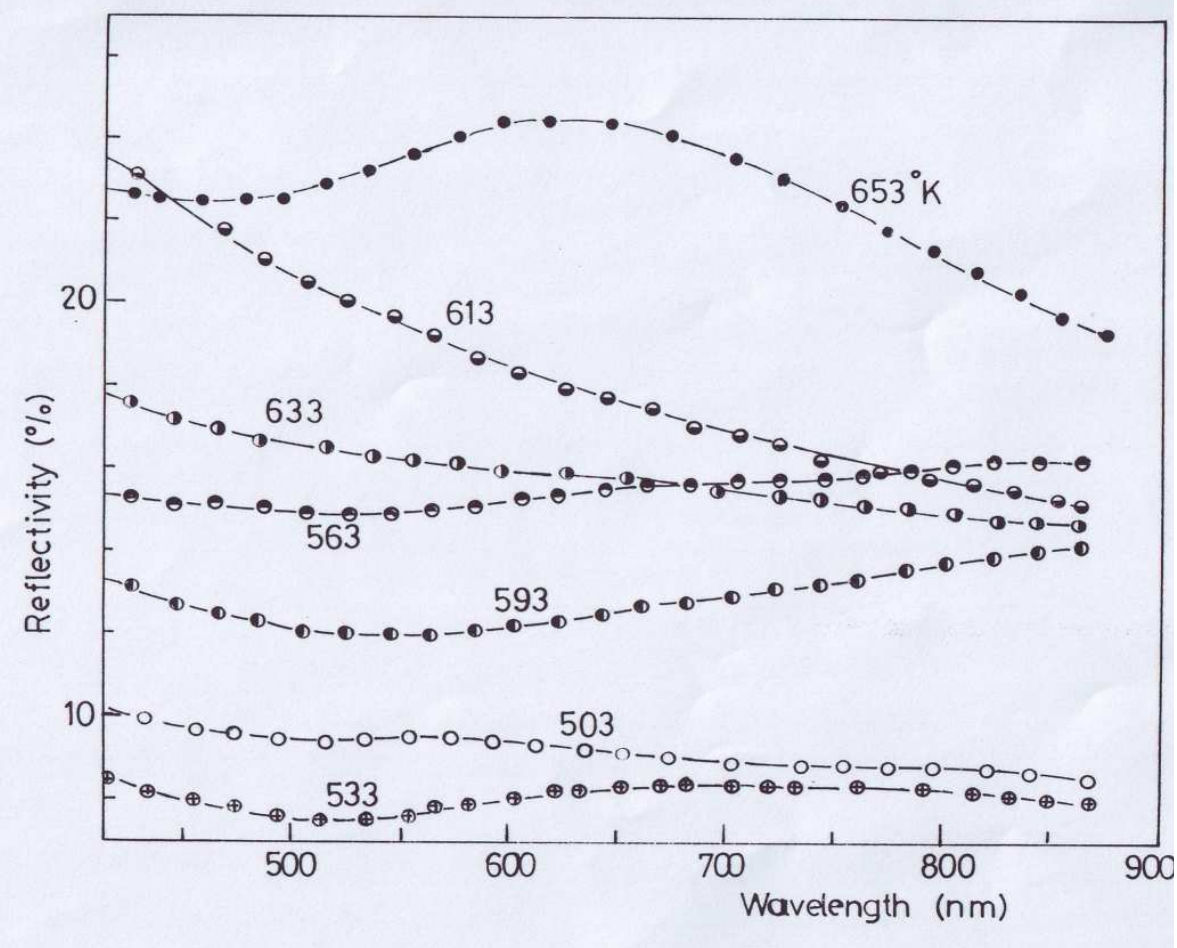

Fig. (3) : Reflectivity spectra of $CuFeS_2$ thin films prepared at different T_s.

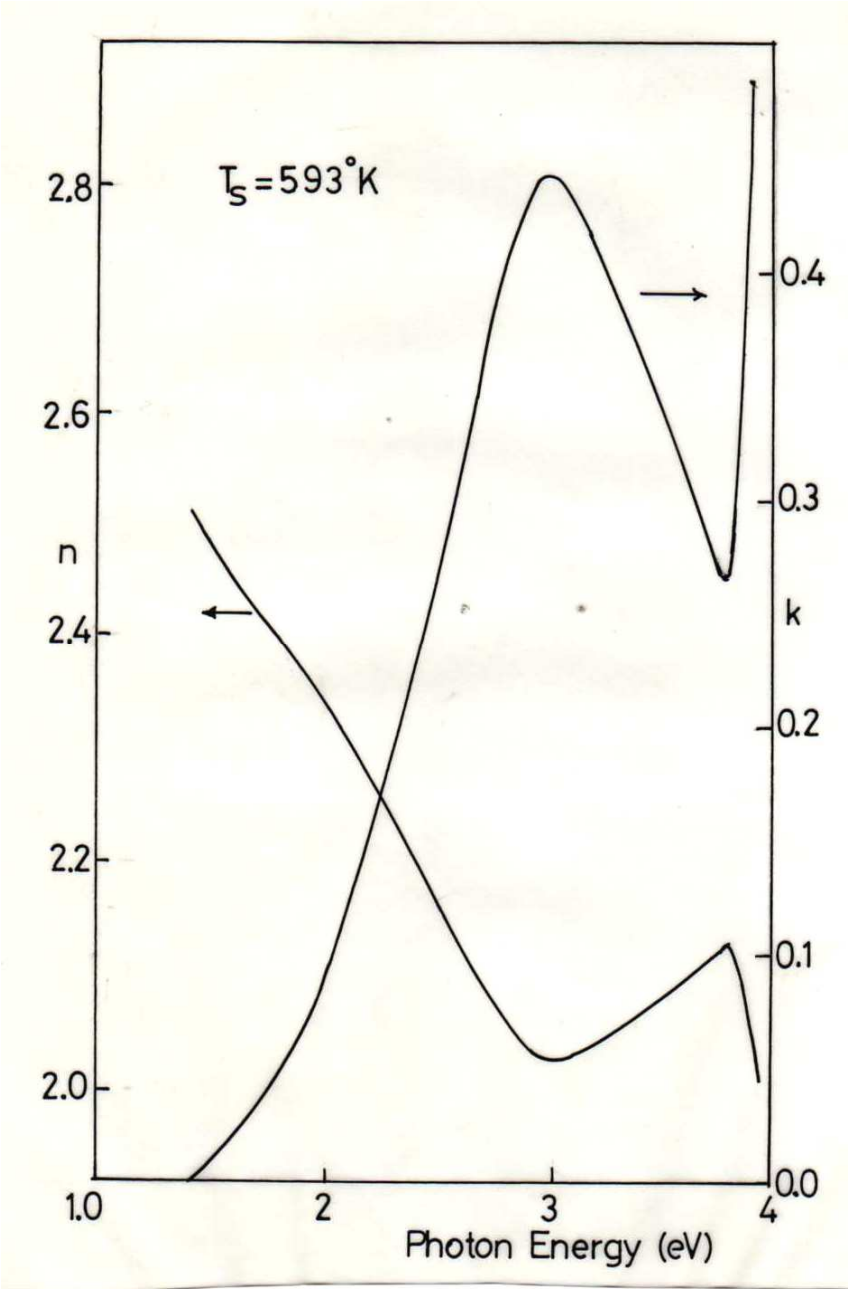

Fig. (4) : The refractive index (n), and the extinction coefficient (k), as a function of photon energy for $CuFeS_2$ thin film prepared at T_s=593˚K.

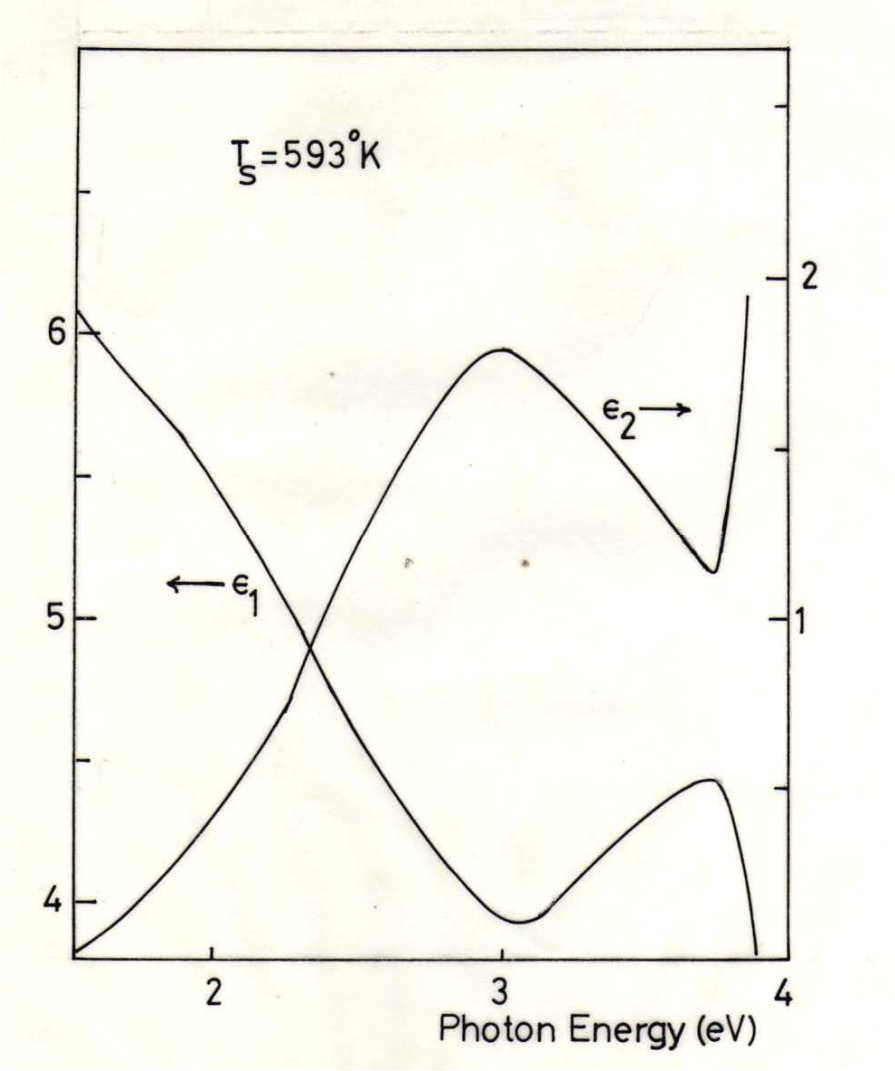

Fig. (5) : Real part, ε_1, and imaginary part, ε_2, of dielectric constant as a function of photon energy for $CuFeS_2$ thin film prepared at T_s=593˚K.

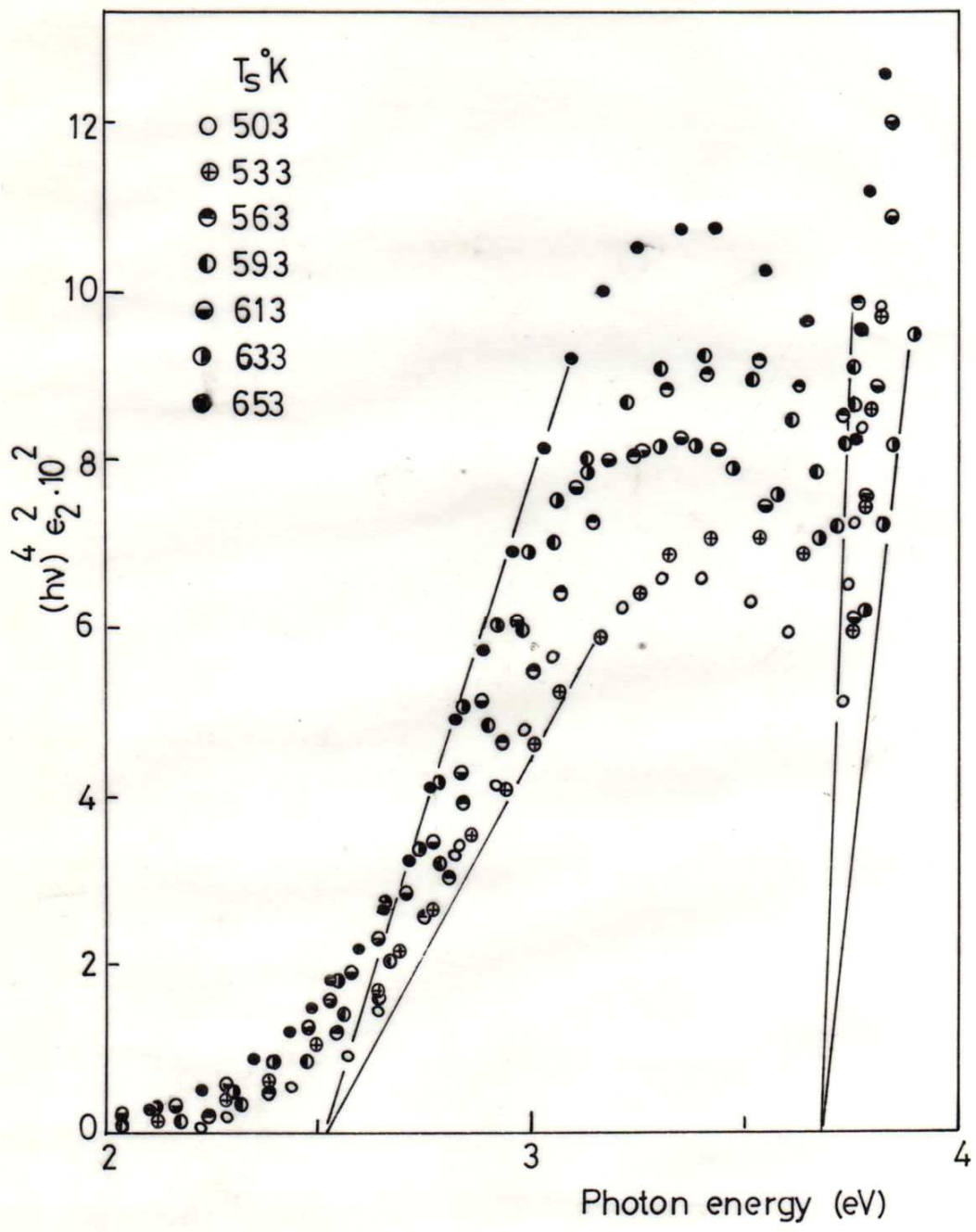

Fig. (6) : The plot of $(h\nu)^4 \varepsilon_2^2$ versus $(h\nu)$ for $CuFeS_2$ thin films prepared at different T_s.

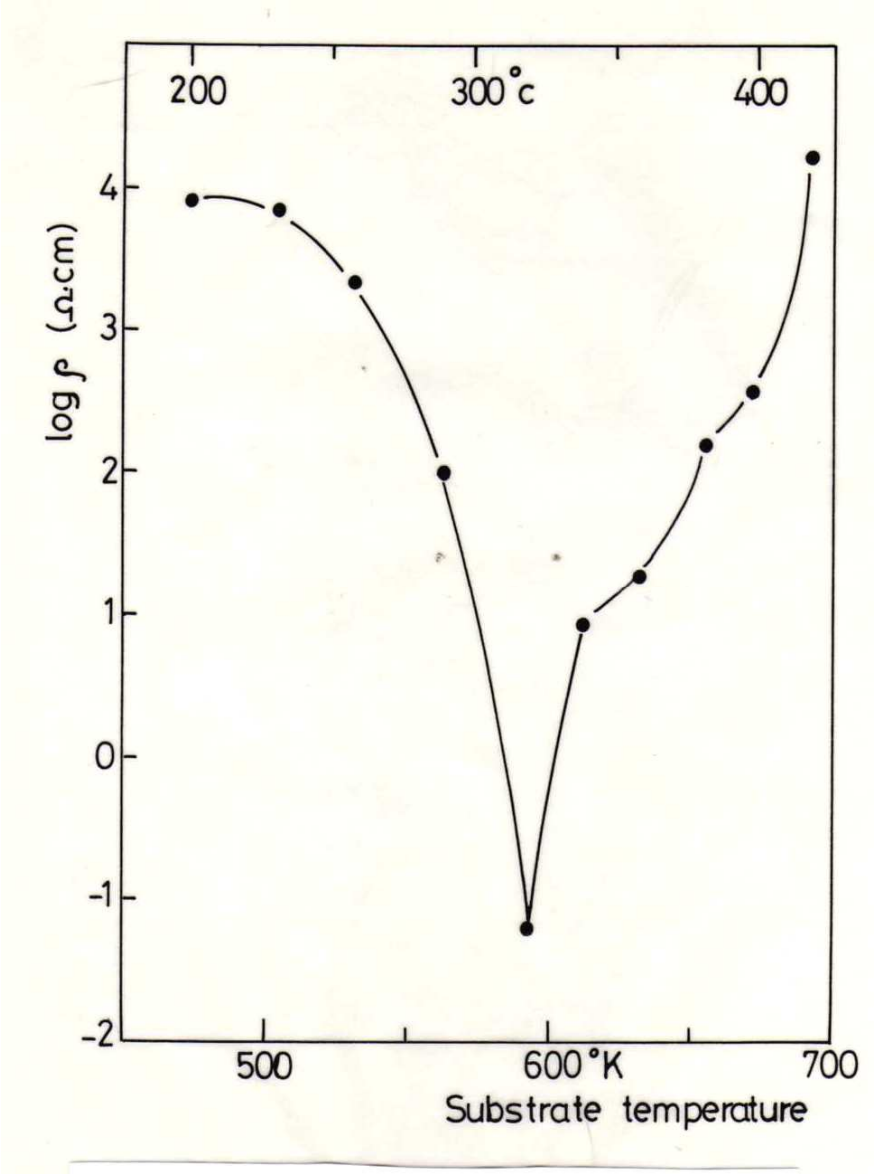

Fig. (7) : The resistivity (ρ) as a function of substrate temperature T_s for $CuFeS_2$ thin films.

Conclusion

In this study, the optical (absorption and reflectivity) and electrical properties of $CuFeS_2$ thin films prepared by spray pyrolysis method, for different substrate temperature, have been investigated. Room temperature optical investigations show two electronic transitions, one is around 2.55 eV and the other is around 3.65 eV. The 3.65eV edge is considered in the present analysis as the true "band-to-band" transition. The Fe^{3+} 3d orbit (or its hybridization with Cu-3p in the presence of S) forms an inter-gap band near the upper edge of the valance band of the thin films formed.

By controlling the heat of formation (i.e. controlling T_s) one can adjust the properties of the sample obtained. First, the temperature of formation is a fundamental factor in varying the structure configuration. Second, temperature plays a fundamental role in the diffusion of the impurities to the grain boundaries. Apparently the non-localization of the Fe^{+3} inter-gap band builds a similar bulk energy band. This is a partially filled inter-gap band near the edge of the

valance band. It can partially overlap with the bulk valance band. Consequently, it behaves like a conduction band. So, one gets a metallic behavior with resistivity in the semiconductor region. Also, it conforms to the p-type semiconductor of the Hot-probe results.

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المستخلص

تم في هذا البحث تحضير اغشيه $CuFeS_2$ بطريقه الرش الكيميائي الحراري . تم مناقشه تاثير درجه حراره القاعده ضمن المدى (713 – 473) كلفن على كل من الخواص الضوئيه والكهربائيه . من درسه طيف الامتصاصيه والانعكاسيه الضوئيه اتضح وجود انتقالات الكترونيه اثنين الاول بحدود 2.55 ev ولاخر بحدود 3.65 ev . اما بالنسبه للتغير بقيمه المقاومه الكهربائيه المستمره المقاسه للاغشيه فقد تبين انها تنخفض بالتوافق مع النتائج الضوئيه.