JOURNAL OF MATERIALS SCIENCE: MATERIALS IN ELECTRONICS 3 (1992) 249–252

Determination of the effective mass for highly degenerate copper selenide from reflectivity measurements

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An investigation was made of the plasma reflection of light and the results were used to find the effective mass of highly degenerate copper selenide, $p > 10^{20}\ \mathrm{cm}^{-3}$, as a function of carrier concentration p. The study of the temperature dependence of effective mass, electrical conductivity, thermoelectric power and Hall mobility carried out in the present work gives an idea of the nature of the valence bands in these materials.

1. Introduction

Copper selenide, $Cu_{2-x}Se$ ($x < 0.2$), is a self-doping superionic semiconductor with a high density of free holes ($> 8 \times 10^{21}\ \mathrm{cm}^{-3}$) due to a high concentration of copper vacancies which supply these holes [1]. X-ray diffraction studies of $Cu_{2-x}Se$ show a solid–solid α–β phase transition at temperatures that depend on the deviation from stoichiometry [2, 3]. The selenium atoms "hop" between the tetragonal, octahedral and trigonal voids in this lattice, making an ionic contribution ($\leqslant 2\%$) to the electrical conductivity [4]. Conductivity and thermo-e.m.f. variation during the phase change undergo anomalous behaviour, which was explained earlier by the existence of a mixture of α- and β-phases near the transition temperature [3, 5, 6].

The present work was a study of the dependence of the effective mass of charge carriers on the hole concentration and temperature. The temperature dependence of the electrical conductivity, thermo-e.m.f. and Hall mobility of large hole densities of copper selenide are reported.

2. Experimental procedure

For the determination of the plasma reflection of light in a variable wavelength range (0.50–2.5 μm), polycrystalline samples with large hole densities ($p > 10^{20}\ \mathrm{cm}^{-3}$) were prepared as described in [7]. The homogeneity of our samples was checked by a search probe and by local measurements of the plasma reflection edge methods.

The reflection spectra $R(\lambda)$ were determined at room temperature and nearly normal incidence of light using a single-beam Zeiss type PMQ3 spectrophotometer in the range 0.3–2.5 μm with a special attachment for reflection. Before measurements of $R(\lambda)$ the samples were optically polished and subsequently etched in HBr + 0.1% Br in order to remove any surface defects formed during polishing.

The electrical conductivity, σ, and Hall coefficient, R_H, were measured by the conventional four-probe method using apparatus that allowed temperature control between 100 and 700 K. The thermoelectric power, Q, was measured simultaneously against copper. Its sign was positive for all samples, indicating free-hole conductivity.

3. Results and discussion

The reflection spectra of semiconductors recorded at infrared wavelengths, beyond the fundamental absorption edge, can yield extensive information on free carriers and lattice vibrations. When the plasma frequency is close to the frequency of transverse optical phonons, the spectral dependence of the reflection coefficient becomes fairly complex.

Fig. 1 shows a typical spectral distribution of the reflection coefficient of four polycrystalline samples of copper selenide with different hole densities at 300 K. The reflection spectra have a minimum typical of degenerate semiconductors, and the position of this minimum is a function of the hole density. It shifts in the direction of shorter wavelength with increasing density.

For a degenerate semiconductor, with a photon energy $h\nu \ll E_f$ (E_f being the Fermi energy) the optical effective mass and other parameters could be determined by solving the following equations for n and k

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

$$n^2 - k^2 = \varepsilon_\infty - 4\pi e^2 \frac{p}{m^*}\left(\frac{\langle\tau\rangle^2}{1 + \omega^2\langle\tau\rangle^2}\right) \tag{2}$$

$$2nk = \varepsilon_0 - 4\pi e^2 \frac{p}{\omega m^*}\left(\frac{\langle\tau\rangle}{1 + \omega^2\langle\tau\rangle^2}\right) \tag{3}$$

TABLE I Results of measurement of copper selenide parameters

Sample		p ($\times 10^{21}$ cm^{-3})	λ_p (μm)	ε_∞	a	m^*/m_0	σ (Ω^{-1} cm^{-1})	μ (cm^2 V^{-1} s^{-1})	$\langle\tau\rangle$ ($\times 10^{15}$ s)	
									Electrical	Optical
$Cu_{1.90}Se$	P_1	1.14	1.75	8.4	1.4	0.445	2500	13.74	2.3	1.57
$Cu_{1.87}Se$	P_2	1.53	1.49	8.0	1.4	0.394	3200	12.60	1.9	1.33
$Cu_{1.85}Se$	P_3	1.95	1.20	7.5	1.4	0.334	4600	14.20	1.6	1.07
$Cu_{1.80}Se$	P_4	2.58	1.01	7.0	1.4	0.336	5800	13.50	1.5	0.90

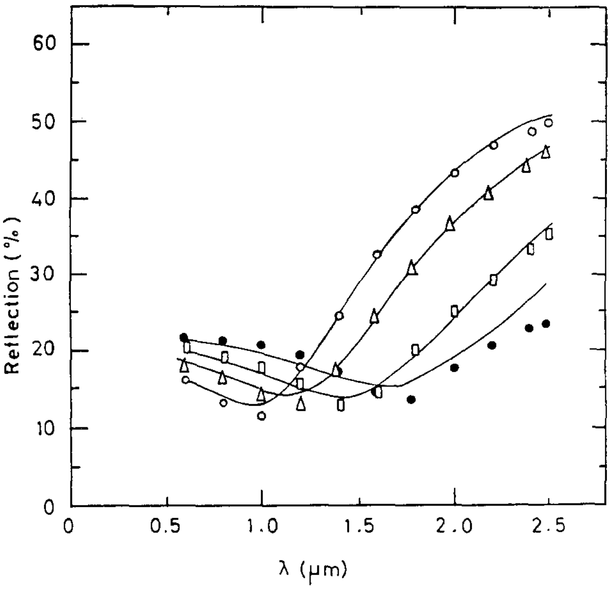

Figure 1 The experimental (●, P_1; □, P_2; △, P_3; ○, P_4) and calculated (full curves) values of the reflection factor of copper selenide.

which give

$$\omega_p = \left(\frac{\pi e^2 \lambda_p}{m^* \varepsilon_\infty}\right)^{1/2} \qquad (4)$$

$$a = \omega_p \langle\tau\rangle \qquad \xi = \omega/\omega_p = \lambda_p/\lambda$$

where ω_p is the plasma frequency, ε_∞ is the high-frequency dielectric constant and $\langle\tau\rangle$ is the carrier relaxation time.

The theoretical dependence $R(\xi)$ for different values of the dimensionless parameters ξ and a, between 0.2 and 5 and 0.1 and 30, respectively, are given in [8]. The calculated dependences, by selecting suitable values for ξ and a (curves in Fig. 1), were compared with the experimental data. Good agreement was obtained, indicating the validity of the values of ξ and a, which are listed with our electrophysical parameters in Table I.

On the other hand, typical results for σ and the thermo-e.m.f., Q, are presented in Fig. 2a and b. The predominant feature in the $\sigma(T)$ and $Q(T)$ curves is the presence of anomalies (minima in σ and peaks in Q) in the vicinity of the phase transition temperatures. These anomalies are explained in detail in our previous work [5–7] by the existence of a mixture of two-phase regions.

Fig. 3a shows the room-temperature dependence of the optical effective mass on concentration for the samples investigated. Comparison of the carrier effective mass values obtained from some of our previous electrical measurements are also shown [5, 6]. It is found that m^*/m_0 decreases with increasing carrier concentration; such a behaviour is expected from a large impurity band which causes a considerable effect in the density of states of the valence band, making that band non-parabolic.

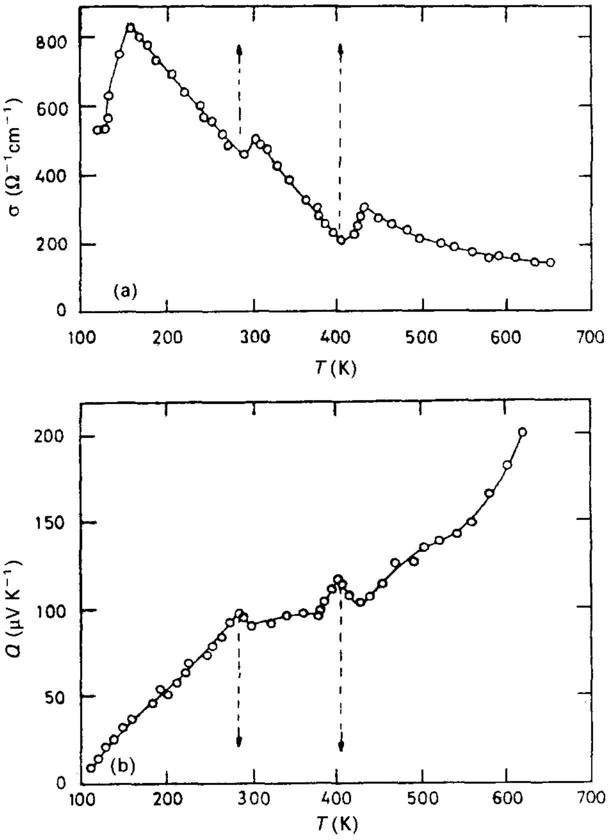

Figure 2 (a) Electrical conductivity (σ) and (b) thermoelectric power (Q) as functions of temperature (T).

The temperature dependence of m^*/m_0 is shown in Fig. 3b. The general trend of m^*/m_0 variation is an increase as T increases for two samples, but the influence of phase transformation appeared as the anomalous behaviour in the $m(T)$ curves for sample I, but was not apparent for sample II, whereas the temperature range of our measurements is beyond the phase transformation range.

The behaviour of m^*/m_0 with p and T has been reported [8, 9] to be governed by either polymorphic transformations at high temperatures inherent in these materials or by the complex structure of the valence bands.

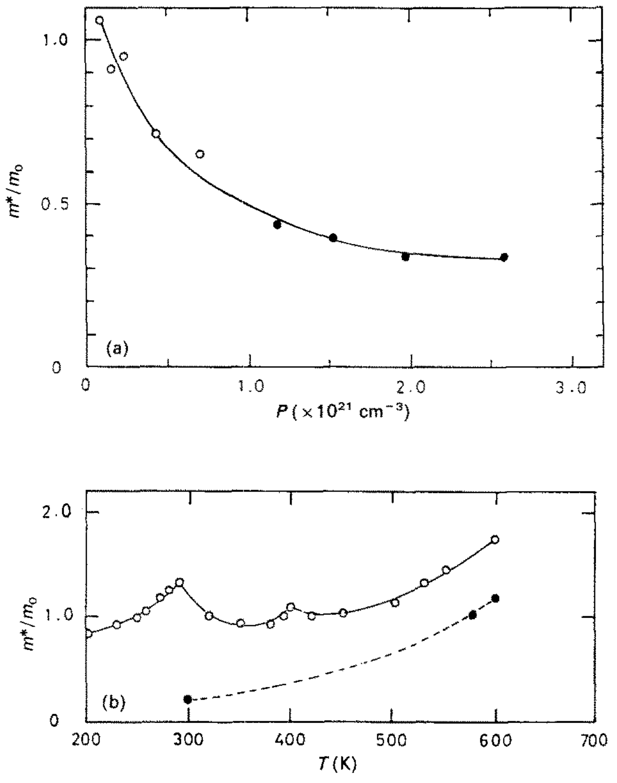

Figure 3 (a) Dependence of m^*/m_0 on concentration: (○) from reflection spectra and (●) from thermo-e.m.f. [5, 6]. (b) Temperature dependence of m^*/m_0: (●) for P_1 and (○) for P_5, $p = 0.92 \times 10^{20}\ \mathrm{cm}^{-3}$.

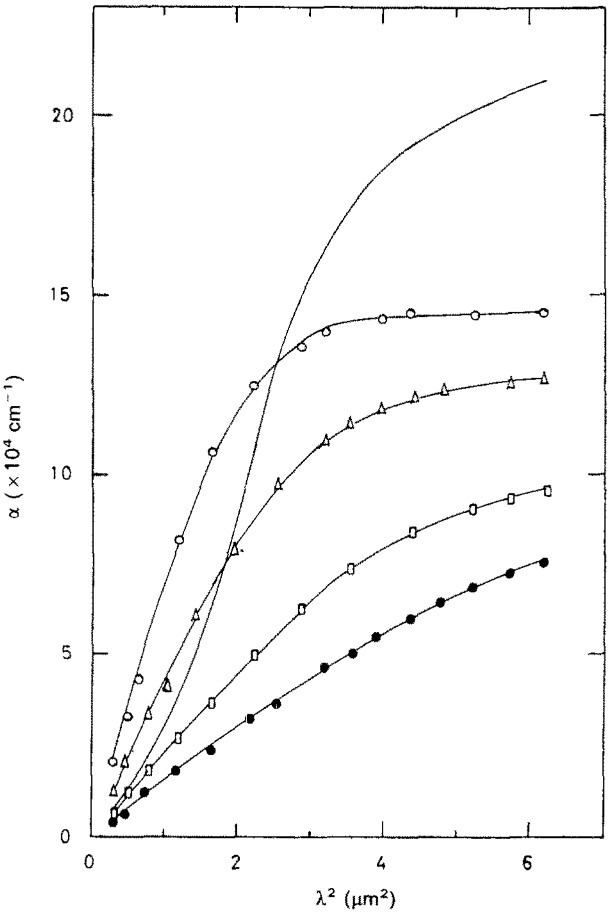

Figure 4 Variation of the absorption coefficient α with λ^2 ((——) data after [8]).

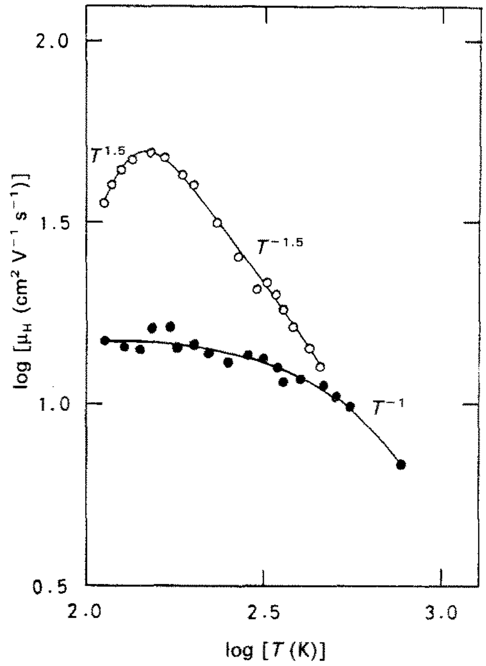

Figure 5 Temperature dependence of the Hall mobility, μ_H: (○) P_5, $p = 0.92 \times 10^{20}\ \mathrm{cm}^{-3}$ and (●) P_1, $p = 2.58 \times 10^{21}\ \mathrm{cm}^{-3}$.

The absorption coefficient (α) was also determined empirically from reflection spectra [10]. Fig. 4 shows the spectral dependence of α for the samples investigated. We observed an increase in α with wavelength, which is usual for the case of scattering by free carriers [11–13]. The absorption process is primarily due to the free carriers where $\omega^2\langle\tau\rangle^2 \gg 1$ ($\tau = 10^{-15}$ s) [14] in this wavelength range.

It was found that, throughout the temperature range investigated, the electrical conductivity of $Cu_{2-x}Se$ increased with the carrier concentration, whereas the Hall mobility of holes remained virtually constant, and equal to $13\ \mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ at 300 K.

Fig. 5 shows the temperature dependence of the Hall mobility, μ_H, in the range $77 \leqslant T \leqslant 600$ K. The Hall mobility decreased proportionally with $T^{-1.5}$ for sample P_5 (near stoichiometric) and with T^{-1} for sample P_1 (highly degenerate), which indicates a predominant scattering of charge carriers by acoustic vibrations of the lattice.

At low temperatures μ_H was nearly constant for sample II but it increased with $T(\mu_H \propto T^{3/2})$ as predicted by the theory of ionized impurity scattering for sample I. The effect of phase transition on $\mu_H(T)$ variation was small, so the power law for sample I was still apparent, but it caused some fluctuation in sample II at the phase transition range. The constant value of $\mu_H(T)$ at low temperatures and the mild variation in $\mu_H(T)$ at high temperatures for sample II can be explained by the large concentration of electrically active copper vacancies.

4. Conclusion

The results of the present work on the plasma reflection of light at room temperature, in parallel with the electrical conductivity σ, Hall mobility μ_H and thermo-e.m.f. Q, in the temperature range 100–650 K are reported.

We have shown how m^*/m_0 (effective mass of holes), σ, μ_H and Q vary with the free carrier concentration and temperature. These properties undergo anomalous effects in the vicinity of the phase transition temperature. The valence band is non-parabolic and the basic scattering mechanism is scattering by acoustic vibrations.

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Received 21 November 1991
and accepted after revision 26 March 1992