

Study of trap levels by electrical techniques in p-type CuInSe_2 thin films prepared using chemical bath deposition

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CuInSe_2 thin films, prepared using the Chemical Bath Deposition (CBD) technique, were analysed using Thermally Stimulated Current (TSC) measurements in order to get a clear picture of the different trap levels present in it. As-prepared samples showed two trap levels: the prominent one was due to the presence of a Se vacancy, while the weak one was due to the presence of a Cu vacancy. After annealing in air, the Se vacancy disappeared and a new level appeared which is suspected to be due to adsorbed oxygen. But annealing in air does not affect the Cu vacancy. On the other hand, annealing in vacuum does not affect Se vacancy, but the presence of an Fe impurity was detected in this case. A possible explanation for this phenomenon is also discussed. The dark conductivity measurements were also conducted on as-prepared as well as annealed CuInSe_2 samples. These results are found to be in good agreement with the results obtained from TSC measurements.

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1. Introduction

CuInSe_2 (CIS) is a promising absorber material for the fabrication of polycrystalline thin film solar cells with CdS as the window layer and this is due to its exceptional opto-electronic properties suitable for photovoltaic device fabrication [1]. CIS based thin film solar cells have shown efficiency >17% in recent times [2] which is the highest efficiency of a thin film single junction solar cell and this indicates the importance of the material in the field of terrestrial photovoltaic applications.

Several methods have been used for the preparation of CIS thin films. Among these, CBD is the simplest technique that offers great promise for the development of low cost devices. One of the factors affecting the efficiency of thin film solar cells is the electrical properties of the film which in turn depends mainly on the presence of different trap levels. TSC measurement is a well-known non-isothermal technique for the investigation of trap levels in semiconducting materials [3–5]. It permits a survey of gap states. TSC measurements were performed in the case of co-evaporated CIS films by Datta *et al.* [6]. But similar studies on this film prepared using CBD have not been reported to the best of our knowledge. In this paper we discuss the results of the TSC experiments on p-type CIS thin films prepared using CBD technique. Dark conductivity measurements were also taken on these samples in order to get more details about the existing trap levels.

2. Theory

The thermally stimulated current (I) due to a single trap of depth E (activation energy) with negligible retrapping and monomolecular kinetics is given by [4, 5]

$$I = I_0 \exp \left[\frac{-E}{kT} - \frac{\nu}{\beta} \int_{T_0}^T \exp \left(\frac{-E}{kT'} \right) dT' \right] \quad (1)$$

where T_0 is the initial temperature, β the heating rate and ν is the attempt-to-escape frequency. Here I_0 , the pre-exponential factor is a weak function of temperature and I exhibits a maximum as a function of temperature. As the temperature increases the trapped charge carriers are released and this gives rise to current peaks. Consequently, a plot of current versus temperature is called the TSC spectrum. The location of TSC peak on the temperature scale gives information on the value of activation energy and capture cross section of the traps. If more than one type of trap is present, curves obtained from TSC studies may be expected to show several maxima depending upon the activation energies of the traps. If carriers are trapped at a single energy level, TSC spectra will show only one peak.

The trap depth can be calculated from Equation 1 as $E = 2kT_m^2/(T_2 - T_1)$ where $(T_2 - T_1)$ is the width of peak at half maximum value and T_m is the temperature of the peak maximum. Mott and Gurney [7] suggested that capture cross section 'a' of the traps may also be calculated from TSC spectra as $a = a_0\nu$ where $a_0 =$

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$10^{-26} \text{ cm}^2 \text{ s}$, $\nu = \beta/T_m (\alpha \exp \alpha)$ and α is defined as E/kT_m .

The variation of dark conductivity (σ) with temperature (T) for an extrinsic semiconductor can be expressed as $\sigma = \sigma_0 \exp(-E/kT)$ where E is the activation energy. Clearly, a plot of $\log \sigma$ versus $10^3/T$ (Arrhenius plot) will be a straight line from the slope of which the activation energy can be calculated as $E = 10^3 m k$, where m is the slope of the graph and k is Boltzmanns constant. When the sample contains different defect levels the Arrhenius plot will have different slopes, giving different activation energies corresponding to the various defect levels.

3. Experimental

Samples were prepared using CBD technique as reported earlier [8, 9]. TSC and dark conductivity measurements were done on as-prepared samples as well as annealed samples. The samples were annealed in air and vacuum (10^{-2} Torr) at 150°C , 175°C , 200°C for 1 hour. In order to conduct TSC measurements, silver paint contacts were given to the sample and was mounted in a metallic vacuum cell at a pressure of 10^{-2} Torr. It was first frozen to 100 K (T_0), which is low enough to make the probability of thermal release of carriers negligible, and then exposed to an optical excitation for a fixed time so that carriers are photoexcited and trapped in the gap states well in excess of their thermal equilibrium concentration. In the present work, the source of excitation was a Tungsten Halogen lamp (25 Watt, Oriel-6394). This process results in the filling of electronic or ionic traps. The excitation was given for a fixed timings (in the range 1–4 minutes) and the sample was heated at a linear rate (β) of 0.05 K/sec always. Current was measured using an electrometer (ECIL-EA815) varying the sample temperature from 100 K to 500 K along the film plane under a dc field of 6 V/cm.

For dark conductivity measurements, thickness of the sample was measured using gravimetric method. Films of thickness 250 nm were used in these measurements. Silver paint contacts were given to the sample. In this case also it was mounted in a metallic vacuum cell at a pressure of 10^{-2} Torr and measurements were carried out by applying a steady voltage of 6 V across the sample. The only difference from TSC measurement was that here samples were not illuminated. The resulting current was measured using the electrometer while the sample temperature was varied from 100 K to 500 K. Conductivity of the sample was calculated for different temperatures and a plot of $\log \sigma$ versus $10^3/T$ gave the Arrhenius plot.

4. Results and discussion

TSC spectra of as-prepared CIS samples are shown in Fig. 1. With 1 and 2 minutes light excitation, the TSC spectra clearly showed only one peak, whose activation energy was calculated to be 70 meV (Table I). But the spectra of same type of sample showed one more peak (of activation energy 40 meV) on increasing the

light excitation time to 4 minutes. Since the sample was not doped, the defect observed must be intrinsic. It was reported earlier that the donor level of 70 meV was probably due to selenium vacancy [10, 11]. Selenium is volatile and vacancies occur during the deposition process itself. Trap level of activation energy 40 meV corresponds to acceptor level [12] and was attributed to Cu vacancy by Migliorato [13]. Presence of acceptor and donor levels due to Cu and Se vacancies respectively

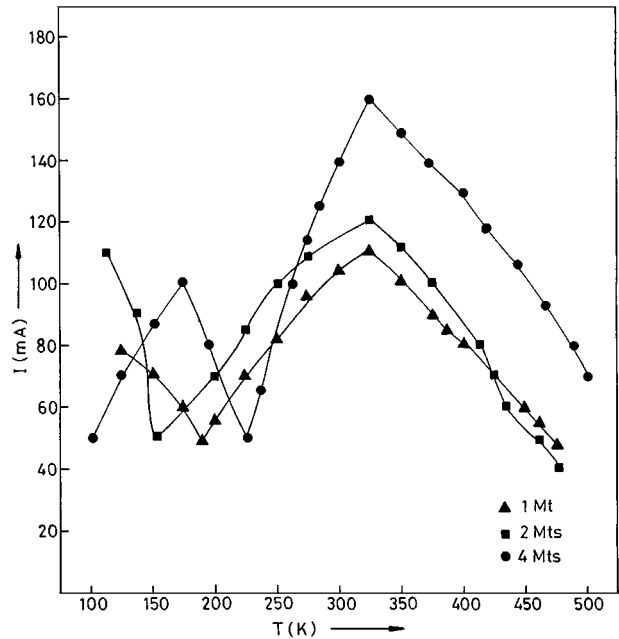


Figure 1 TSC spectra of as-prepared CuInSe₂ thin film samples for different light excitation time.

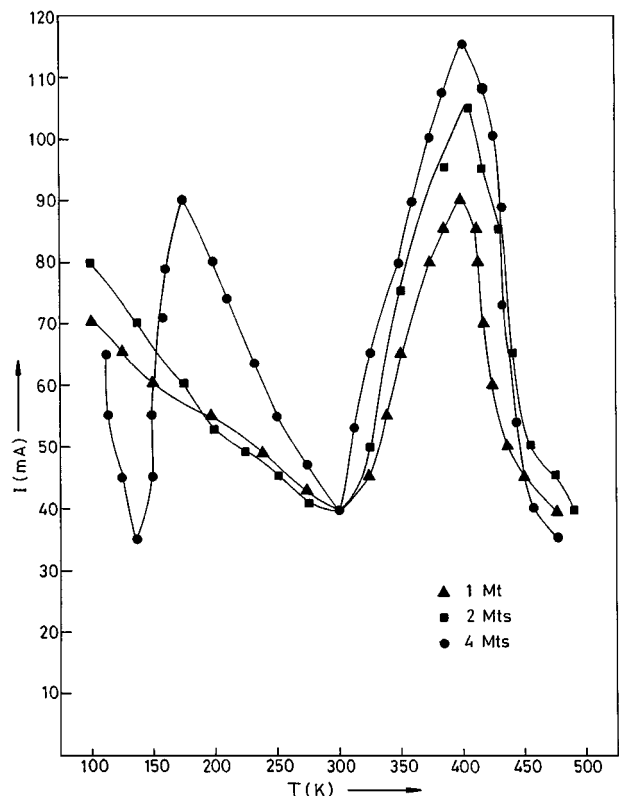


Figure 2 TSC spectra of CuInSe₂ thin film samples air annealed at 150°C for different light excitation time.

TABLE I Values of activation energy of various trap levels in CuInSe₂ thin film samples obtained from TSC measurement

Sample type		Activation energy (meV) for different light excitation time		
		1 mt.	2 mts.	4 mts.
Unannealed		70.08 ± 0.52	70.08 ± 0.81	1) 70.08 ± 0.54 2) 40.63 ± 0.58
Air annealed at	150 °C	220.8 ± 1.38	219.8 ± 1.35	1) 220.7 ± 1.48 2) 40.63 ± 0.58
	175 °C	220.8 ± 1.38	220.8 ± 1.38	1) 220.8 ± 1.38 2) 85.28 ± 1.01
	200 °C	220.8 ± 1.38	220.6 ± 1	1) 220.8 ± 1.38 2) 85.18 ± 1.07
Vacuum annealed at	150 °C	70.89 ± 0.55	70.62 ± 0.54	1) 70.89 ± 0.55 2) 400.2 ± 4.85
	175 °C	70.02 ± 0.60	70.89 ± 0.55	1) 70.89 ± 0.55 2) 400.43 ± 4.56
	200 °C	70.62 ± 0.54	70.02 ± 0.6	1) 70.89 ± 0.55 2) 400.23 ± 2.94

TABLE II Values of capture cross sections of various trap levels in CuInSe₂ thin film samples obtained from TSC measurements

Sample type		Capture cross section (10 ⁻²⁶ cm ²) for different light excitation time		
		1 mt.	2 mts.	4 mts.
Unannealed		4.62 × 10 ⁻³	4.68 × 10 ⁻³	1) 4.62 × 10 ⁻³ 2) 0.10 × 10 ⁻³
Air annealed at	150 °C	0.481	0.402	1) 0.475 2) 0.011
	175 °C	0.481	0.481	1) 0.481 2) 0.142
	200 °C	0.481	0.475	1) 0.481 2) 0.160
Vacuum annealed at	150 °C	4.81 × 10 ⁻³	4.68 × 10 ⁻³	1) 4.81 × 10 ⁻³ 2) 3.28 × 10 ⁻³
	175 °C	4.62 × 10 ⁻³	4.81 × 10 ⁻³	1) 4.81 × 10 ⁻³ 2) 3.80 × 10 ⁻³
	200 °C	4.68 × 10 ⁻³	4.68 × 10 ⁻³	1) 4.81 × 10 ⁻³ 2) 3.26 × 10 ⁻³

had been reported by Yu [14]. It had been suggested that copper vacancies were easily formed in CIS because copper could participate weakly in the covalent bonding [15]. From photoluminescence study, an acceptor level of 40 meV was attributed to Cu vacancy by Tanda also [10]. The values of capture cross section of these trap levels are given in Table II. It indicates that value corresponding to the acceptor level is small compared to that of the donor level (Se vacancy). Probably this may be the reason why the level corresponding to Cu vacancy becomes “visible” only after the irradiation for 4 minutes.

TSC spectra of air annealed films are depicted in Figs 2–4. With 1 and 2 minutes light excitation TSC spectra of all samples show only one peak (irrespective of annealing temperature) corresponding to a level having activation energy of 220 meV. It was reported that this level of 220 meV is a donor level and no clear reason for its existence has not been given [16, 17]. But here the Se vacancy, which existed in as-prepared sample, disappeared on air annealing and donor level of 220 meV appears. Under this circumstance, we conclude that the 220 meV donor level may be due to the adsorption

of oxygen during air annealing in the Se vacancy of as-prepared samples. With 4 minutes excitation time, these samples gave one more peak of smaller capture cross section compared to that of the previous one and this corresponds to Cu vacancy. In the case of sample annealed at 150 °C, the activation energy is 40 meV (Cu vacancy) while the samples annealed at 175 °C and 200 °C have it to be 85 meV. It was reported by Tanda that the level corresponding to 85 meV was also due to Cu vacancy [10]. Hence it is concluded that air annealed samples have Cu vacancy with smaller capture cross section as in the case of as-prepared samples.

TSC spectra of samples annealed in vacuum are shown in Figs 5–7. As in the case of air annealed samples, these samples also showed one peak irrespective of annealing temperature under 1 and 2 minutes light excitation. Activation energy of this trap level was found to be 70 meV, which is the donor level of Se vacancy similar to the case of as-prepared samples. After 4 minutes light excitation, these samples showed an additional peak of smaller capture cross section having trap depth of 400 meV. A similar acceptor level was detected by Wasim [18] in CIS from thermal conductivity

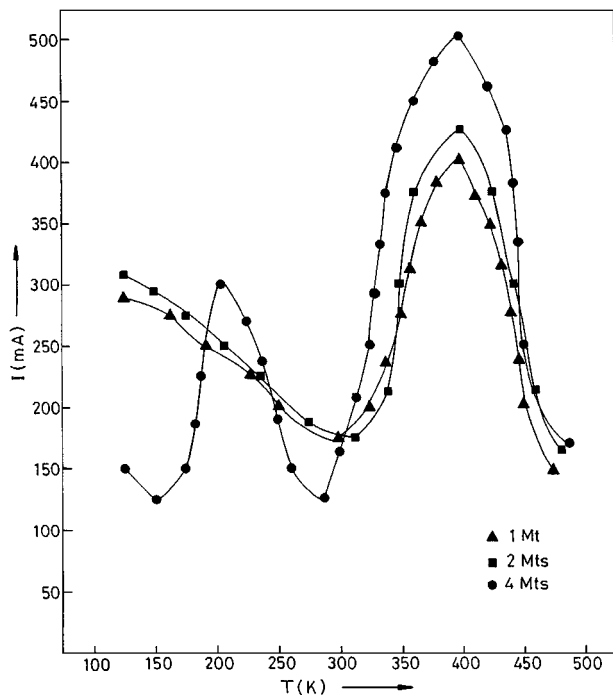


Figure 3 TSC spectra of CuInSe₂ thin film samples air annealed at 175 °C for different light excitation time.

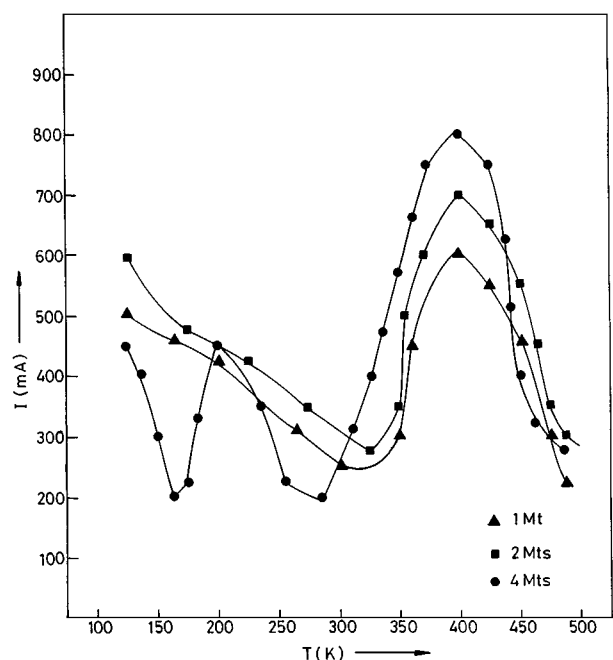


Figure 4 TSC spectra of CuInSe₂ thin film samples air annealed at 200 °C for different light excitation time.

measurements and this was attributed to be due to Fe impurity. Many other authors [16, 19, 20] detected Fe impurity in CIS samples. The existence of Fe impurity in CIS as a contamination in Cu was observed from electron paramagnetic resonance [21, 22] also. In the present investigation, we prepared the CIS samples using CBD from a reaction bath containing aqueous solutions of copper citrate, indium citrate and sodium selenosulphate [8,9]. Fe impurity can come from the copper salt. When Fe is present in the reaction mixture with a pH ~7, Fe(OH)₃ may be formed which decomposes and deposits as γ -FeO along with CIS film. When

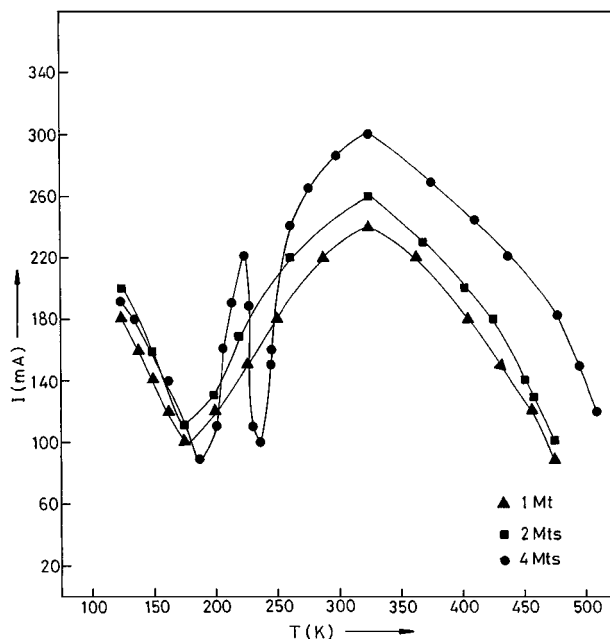


Figure 5 TSC spectra of CuInSe₂ thin film samples vacuum annealed at 150 °C for different light excitation time.

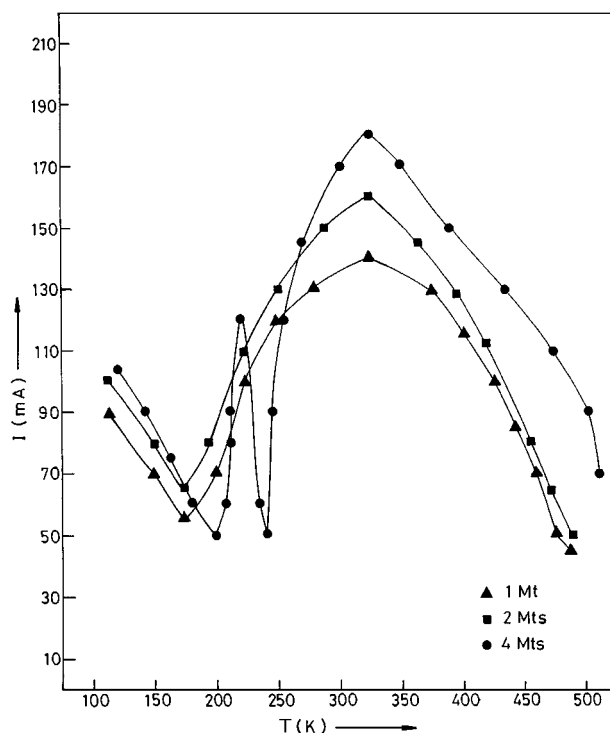


Figure 6 TSC spectra of CuInSe₂ thin film sample vacuum annealed at 175 °C for different light excitation time.

this film is annealed in air Fe₂O₃ may be formed and this will not give any TSC peak. But when the sample is annealed in vacuum FeO may be transformed into FeSe and SeO₂. FeSe is unstable and will be associated with other molecules or defects. This may give rise to a TSC peak. The peak observed in vacuum annealed samples may be explained in this way.

Arrhenius plot of conductivity of as-prepared and vacuum annealed (200 °C) samples are shown in Fig. 8 and of air annealed sample (220 °C) in Fig. 9. Each of these graphs indicated two distinct slopes, from which

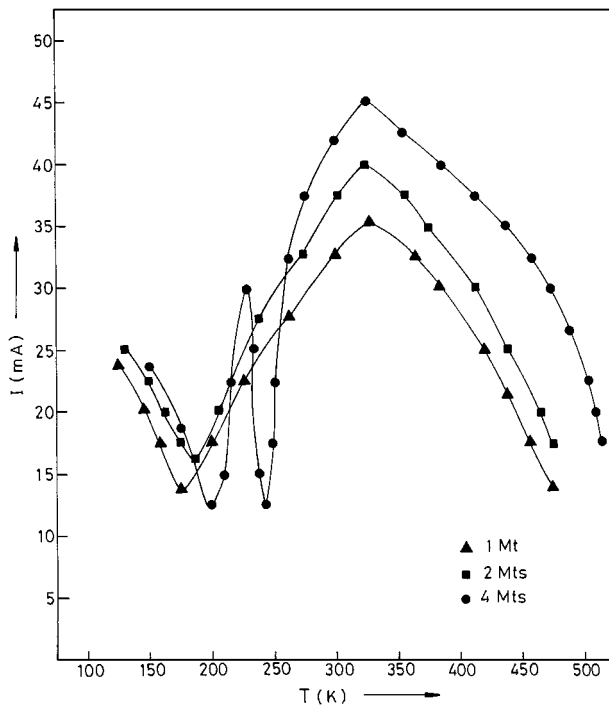


Figure 7 TSC spectra of CuInSe₂ thin film sample vacuum annealed at 200 °C for different light excitation time.

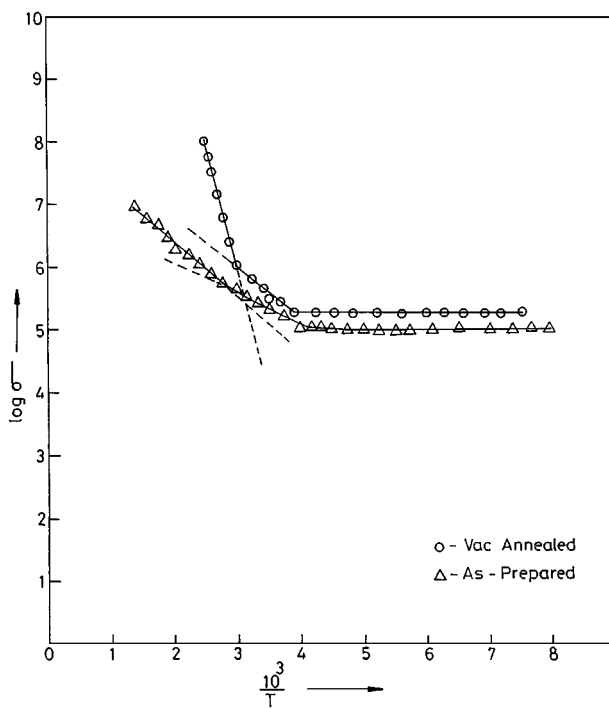


Figure 8 Arrhenius plot of conductivity of as-prepared and vacuum annealed (200 °C) CuInSe₂ thin film samples.

activation energies were calculated (Table III). As-prepared sample had trap levels of activation energies 70.72 meV and 40.5 meV indicating the presence of Se vacancy and Cu vacancy. Again vacuum annealed sample had levels of activation energy values at 70.29 meV and 414.5 meV which supported the existence of Se vacancy and Fe impurity. In the case of air annealed (200 °C) samples, the arrhenius plot indicated two activation energy values at 40.5 meV and 103 meV, which are attributed to Cu vacancy as obtained by Sridevi *et al.* [23]. From this it is clear that results of the elec-

TABLE III Values of activation energies obtained from dark conductivity measurements on CuInSe₂ thin film samples

Sample type	Activation energy (meV)	
As-prepared	1) 70.72	2) 40.5
Air annealed at 200 °C for 1 hour	1) 103	2) 40.5
Vacuum annealed at 200 °C for 1 hour	1) 70.29	2) 414.5

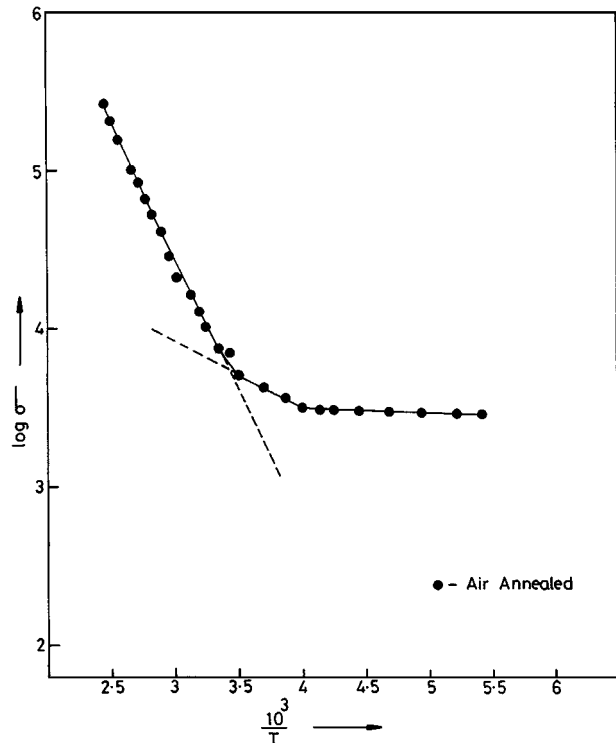


Figure 9 Arrhenius plot of conductivity of air annealed (200 °C) CuInSe₂ thin film samples.

trical conductivity measurement very well corroborate the TSC measurement result.

5. Conclusion

Trap level detection of CIS films prepared using a CBD technique was performed by a TSC measurement technique on samples in the as-prepared and annealed condition. The former type had a Se vacancy as a prominent trap and Cu vacancy of smaller capture cross section. But when these samples were annealed in air, the Se vacancy of the as-prepared sample disappeared, and another donor level supposed to be due to the adsorption of oxygen in the Se vacancy came into existence. Cu vacancies continued to exist in air annealed samples. Vacuum annealing did not affect the presence of the Se vacancy as a prominent one since oxygen adsorption is quite difficult under this condition. Interestingly, these samples also showed the presence of an Fe impurity. Dark electrical conductivity measurements on these samples were found to be in good agreement with the results obtained from TSC measurements.

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