Defect band transport in p-type $CuGaSe_2$

2005 J. Phys.: Condens. Matter 17 2699

(http://iopscience.iop.org/0953-8984/17/17/018)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) 2699–2704 doi:10.1088/0953-8984/17/17/018

Defect band transport in p-type $CuGaSe_2$

Ernest Arushanov[1], Susanne Siebentritt, Thomas Schedel-Niedrig and Martha Ch Lux-Steiner

Hahn-Meitner Institut GmbH, Glienicker Straße 100, D-14109 Berlin, Germany

Received 15 December 2004, in final form 10 March 2005
Published 15 April 2005
Online at stacks.iop.org/JPhysCM/17/2699

Abstract

The Hall effect and electrical resistivity are measured on slightly Cu-rich epitaxial $CuGaSe_2$ films in the temperature range 15–300 K. The temperature dependence of the Hall coefficient is described by the two-band model with holes in both the valence and defect bands, as manifested by a maximum in the Hall coefficient. The model can be used to separate holes in the valence band and the defect band, allowing the determination of the activation energies and concentrations of the acceptors, and the concentration of the compensating donors.

1. Introduction

$CuGaSe_2$ is a promising material for use in red-light-emitting devices, light detectors, and as an absorber for solar cells. So far, $CuGaSe_2$ solar cells have achieved efficiencies of 9.5% and 9.7% as thin film [1] and single crystal solar cells [2], respectively. This is only about half of the efficiency achieved for $Cu(In, Ga)Se_2$ solar cells [3]. Great interest exists in the further development of $CuGaSe_2$ solar cells, since a tandem arrangement of $CuInSe_2$ and $CuGaSe_2$ could increase efficiency above 25% [4, 5]. For a further improvement a better understanding of the material properties are needed.

Electrical transport phenomena measurements were carried out on $CuGaSe_2$ films [6–11] and single crystals [12–16]. It has been shown previously that Cu-rich $CuGaSe_2$ with only a slight Cu excess contains high concentrations of defects and thus exhibits a conduction mechanism dominated by transport via defect states at temperatures below 200–250 K [9, 11]. By defect transport we do not necessarily imply extended defect states; it could be hopping transport or actual band transport in extended states. Extended states in a defect band occur when the average distance between defects is close to the diameter of the Bohr orbit of the defect. The properties and the conduction mechanism of such semiconductors at low temperatures are completely determined by the behaviour of the electrons or holes in the defect band.

To extract data on the defect states responsible for doping, like defect ionization energies and defect concentrations, it is necessary to fit the temperature dependence of the charge carrier

[1] Permanent address: Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD 2028, Moldova.

density where it is dominated by transport in the valence band without influence from transport in defects. If the transport in defects already dominates at high temperatures around 250 K, the temperature range that can be used to extract defect data becomes very small, rendering the obtained data unreliable.

Here we apply for the first time to p-type $CuGaSe_2$ a model that takes the transport in defect states explicitly into account [17, 18] and allows the extraction of the charge carrier concentration in the valence band. Therefore it makes possible a more reliable determination of doping defect data.

2. Film growth and Hall measurements

The epitaxial films are prepared by metal organic vapour phase epitaxy (MOVPE) on semi-insulating (001) GaAs at substrate temperatures of 570 °C, using cyclopentadienyl copper tri ethyl phosphine tertiarybutylisocyanide, ditertiarybutyl selenium and triethyl gallium as Cu, Se, and Ga source, respectively. The typical thickness of these films is 0.4 μm. Epitaxial quality has been shown by x-ray diffraction, electron channelling pattern, and scanning electron microscopy. Further details of the film growth can be found in [19, 20]. Growth rates are low, about 100 nm h^{-1}. In the growth process of the samples discussed here the rotation of the substrate was switched off to make use of the Cu gradient occurring along the flow direction. This allowed us to grow samples with varying Cu excess in one process. The wafer was cut after the process into small pieces, which were contacted for Hall measurements. Both samples discussed in this paper were cut from a position very close to the position where [Cu]/[Ga] = 1, with sample A closer to [Cu]/[Ga] = 1 than sample B, i.e. both were grown under Cu excess, but only slight, with a lower Cu excess in sample A than sample B.

The resistivity ρ was measured in the temperature range from 15 to 300 K and the Hall coefficient R from 100 to 300 K in a static magnetic field, H, up to 1 T. The contact arrangement used was a four-point probe in the van der Pauw geometry. Current and field reversal was applied. The films are p-type.

3. The two-band model

Here we present a brief description of features of the two-band model [17, 18] that we use in the analysis of our data.

In a semiconductor with high concentration of defects transport not only takes place in the bands but it can also take place via defect states. This can occur either by the formation of extended states by the overlapping of defect states or by hopping between localized defect states. For a detailed discussion of these transport mechanisms see for example [21, 22].

Due to the presence of transport in defects, an analysis of the temperature dependence of the Hall coefficient $R(T)$ at low temperature has to be made on the basis of the two-band model [17, 18]. If carriers in a crystal can be divided into two groups, characterized by their mobilities (μ and μ_1) and concentrations (p and p_1) which contribute to the total electrical conductivity σ_0 of the crystal, $\sigma_0 = \sigma + \sigma_1$, then according to the theory of two-band conduction and assuming a Hall factor of 1,

$$R = \frac{p\mu^2 + p_1\mu_1^2}{e(p\mu + p_1\mu_1)^2} \tag{1}$$

where μ, μ_1, σ, σ_1 and p, p_1 are the mobility, conductivity and the hole concentration in the main band (valence band) and in the defect states, respectively. In the following it is assumed that the available holes are either located in the acceptors or in the valence band, with the total

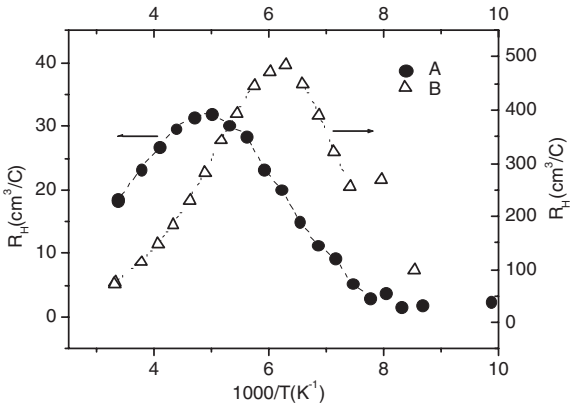

Figure 1. Temperature dependence of the Hall coefficient $R(1/T)$ for two samples A and B of $CuGaSe_2$. The lines are calculated according to equation (1) and using the parameters extracted from the measured curves. The maximum in R indicates two-path transport.

concentration of holes $p + p_1 = p_f = \text{constant}$. A possible contribution of deeper defects is neglected. This means that the Hall coefficient at high temperatures and at low temperatures equals $R_f = 1/ep_f$ with a maximum at intermediate temperatures. This maximum is a clear indication of two-band transport.

To analyse equation (1) further we introduce $b = \mu/\mu_1$, $x = p_1/p$ and obtain

$$\frac{R}{R_f} = \frac{(x + b^2)(x + 1)}{(x + b)^2}. \tag{2}$$

Taking into account that the relative hole concentration x changes by many orders of magnitude, while the relative mobility will change much less, we can assume b independent of temperature and can obtain the condition for the maximum in R by forming the derivative on x and setting it equal to zero. The maximum occurs at the temperature where $\sigma = \sigma_1$ and the value of the maximum is given by

$$\frac{R_{\max}}{R_f} = \frac{(b + 1)^2}{4b}. \tag{3}$$

4. Results and discussion

The samples studied show an exponential growth of the Hall coefficient with decreasing temperature down to about 160–170 K and a well-pronounced maximum of R (figure 1), the characteristic sign of the presence of conduction in a defect band. Sample B shows a higher $R_{\max}$ at lower temperatures; this can be attributed to a lower defect concentration. The resistivity of the two samples studied increases with decreasing temperature (figure 2). The $1/T$ dependence of the resistivity shows an activated type of conductivity down to temperatures somewhat lower than the temperature of $R_{\max}$. The temperature dependence of $\mu = R/\rho$ is given in figure 3. The value of R/ρ increases with decreasing temperature as T^{-n} (where $n = 1.4$–2.0) down to 220–180 K, reaches a maximum and then decreases rapidly, as has been shown before [9, 23].

Using equation (3), an approximation for the parameter b can be determined from the R versus T curves. This can also be estimated from the conditions ($p\mu = p_1\mu_1$) at the temperature where R is maximum.

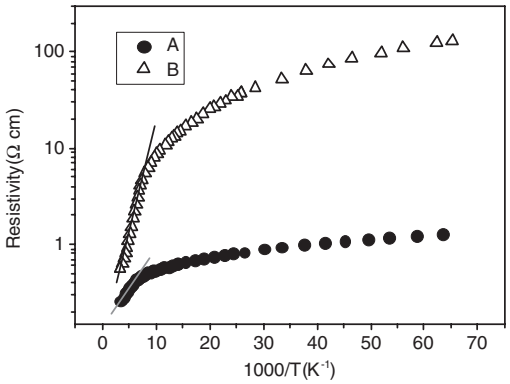

Figure 2. Temperature dependence of the resistivity $\rho(1/T)$ of the same samples as in figure 1.

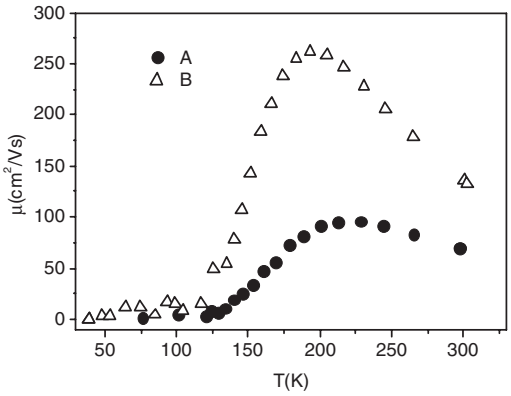

Figure 3. Temperature dependence of $\mu = R/\rho(T)$, obtained from the data in figures 1 and 2.

Table 1. Parameters of p-type $CuGaSe_2$ epitaxial films.

Sample	R_{max} ($cm^3\ C^{-1}$)	R_f ($cm^3\ C^{-1}$)	μ/μ_1	N_a ($10^{18}\ cm^{-3}$)	N_d ($10^{18}\ cm^{-3}$)	N_d/N_a (%)	E_a (meV)
A	32	1.7	74	12	8.42	70	73
B	485	7.8	247	9.3	8.5	91	67
Values obtained from previous fit [11]							
A				39.3	37.1	95	14
B				12.8	12.3	96	46

b is found to be up to 246 in our samples (table 1). The relation (2) and $p + p_1 = p_f$ = constant allow us to determine from the experimental curves $R(T)$ (figure 1) the concentrations p and p_1 as a function of temperature (figure 4). The value of R_f is estimated as the smallest value of R at low temperatures. This estimation is clearly more reliable for sample A, where $R(T)$ levels off at low temperatures. For sample B this is only a rough estimate. This permits us to estimate the value of the net doping $(N_a - N_d) = 1/eR_f$. The calculation of the concentrations becomes impossible at the lowest temperature, where the Hall coefficient becomes a constant or even begins to increase. It is worth mentioning that

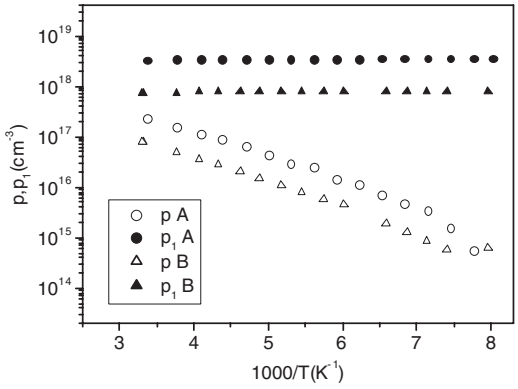

Figure 4. Hole concentrations in the valence band and in the defect states p and p_1 versus temperature, as extracted from the data in figure 1 according to the two-band model.

the Hall coefficient values calculated backwards using equation (1) and the values for b, p and p_1 agree well with the experimental data (figure 1). This indicates that the assumption of $b =$ constant (T) did not introduce a too large error.

The carrier density in the valence band as a function of temperature is given by the following expression [24]:

$$p = -A + \sqrt{A^2 + gN_v(N_a - N_d)\exp(-E_a/kT)}$$
$$\text{with } A = \tfrac{1}{2}(N_d + gN_v \exp(-E_a/kT)) \tag{4}$$

where $N_v = 2(2\pi m^* kT/h^2)^{3/2}$ is the effective density of states in the valence band, N_a is the concentration of acceptor levels, E_a is the activation energy of acceptor levels, g is the degeneracy factor ($g = 1/2$), and N_d is the concentration of donors. Fitting equation (4) to the p data in figure 4, assuming an effective mass $m^* = m_e$ and taking $(N_a - N_d) = 1/eR_f$ into account, the values of E_a, N_a and N_d are obtained (table 1). The activation energies E_a are now around 70 meV for both samples, the acceptor concentrations are around 10^{19} cm^{-3}, and compensation is high at 70% and 90%. We compare these to the data obtained from previous fits [11], where only the few data points before the maximum in R were taken into account. As expected, the discrepancy is larger in the case of sample A, where only four data points were available for the conventional fit. For both samples, the new approach results in a lower degree of compensation and a higher activation energy. Higher activation energies are expected for lower acceptor concentrations [11].

5. Conclusion

In summary, we conclude that the observed temperature dependence of the Hall coefficient in p-type $CuGaSe_2$ is explained by assuming a two-path model with transport in the valence band and in the acceptor levels. The values of the activation energies of the acceptors, their concentrations and the concentration of the compensating donors were calculated using the two-band model, which gives more reliable data than those obtained from a fit to just the few data points at temperatures above the maximum of the Hall coefficient.

Acknowledgment

This work was partly supported by the German Research Ministry BMBF.

References

[1] Young D L, Keane J, Duda A, AbuShama J A M, Perkins C L, Romero M and Noufi R 2003 *Prog. Photovolt. Res. Appl.* **11** 535
[2] Saad M, Riazi H, Bucher E and Lux-Steiner M C 1996 *Appl. Phys.* A **62** 181
[3] Ramanathan K, Contreras M A, Perkins C L, Asher S, Hasoon F S, Keane J, Young D, Romero M, Metzger W, Noufi R, Ward J and Duda A 2003 *Prog. Photovolt. Res. Appl.* **11** 225
[4] Coutts T J, Ward J S, Young D L, Emery K A, Gessert T A and Noufi R 2003 *Prog. Photovolt. Res. Appl.* **11** 359
[5] Siebentritt S 2002 *Thin Solid Films* **403/404** 1
[6] Schumann B, Tempel A, Kühn G, Neumann H, Nam N V and Hänsel T 1978 *Krist. Tech.* **13** 1285
[7] Schroeder D J, Hernandez J L, Berry G D and Rockett A A 1998 *J. Appl. Phys.* **83** 1519
[8] Rusu M, Gashin P and Simashkevich A 2001 *Sol. Energy Mater. Sol. Cells* **70** 175
[9] Siebentritt S, Gerhard A, Brehme S and Lux-Steiner M 2001 *Mater. Res. Soc. Symp. Proc.* **668** H.4.4.1
[10] Schuler S, Nishiwaki S, Beckmann J, Rega N, Brehme S, Siebentritt S and Lux-Steiner M C 2002 *Proc. 29th IEEE Photovoltaic Specialist Conf. (New Orleans, 2002)* p 504
[11] Schuler S, Siebentritt S, Nishiwaki S, Rega N, Beckmann J, Brehme S and Lux-Steiner M C 2004 *Phys. Rev.* B **69** 045210
[12] Mandel L, Tomlinson R D and Hampshire M J 1976 *J. Cryst. Growth* **36** 152
[13] Mandel L, Tomlinson R D and Hampshire M J 1977 *J. Appl. Crystallogr.* **10** 130
[14] Mandel L, Tomlinson R D, Hampshire M J and Neumann H 1979 *Solid State Commun.* **32** 201
[15] Stankiewicz J, Giriat W, Ramos J and Vecchi M P 1979 *Sol. Energy Mater.* **1** 369
[16] Schön J H, Baumgartner F P, Arushanov E, Riazi-Nejad H, Kloc C and Bucher E 1996 *J. Appl. Phys.* **79** 6961
[17] Hung C S 1950 *Phys. Rev.* **79** 727
[18] Emel'yanenko O V, Lagunova T S, Nasledov D N and Talalakin G N 1965 *Sov. Phys.—Semicond.* **7** 1063
[19] Artaud-Gillet M C, Duchemin S, Odedra R, Orsal G, Rega N, Rushworth S and Siebentritt S 2003 *J. Cryst. Growth* **248** 163
[20] Bauknecht A, Siebentritt S, Albert J and Lux-Steiner M C 2001 *J. Appl. Phys.* **89** 4391
[21] Shklovskii B I and Efros A L 1984 *Electronic Properties of Doped Semiconductors* (Berlin: Springer)
[22] Mott N F 1974 *Metal–Insulator Transitions* (London: Taylor and Francis)
[23] Siebentritt S 2005 *Thin Solid Films* at press
[24] Seeger K 2002 *Semiconductor Physics* (Heidelberg: Springer)