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Effect of hydrogen on electrical transport properties of polycrystalline $CuInTe_2$ thin films

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The effect of molecular hydrogen on the electrical transport properties of p-type $CuInTe_2$ films was studied by exposing the films at high pressures (up to 700 psi). It was observed that the Hall coefficient increased initially with the increase of pressure up to 500 psi and then started decreasing. The mobility was found to increase with pressure of the gas. The results are explained in terms of a grain-boundary scattering mechanism and in terms of donor action provided by hydrogen diffusion into the thin film.

1. Introduction

Solid solutions of group III–VI layer compounds with I–VI or II–VI compounds, i.e. ternary chalcopyrite crystals in general and $CuInSe_2$, $CuInS_2$ and $CuInTe_2$ in particular have drawn considerable interest in recent years because of their important technological applications [1–6] in the areas of visible and infrared light emitting diodes, infrared detectors, optical parametric oscillators, upconverters and solar energy conversions. These ternary compounds are reported to have high potential in photovoltaic devices particularly as heterojunction solar cells [4, 7]. Shay *et al.* [8] have demonstrated the first single crystal $CuInSe_2$/CdS heterojunction solar cell with 12% efficiency. In spite of the wide application of these materials, very little work has been reported on the fabrication, characterization and optimization of thin films for these materials. Kazmerski and Shieh [9] have reported on the growth of thin films of $CuInTe_2$ and other chalcopyrites utilizing single and multiple sources. It has been reported by Kazmerski and Juang [10] that the films of $CuInTe_2$ are always polycrystalline in nature and the mobilities are of the order of $10\,cm^2\,V^{-1}\,sec^{-1}$ for p-type films which is far below the mobility of the holes in the bulk crystalline material.

Many workers [11–14] have investigated the effect of surrounding ambient gases on the electrical properties of metals and semiconductors. The gases in general have been found to affect the properties of a semiconductor in a number of ways, e.g. acting as donors or acceptors [14, 15], changing the lattice spacing [16], affecting the work function [17], forming an interfacial compound [18] with the host material, etc. Spear and Lecomber [19] have reported that hydrogenation decreases the density of states in amorphous silicon. Robinson and D'Aiello [20] have shown that hydrogenation reduces the grain boundary potential barrier in polycrystalline solar cells. In the present work, the effect of molecular hydrogen on p-type $CuInTe_2$ films has been studied by exposing the films to high pressures (up to 700 psi§). The studies revealed that the carrier concentration decreased with the increase of pressure up to 500 psi and then started increasing with a further increase of pressure. The mobility, on the other hand, is found to increase significantly with the increase of pressure (up to 500 psi) of gas to which the films were exposed. The results have been explained on the basis of existing theories.

2. Experimental details

$CuInTe_2$ was prepared by heating the elements (5 N pure) in stoichiometric proportion in a vacuum-sealed quartz ampoule to a temperature of about 850° C for 20 h. The temperature was then lowered to about 300° C in about 6 h. The ampoule was then quenched in ice cold water.

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§1 psi = 6.89×10^3 Pa.

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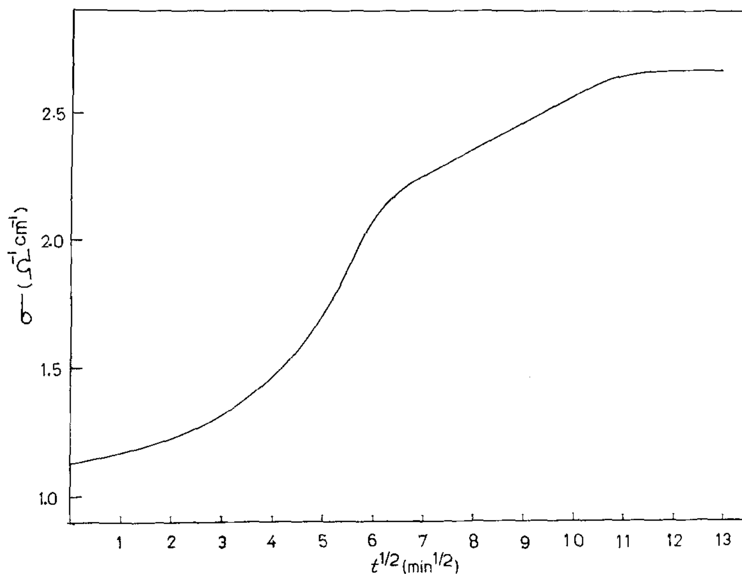

Figure 1 Variation of the d.c. conductivity with exposure time at a hydrogen pressure of 500 psi.

The thin films of dimensions 22 mm x 4 mm were grown at a deposition rate of about 150 Å sec^{-1} by evaporating the charge thus prepared from a tantalum boat under a vacuum (5×10^{-6} torr) onto mica substrates preheated to a temperature of 200° C. These deposition parameters were chosen in order to fabricate single phase films as reported by Kazmerski and Juang [10]. Electron micrograph studies on unexposed as well as on films exposed to hydrogen showed that these films were single phase and polycrystalline in nature. The thickness of the films was monitored with a quartz thickness monitor [21].

Films from the same batch were then annealed in an argon atmosphere at a pressure of about 2 atm at 400° C for 2 h. After annealing, ohmic contacts were made by evaporating high purity indium onto the films under vacuum through tantalum masks. These films were then exposed to hydrogen at room temperature in a specially designed cell at various pressures and for different durations. The exposed films were kept in a desiccator for 24 h in order to stabilize their behaviour. The details of the set-up for the measurements of the d.c. conductivity and the Hall coefficient are given in our earlier paper [22].

3. Results and discussion

The films exposed to hydrogen at pressures < 100 psi and for a duration of 2 h showed a small change in the electrical conductivity. However the conductivity regained its initial values within about 12 h after stopping the exposure. The duration within which the conductivity reached its initial value was found to depend on the exposure time and pressure of the gas. Typically, the films exposed to hydrogen at a pressure of 100 psi for 30 min were found to approach their initial behaviour after 6 h. However films exposed at higher pressures were found to exhibit a significant irreversible change in their electrical behaviour which did not have any aging effect for 60 days and the results were reproducible.

Fig. 1 shows the variation of the d.c. conductivity σ during exposure as a function of exposure time t (σ against $t^{1/2}$) for a typical film of thickness 0.5 μm and at a hydrogen pressure of 500 psi. It can be seen from the figure that this plot is nonlinear up to 1 h, after which it becomes linear and ultimately saturates after 2 h. The initial nonlinear rise in σ shows that adsorption process [23] is predominant for low exposure durations up to about 40 min, while the linearity for the longer duration range shows the predominance of the diffusion process [24]. The hydrogen molecules may diffuse through the films, presumably via interstitials, until they come to the vicinity of relatively static doping defects. The reaction of the defect with the hydrogen molecules may cause these molecules to become electrically active and immobilized.

The observed variation of the Hall coefficient R_H as a function of pressure P of hydrogen at 300 K is shown in Fig. 2. These results are for a typical thickness of 0.5 μm and the films were exposed for a duration of 2 h (exposure time cor-

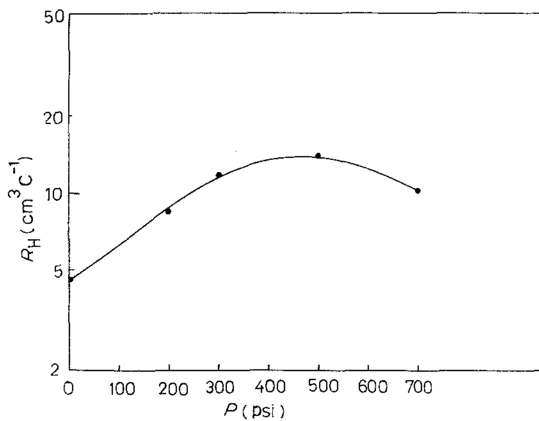

Figure 2 Variation of the Hall coefficient R_H with hydrogen pressure at 300 K.

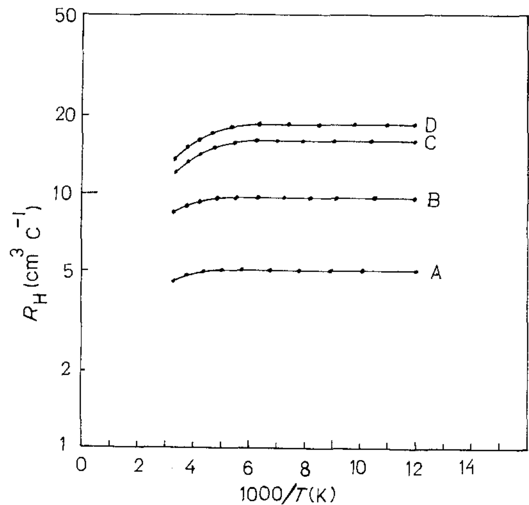

Figure 3 Variation of the Hall coefficient R_H with temperature ($\log R_H$ against $1/T$) for p-type $CuInTe_2$ films exposed to typical pressures of hydrogen. Curve A unexposed, curve B 200 psi, curve C 300 psi and curve D 500 psi.

responds to the saturation in conductivity). It is observed that the Hall coefficient R_H increases initially with the increase of hydrogen pressure and attains a maximum value at about 500 psi. With a further increase of pressure P the value of R_H starts decreasing. Similar results have been observed in films of other semiconductor materials e.g. PbTe [15, 25], PbSe [26, 27] etc.

The variation of R_H with pressure can be explained on the basis of the following two hypotheses.

(a) The diffusion of hydrogen into the film provides donor action [15] which increases with the increase of pressure. The Hall coefficient in this case can be explained as

$$R_H = \frac{1}{pe}\left[\frac{1 - xb^2}{(1 + xb)^2}\right] \quad (1)$$

where $x = n/p$ and $b = -\mu_n/\mu_p$, where n and p are the concentrations of free electrons and holes and μ_n and μ_p are their respective mobilities. The Hall coefficient reaches a maximum ($R_{H\max}$) at a pressure at which the contributions of the electrons provided by hydrogen and extrinsic holes are equal and

$$x = \frac{1}{b(1 + 2b)}. \quad (2)$$

The decrease in the value of R_H with a further increase of P can also be explained on the basis of Equation 1 for higher values of x.

(b) The absorbed hydrogen molecules may remove the acceptors tellurium in the $CuInTe_2$ lattice to the surface of the film and form a loosely bound molecule H_2Te_2 thereby making the film intrinsic. The value of R_H, therefore, will increase with the increase of pressure indicating a decrease of extrinsic hole concentration.

If the second process is predominant, then a situation should be reached when the film should become intrinsic and the carrier concentration and the mobility for this pressure should correspond to intrinsic values. Such results have been reported by Parker and Williams [28] where the oxygen sorption on n-type PbTe films makes them intrinsic. However in the present case the value of $R_{H\max}$ does not correspond to the intrinsic value. Therefore this process alone cannot explain the observed results.

Fig. 3 shows the observed variation of R_H with temperature ($\log R_H$ against $1/T$) for films exposed to hydrogen at typical pressures of 200, 300 and 500 psi for a duration of 2 h. It is evident that R_H remains practically constant up to about 190 K which is characteristic of degenerate semiconductor. The value of R_H starts decreasing with the increase of temperature beyond about 190 K which indicates that the contribution of intrinsic carrier concentration starts beyond this temperature.

The variation of the d.c. conductivity with temperature ($\log \sigma$ against $1/T$) for the films exposed to hydrogen at different pressure is shown in Fig. 4a. It is observed that for all the films the conductivity in the high temprature regions obeys the relation

$$\sigma \propto \exp(-E_a/kT) \quad (3)$$

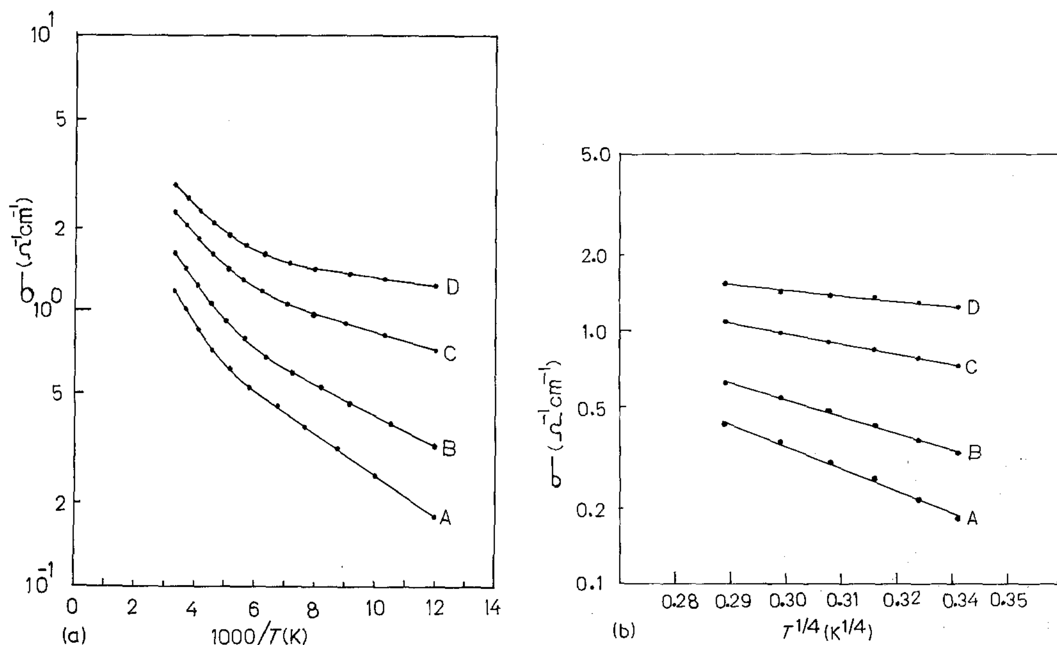

Figure 4 (a) Variation of the d.c. conductivity σ with temperature (log σ against $1/T$) for p-type $CuInTe_2$ films exposed to hydrogen pressures. Curve A unexposed, curve B 200 psi, curve C 300 psi and curve D 500 psi. (b) Variation of the d.c. conductivity σ with temperature (log σ against $1/T)^{1/4}$, for p-type $CuInTe_2$ films exposed to hydrogen pressures. Curve A unexposed, curve B 200 psi, curve C 300 psi and curve D 500 psi.

where E_a is the conductivity activation energies, values of which are given in Table I. Since the films were polycrystalline, the activation energy corresponds to the grain boundary potential barrier. It can be observed from Table I that the value of E_a decreases with an increase of hydrogen pressure. This shows that the grain boundary potential decreases with an increase of hydrogen pressure. It can be further observed from Fig. 4a that the values of activation energy in the low-temperature range are much smaller as compared to those in the high-temperature range, possibly because of the fact that the variable range hopping mechanism is more predominant in the low-temperature region. This has been verified by plotting the curves between log σ against $(1/T)^{1/4}$ shown in Fig. 4b, in accordance with relation [29]

$$\sigma \propto \exp(-T_0/T)^{1/4} \tag{4}$$

The linearity of these curves, indicates the occurrence of the variable-range hopping conduction mechanism. The existence of the localized states necessary for such a conduction process is a consequence of imperfections associated with polycrystalline films [30]. The values of T_0 for all the films, which are shown in Table I, are related to the density $N(E)$ of localized states by [29]

TABLE I

Film	Conductivity activation energy E_a (eV)	Grain boundary barrier potential ϕ_B (eV)	T_0 (K)	$N(E)$ ($eV^{-1} cm^{-3}$)
Unexposed	0.043	0.038	2.1×10^5	8.8×10^{20}
Exposed to hydrogen at pressure 200 psi	0.038	0.035	5.6×10^4	3.3×10^{21}
Exposed to hydrogen at pressure 300 psi	0.030	0.026	7×10^3	2.7×10^{22}
Exposed to hydrogen at pressure 500 psi	0.027	0.024	5.1×10^2	3.6×10^{23}

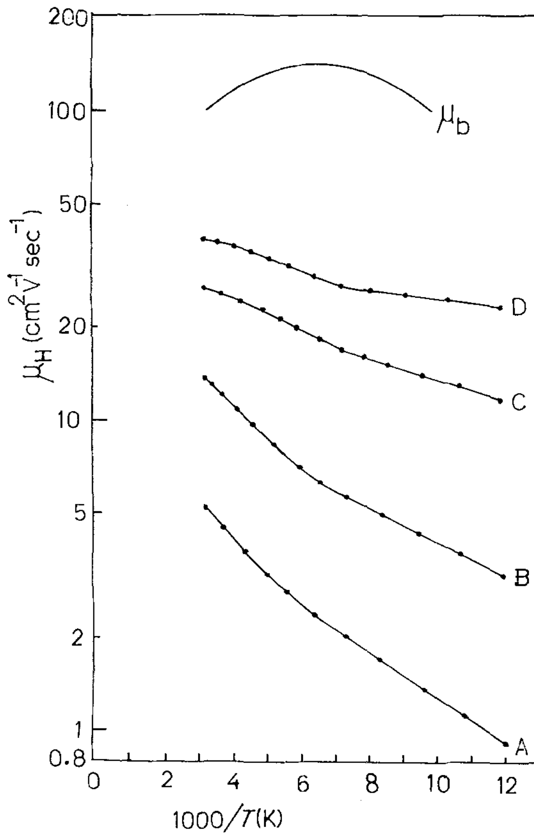

Figure 5 Variation of the Hall mobility μ_H with temperature (log μ_H against $1/T$) for p-type $CuInTe_2$ film exposed to hydrogen pressures. Curve A unexposed, curve B 200 psi, curve C 300 psi and curve D 500 psi.

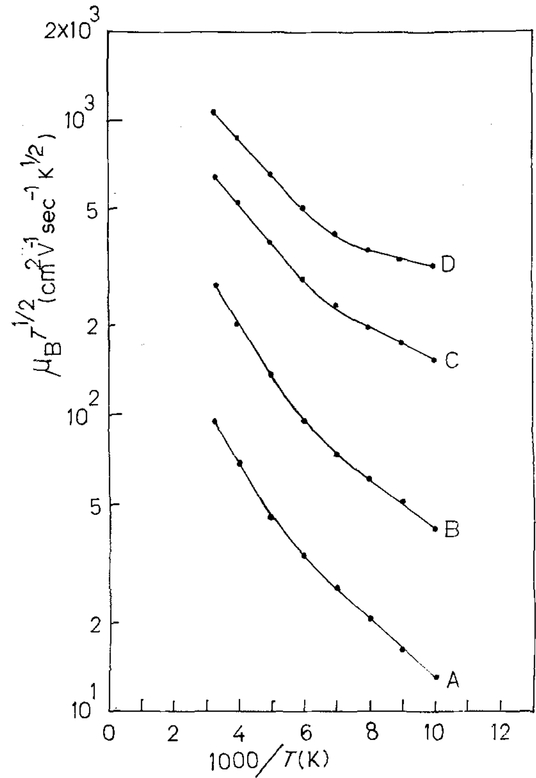

Figure 6 Variation of the mobility μ_B limited by grain boundary potential barrier with temperature (log $\mu_B T^{1/2}$ against $1/T$) for p-type $CuInTe_2$ films exposed to hydrogen pressures. Curve A unexposed, curve B 200 psi, curve C 300 psi and curve D 500 psi.

$$N(E) = \frac{16\alpha^3}{kT_0} \quad (5)$$

where $\alpha = 10^7 \text{cm}^{-1}$. The values of $N(E)$ are also shown in Table I.

The variation of the Hall mobility with temperature (log μ_H against $1/T$) for all these films is shown in Fig. 5. The value of the mobility for the bulk sample (μ_b) is also shown in Fig. 5 for comparison. It is observed that the value of the mobility for the unexposed film is very low as compared to the bulk specimen. The mobility however increases with the increase of pressure. It can be further observed that the value for the mobility increases with the increase of temperature which indicates the predominance of grain boundary and/or ionized impurity scattering mechanism in these films.

Since the films are polycrystalline, it is reasonable to assume that the mobility is limited mainly by the grain-boundary potential barrier. The values of the mobilities limited by the grain boundary (μ_B) have been calculated using the relation

$$\frac{1}{\mu_H} = \frac{1}{\mu_b} + \frac{1}{\mu_B} \quad (6)$$

The exponential temperature dependence of the mobility (μ_B) can be represented by the Petritz relation [31]

$$\mu_B = \frac{\mu_0}{T^{1/2}} \exp\left(-\frac{\phi_B}{kT}\right) \quad (7)$$

where ϕ_B is the grain boundary barrier potential. The term μ_0 depends on the average grain size l by the relation

$$\mu_0 = el\,(8/\beta\pi k m^*)^{1/2} \quad (8)$$

where β is a numerical constant, m^* the effective mass of the charge carriers, e the electron charge and k is the Boltzmann constant.

The value of grain boundary potential ϕ_B can be estimated from the plot of log $\mu_B T^{1/2}$ against $1/T$. Such plots are given in Fig. 6 and the values of ϕ_B thus calculated are given in Table I. The value of the grain boundary potential barrier

observed in these films is in the range 0.024 to 0.038, which agrees well with the values reported by Kazmerski and Juang [10] for polycrystalline $CnInTe_2$ films. It can be seen from Fig. 5 that the mobility increases appreciably with the increase of pressure of the gas. This is because of two reasons. Firstly the grain boundary potential decreases with the increase of pressure as can be seen from Table I. Secondly, the hydrogen removes tellurium acceptors and hence reduces the number of scattering centres thereby increasing the overall mobility.

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