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Effect of indium annealing on the electrical properties of polycrystalline n-type CdTe

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Polycrystalline n-type CdTe samples were annealed in molten indium at 800° C for different times (150 to 350 h). D.c. conductivity (σ) and Hall coefficient (R_H) studies were made on these samples in the temperature range 77 to 400 K. R_H and σ data were analysed based on the various models existing for polycrystalline semiconductors. The temperature variation of mobility data were analysed in the light of various scattering mechanisms; the role of grain-boundary scattering being examined in particular detail.

1. Introduction

Many emerging applications of polycrystalline semiconductors have drawn considerable interest in recent years due to their high potential in fabrication of devices at low cost. Therefore, the study of electrical and optical properties of polycrystalline semiconductors has become the subject of broad investigations [1–4]. It is necessary to understand the mechanism of electron transport in polycrystalline materials under the varying conditions of temperature, electric field and illumination [5–6]. Most of the work in the polycrystalline materials has been done on silicon [7–10], and other semiconductor compounds, such as CdTe, have been less studied. CdTe has been used in nuclear detectors, infrared detectors, solar cells, γ-ray detectors and laser window materials [11, 12].

The intergranular regions in polycrystalline semiconductors, which distinguish them from their single-crystal counterparts, are the grain boundaries, acting as sinks for the impurity atoms, segregating the impurities from the grain [2]. These grain boundaries are two-dimensional imperfections containing highly complex structural defects and in most of the cases are electrically active [13]. The polycrystalline semiconductors can tolerate a higher degree of impurities. Owing to the segregation effect, the concentration of free charge carriers in polycrystalline semiconductors is lower, compared to that in its single-crystal counterpart. Because of the presence of a large number of defect states in the forbidden gap from dangling bonds, a space charge region is formed, thereby creating a potential energy barrier at the grain boundaries [1, 2] and reducing the carrier mobility compared to that in single-crystal material.

The transport properties of a polycrystalline material depend largely on the ratio of the grain size, l, and the Debye length [1], L_D, which is given as

$$L_D = (k_s \varepsilon_0 k_B T / e^2 N)^{1/2} \qquad (1)$$

where k_s is the static (or low-frequency) dielectric constant, ε_0 is the permittivity of free space, k_B is the Boltzmann constant, e is the electronic charge magnitude and N is the doping concentration. If the Debye length is comparable or greater than the grain size ($L_D > l$), the free charge carriers are mainly confined to the grain-boundary region and the transport is determined by the depletion or the space charge region [1, 13]. On the other hand, if $L_D \ll l$, the grains are partly depleted of the free charge carriers and the thermal activation of the carriers over the grain-boundary potential barriers is predominant. The height of the potential barrier, ϕ_b, depends on the ambient temperature, T, and the value of potential barrier height, ϕ_b, becomes vanishingly small above the critical temperature, T_c, and the mobility is then limited by lattice scattering above this temperature. The temperature variation of ϕ_b is governed by the relation [14]

$$\phi_b = \phi_0(1 - aT) \qquad (2)$$

where ϕ_0 is the value of ϕ_b extrapolated to 0 K and a is a constant having the dimensions of the inverse temperature.

In the present paper we report the temperature variation of d.c. galvanomagnetic properties, namely Hall coefficient, R_H, low-field d.c. conductivity, σ, and Hall mobility, μ^H, in the temperature range 77 to 400 K on CdTe polycrystalline samples that were annealed in molten metal indium (In) at a high temperature (800° C) for different durations in the range 150 to 350 h. The experimental data on R_H, σ and μ^H in all the annealed samples have been analysed in the light of various existing models. In the high- and low-temperature range, conductivity data have been analysed in the light of thermally activated and variable range hopping conduction mechanisms, respectively. Hall mobility is analysed over the entire temperature region by taking into account the possible charge carrier scattering mechanisms operating in the conduction band (lattice and impurity scattering mechanisms) and the grain-boundary effects for all the annealing times. Above the critical temperature (T_c), the effect of the grain boundary diminishes and the grain-boundary effect also diminished with longer annealing

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times. For longer annealing times the carrier conduction is mobility limited rather than barrier-limited conduction. The grain size, l, and grain-boundary potential barrier height, ϕ_b, are computed for all the annealed samples.

2. Experimental details

The polycrystalline CdTe was prepared from the reaction of pure elements of cadmium and tellurium of 99.999% grade. Stoichiometric proportions were weighed and placed in a quartz ampoule 18 cm long and 2 cm diameter. The ampoule was sealed under a vacuum of less than 10^{-5} torr. By gradually raising the temperature to $\approx 700°$C within 4 d, homogeneous CdTe was obtained. The Laue diffraction pattern has shown the polycrystalline nature of the grown material. The n-type conductivity of the material was tested with the help of a hot-probe technique. From the as-grown boule, samples of rectangular bar geometry about 6.0 mm × 1.5 mm × 1.0 mm in size were cut using a Microslice Precision Annular Saw. These samples were annealed in high-purity molten metal indium at $\sim 800°$C for different times in the range 150 to 350 h. Annealing for shorter times resulted in very little change in the electrical properties of the samples. The annealing of the sample was done by keeping it in an evacuated quartz ampoule along with the annealing metal whose weight was about ten times the sample weight.

Before making the ohmic contacts on the annealed samples, the samples were lapped by using fine-grained abrasive powder (3 μm silicon carbide). After chemomechanical polishing, the samples were etched in a solution of one part HF, one part HNO_3 and two parts distilled water for 2 min. After etching, the samples were treated by boiling in 50% NaOH solution for 1.5 min followed by washing in distilled and deionized water.

Ohmic contacts on the etched samples were provided by diffusing high-purity indium at 250° C in an inert atmosphere of high-purity argon. The voltage contacts were about 0.6 mm in size, whereas the current contacts were spread over the entire end cross-sections of the samples. The ohmic nature of the contacts was verified for the operative voltages by observing the linearity of current voltage characteristics throughout the temperature range of interest.

The temperature variation of Hall coefficient, R_H, and low-field d.c. conductivity, σ, were measured by employing the five-probe technique [15] (where one voltage probe was taken common in the six probe technique). Annealed samples were mounted in the dark in a double-walled metal vacuum cryostat [16]. The temperature was measured by means of a precalibrated copper/constantan thermocouple in direct contact with the sample surface. The temperature variation during each measurement was kept below 0.5° C with the help of a temperature controller. The Hall coefficient is found to be independent of magnetic field up to 0.6 T which was the highest magnetic field available to us. The Hall voltage was measured to within an accuracy of about 1% and found to be proportional to the applied magnetic field and the sample current. In order to avoid thermoelectric and thermomagnetic effects, the direction of both the sample current and magnetic field were reversed for each Hall measurement. The error in measurement of R_H was estimated to be about 2% including errors in the measurements of Hall voltage, magnetic field and sample current. The d.c. conductivity was measured to within an accuracy of about 1.5% and therefore the overall maximum error in the estimation of Hall mobility was found to be about 3%.

3. Results and discussions

3.1. Hall coefficient data

The temperature variation of Hall coefficient, R_H (log R_H against $10^3/T$) over the entire temperature range studied, i.e. 77 to 400 K, is shown in Fig. 1, for all CdTe samples that were annealed in molten In for 150, 250 and 350 h. It is observed from the figure that the value of R_H decreases slowly with increasing ambient temperature in the low-temperature region (77 to 120 K) in the as-grown, as well as for samples annealed for less than 250 h. In the high-temperature region, R_H decreases at a faster rate and finally tends

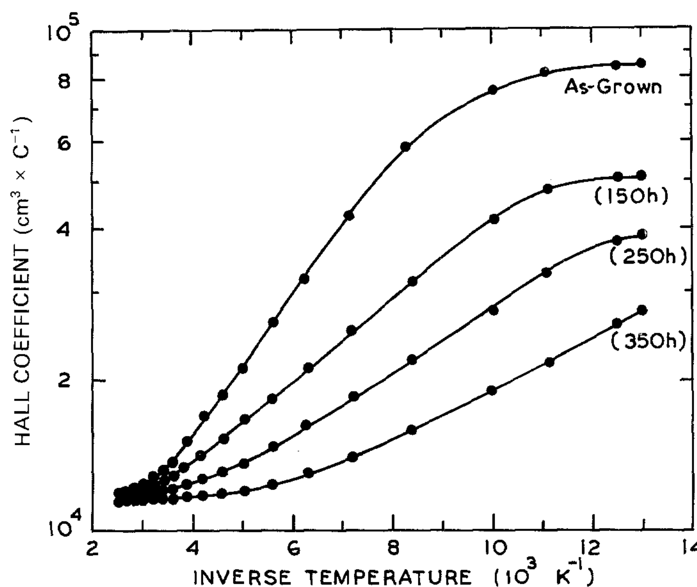

Figure 1 The temperature variation of observed Hall coefficient R_H in n-type CdTe polycrystals annealed in molten indium for 150, 250 and 350 h, respectively.

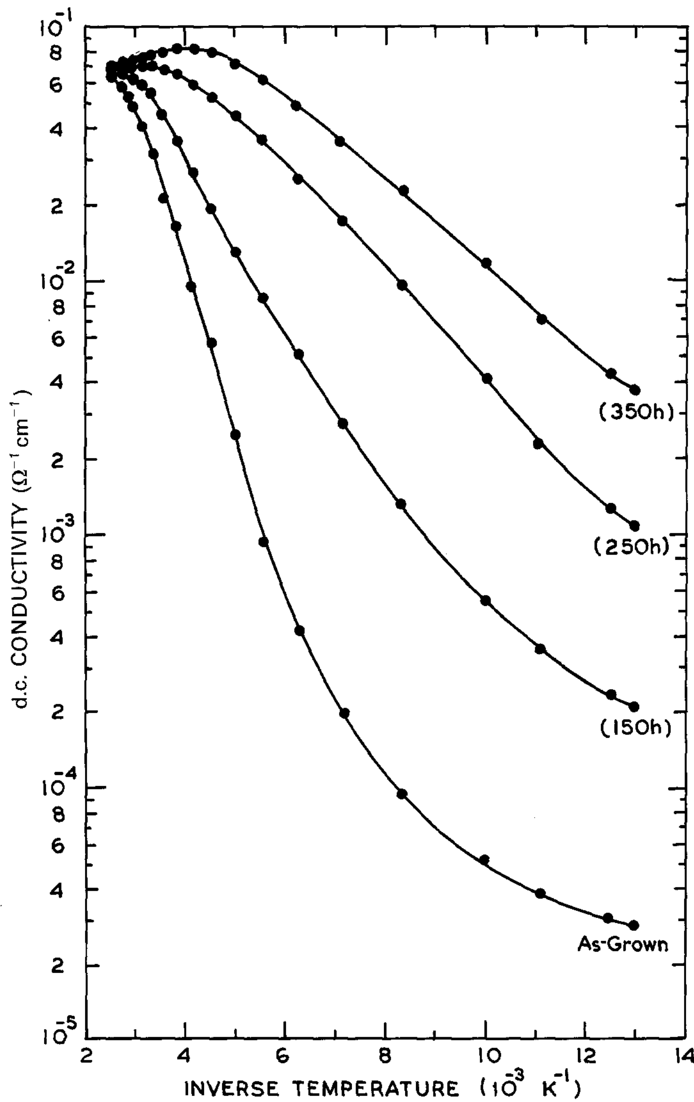

Figure 2 The temperature variation of obseved d.c. conductivity σ, in n-type CdTe polycrystals annealed in molten indium for 150, 250 and 350 h, respectively.

to become a slowly varying function of temperature above 250 K.

In the low-temperature region, 77 K $< T < T_s \approx$ 120 K, the Fermi level is very close to the conduction band edge, most of the grain-boundary interface states are filled with the trapped free electrons and the free-electron concentration in the bulk of the grain remains more or less constant. The Hall effect measurements record only the free electrons in the bulk of the grain, and therefore the Hall coefficient, R_H, in the material remains constant. But for samples annealed for 350 h, R_H decreases significantly in the low-temperature region and becomes saturated at higher temperatures.

As the temperature rises above the saturation temperature, T_s, the Fermi level shifts towards the intrinsic Fermi level and trapped free electrons in the grain boundaries are liberated through thermal activation. The Hall coefficient in the bulk of the grain drops exponentially with increasing temperature, for all the annealed samples, as in a single crystal and, therefore, the total Hall coefficient, R_H, decreases exponentially with increasing temperature. Below the critical temperature, T_c, according to Berger and coworkers [17, 18], the conduction process is largely grain-boundary interface-barrier-limited and R_H exhibits an exponential temperature dependence

$$R_H = R_0 \exp(-E_n/k_B T) \quad (3)$$

where R_0 is the extrapolated value of R_H for $1/T \to 0$ and E_n is the carrier concentration activation energy. The value of E_n is found to be temperature dependent. As the critical temperature (T_c) is reached, trapped free-electrons are released from the grain-boundary interface states and hence the interface barrier of grain boundaries tends to become vanishingly small. At this stage, the conduction is no longer barrier limited but mobility limited, as in the case of single crystals. Owing to the complete ionization of donors at such a high temperature, the Hall coefficient, R_H, tends to become a very slowly varying function of temperature for all the annealed samples, and corresponds to that in its single crystalline counterpart with the same doping level.

3.2. D.c. conductivity

It can be observed from Fig. 2 that the as-grown sample conductivity varies slowly in the low-temperature range ($T_s \approx$ 120 K), increases rapidly in the region $T_c < T < T_s$, and tends to decrease at temperatures above T_c. This behaviour can be explained on the basis of variable range hopping conduction in the low-temperature region and thermionic emission in the temperature range $T_c < T < T_s$. At temperatures above T_c the conduction is expected to be mobility limited, as in the case of single crystals.

In the annealed samples, the conductivity increases

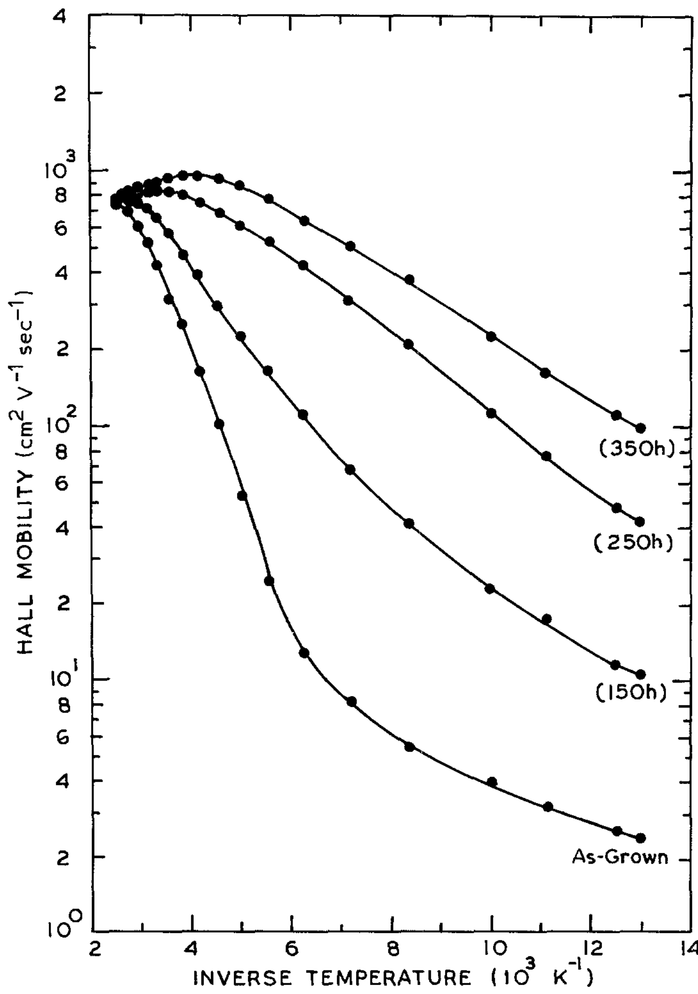

Figure 3 The temperature variation of observed Hall mobility, μ^H, in n-type CdTe polycrystals annealed in molten indium for 150, 250 and 350 h, respectively.

at a faster rate and the conduction is due to the thermionic emission of the carriers over the grain boundaries. In the high-temperature region, mobility-limited conduction is predominant. The d.c. conductivity in the thermionic emission region has been found to follow the relation [1, 3]

$$\sigma = e^2 \ln_{av} (2\pi m^* k_B T)^{-1/2} \exp(-E_\sigma/k_B T) \quad (4)$$

where E_σ is the conductivity activation energy [17, 19–24] and other symbols have their usual meanings. The value of E_σ is found to decrease with increasing annealing time. This could either be due to a decrease in E_n, the carrier concentration activation energy, or to a decrease in the barrier potential height, ϕ_b, or both.

3.3. Hall mobility

The observed variation of Hall mobility as a function of temperature (e.g. log μ^H against $10^3/T$) is shown in Fig. 3 for the as-grown and annealed samples of polycrystalline CdTe. It can be observed from the figure that the mobility variation has three distinct regions for the as-grown and indium-annealed samples for durations $\leqslant 150$ h. In the low-temperature region, μ^H increases slowly with increasing temperature up to $T_s \approx 120$ K; above T_s the value of μ^H increases sharply up to the critical temperature, T_c, above which μ^H decreases with increasing temperature. In the polycrystalline samples, the Hall mobility is expected to have lower values than the single crystals, due to the presence of grain boundaries.

The mobility variation for the samples annealed for 250 and 350 h shows that the mobility increases sharply in the low-temperature region due to the thermionic emission of the trapped free electrons over the grain-boundary interface barrier, giving rise to an exponentially temperature dependent Hall mobility μ^{H2} in the grain-boundary region which, when added to another thermally activated Hall mobility, μ^{H1}, in the bulk of the grain, yields the total mobility, μ^H, in the material. Therefore, μ^H increases exponentially with increasing temperature with a large activation energy.

At the critical temperature, T_c, most of the trapped free electrons from the grain-boundary interface are released, causing the interface barrier to have vanishingly small values ($\phi_b \rightarrow 0$). The grain-boundary region almost vanishes and consequently the overall mobility, μ^H, corresponds to the single-crystalline counterpart with the same doping level.

The observed Hall mobility data are examined by taking into account the various possible charge carrier scattering mechanisms, and they exhibit an additive nature as predicted by Mattheisen's rule

$$\frac{1}{\mu^H} = \frac{1}{\mu^H_{OPS}} + \frac{1}{\mu^H_{IIS}} + \frac{1}{\mu^H_{GBS}} \quad (5)$$

where μ^H_{IIS}, μ^H_{OPS} and μ^H_{GBS} are the mobilities limited by scattering due to ionized impurities, optical phonons and grain boundaries. This rule is valid only when the Hall scattering factor [25], for each scattering process is unity

$$r_H = \langle E\tau^2 \rangle \langle E \rangle / \langle E\tau \rangle^2 \quad (6)$$

which is true for polycrystalline semiconductors. In Equation 6 the angular brackets are the Maxwelllian averages, E is the carrier energy, τ is the relaxation time of charge carriers as limited by the scattering processes.

The polar optical phonon scattering operates through a strong interaction between optical phonons and free-electrons through the polarization produced by the optical vibrations due to the ionic charges associated with the atoms [26, 27]. The Hall mobility, μ^{H}_{OPS}, limited by this scattering is estimated over the entire temperature range using the equation [28, 29]

$$\mu^{H}_{OPS} = (4e/3\pi^{-1/2}\alpha\omega_l m^*)Z^{-1/2}\psi_Z(\exp Z - 1)R_H \quad (7)$$

where Z is the reduced reciprocal temperature and is the ratio of the Debye temperature, $\theta_D(=\hbar\omega_l/k_B)$ [30], ψ_Z is a slowly varying function which has been evaluated by Howarth and Sondheimer [29] and later generalized by Ehrenreich [31] so as to include the carrier screening effects, ω_l is the angular frequency of longitudinal optical phonons, α is the polaron coupling constant of the material. The Hall scattering factor R_H for the polar optical phonon scattering has been taken to be unity by assuming the energy independence of the relaxation time for this scattering for $E \ll \hbar\omega_l$ [26, 29] i.e.

$$\tau_{OPS} = \hbar^{3/2}(4\pi\varepsilon_0)(\exp Z - 1)/ e^2(2m^*\omega_l)^{1/2}(n_0^{-2} - k_s^{-1}) \quad (8)$$

where n_0, the refractive index of the material at optical frequencies, equals the square-root of the optical dielectric constant. The free electron effective mass, m^*, is replaced by polaron effective mass

$$m^*_p \approx m^*(1 + \alpha/6) \quad (9)$$

due to the polaron effect [32, 33], is the polaron coupling constant

$$\alpha = e^2/\hbar(m^*/2\hbar\omega_l)^{1/2}(k_\alpha^{-1} + k_s^{-1}) \quad (10)$$

where $\hbar\omega_l = 0.0212\,\text{eV}$ [33] is the longitudinal optical phonon energy and k_∞, the optical dielectric constant, is a measure of the degree of interaction. The temperature variation of static (or low-frequency) dielectric constant, k_s, is expressed by [34]

$$k_s(T) = k_s(0)(1 + \lambda T) \quad (11)$$

where $k_s(0) = 10.31$ is the static dielectric constant extrapolated to 0 K and $\lambda = 2.27 \times 10^{-14}\,\text{K}^{-1}$ is a constant for the material. The estimated values of Hall mobility, μ^{H}_{OPS}, have been plotted.

The Hall mobility, μ^{H}_{IIS}, for ionized impurity scattering which results from either impurities or lattice defects generated by nonstoichiometric composition of the compound, have been estimated over the entire temperature range using the Brooks–Herring formula for non-degenerate and compensated semiconductors [34, 35],

$$\mu^{H}_{IIS} = 2^{7/2}(4\pi\varepsilon_0 k_s)^2(k_B T)^{3/2} / \pi^{3/2}e^3 m^{*1/2} N_I \ln\left[\frac{6m^*(k_B T)^2 4\pi\varepsilon_0 k_s}{\pi e^2\hbar^2 n'(2 - n'/N_I)}\right] \quad (12)$$

where

$$n' = n_c + \left(1 - \frac{n_c + N_a}{N_d}\right)(N_a + n_c) \quad (13)$$

is the effective screening concentration and N_I is the sum of ionized acceptor and donor impurity concentrations, N_a and N_d. The values of N_a and N_d are shown in Table I for all the annealed samples. The free-electron relaxation time, τ_{IIS}, for the ionized impurity scattering has the energy dependence

$$\tau_{IIS} = (2m^*)^{1/2}(4\pi\varepsilon_0 k_s)^2(k_B T)^{3/2}(E/k_B T)^{3/2} / e^4\pi N_I\left[\ln(1 + b^1) - \frac{b^1}{(1 + b^1)}\right] \quad (14)$$

where the scattering index is $\frac{3}{2}$.

Having estimated the ionized impurity scattering and optical phonon scattering, we have estimated the Hall mobility, μ^{H}_{GBS}, arising from the grain-boundary scattering using Mattheissen's rule. These estimated values of μ^{H}_{GBS} are shown in Figs 4 to 6 for the as-grown and indium annealed samples. It is observed from the figures that μ^{H}_{GBS} is dominant at low temperatures for the as-grown and 150 h annealed samples and its effect decreases for 250 and 350 h annealing times, whereas at higher temperatures, it rises sharply with increasing temperature for all the samples (as-grown and annealed) and follows the following temperature dependence [29, 36]

$$\mu^{H}_{GBS} = (e^2 l^2/8\pi m^* k_B T)^{1/2}\exp(e\phi_b/k_B T) \quad (15)$$

where ϕ_b is the grain-boundary potential barrier height which decreases with annealing time. The values of ϕ_0 have been estimated from $\log \mu^{H}_{GBS} T^{1/2}$ against $1000/T$ curves and are shown in Table I. We have calculated the overall grain size, l, for all the annealed samples by extrapolating the value of $\log \mu^{H}_{GBS} T^{1/2}$ for $1/T \to 0$. The estimated values of grain size, l, and these of found from X-ray diffraction studies are given in Table I. The thickness, l_2, of the grain-boundary region is temperature dependent as per Equation 7 [37]

TABLE I Grain size l, E_σ, N_a, and ϕ_0 for as-grown and indium-annealed n-type polycrystalline CdTe

Annealing time (h)	l (μm)	ϕ_0 (meV)	E_σ (meV)	N_a ($10^{16}\,\text{cm}^{-3}$)	N_d ($10^{16}\,\text{cm}^{-3}$)
As-grown	0.094 (0.10)	149.1	114.2	6.00	6.06
150	0.110 (0.105)	122.39	103.7	4.62	4.67
250	0.133 (0.135)	109.43	98.75	3.22	3.27
350	0.147 (0.149)	99.07	94.3	1.98	2.035

The values in parentheses are those of grain size, l, found from X-ray diffraction studies.

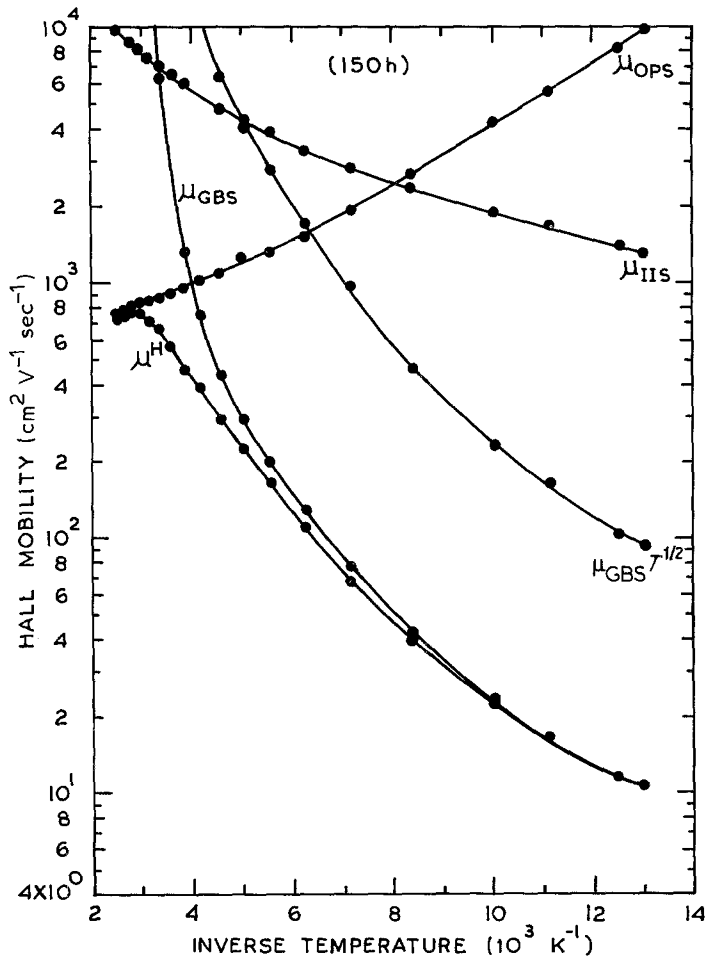

Figure 4 The temperature variation of observed Hall mobility, μ^H, and theoretically estimated components, μ^H_{OPS}, μ^H_{IIS} and μ^H_{GBS} in n-type CdTe polycrystal samples annealed in molten indium for 150 h.

$$l_2 = (8k_s\varepsilon_0\phi_b/en_1)^{1/2} \tag{16}$$

that is, l_2 decreases with increasing temperature because of the decrease in ϕ_b, and the free electron concentration, n_1, in the bulk of the grain increases with increasing temperature.

4. Conclusions

Annealing of polycrystalline CdTe for durations up to 350 h at 800° C in indium has been found to improve the electrical properties significantly. Mobility and carrier concentration have been found to increase with increasing annealing time. Grain size (l) was also found to increase and the barrier height was found

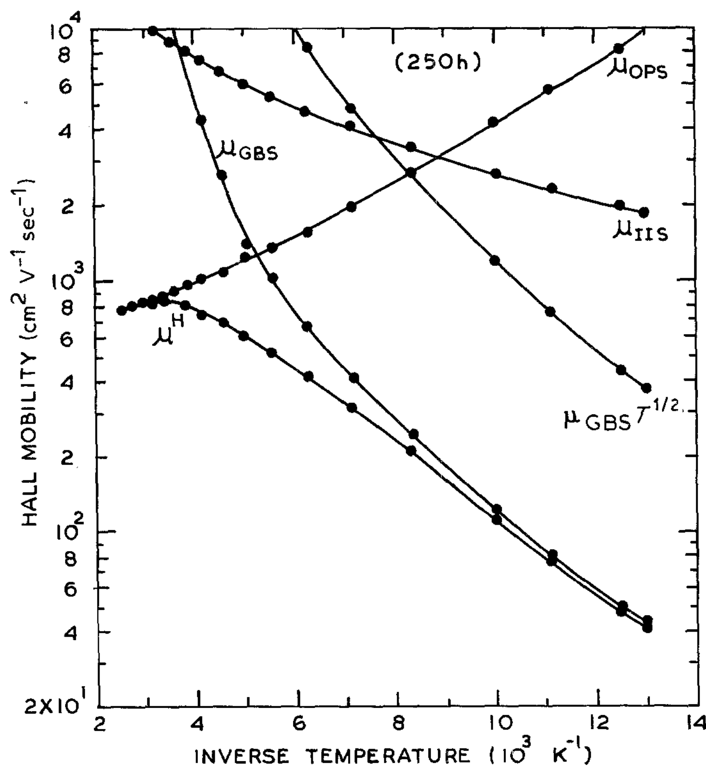

Figure 5 The temperature variation of observed Hall mobility, μ^H, and theoretically estimated components, μ^H_{OPS}, μ^H_{IIS}, and μ^H_{GBS} in n-type CdTe polycrystal samples annealed in molten indium for 250 h.

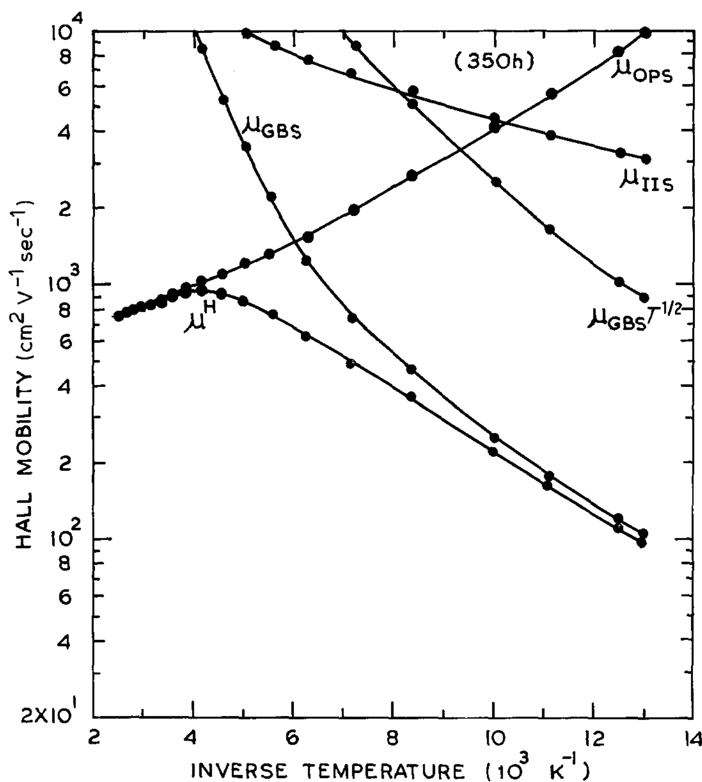

Figure 6 The temperature variation of observed Hall mobility, μ^H, and theoretical estimated components μ^H_{OPS}, μ^H_{IIS} and μ^H_{GBS} in n-type CdTe polycrystal samples annealed in molten indium for 350 h.

to decrease with increasing annealing time. Grain boundaries limit the mobility at low temperatures in as-grown and 150 h annealed samples and its effect decreases at higher temperatures and longer annealing times.

Acknowledgements

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