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Temperature Dependences of Concentrations of Photo-generated Free Electrons and Holes in p-$CuInS_2$

In a previous work [1] the strongly sublinear dependence of the concentration of photo-excited free holes on excitation strength was calculated using a model [2] of the p-type partly compensated semiconductor with two classes of recombination centres and one class of hole traps. It was assumed that the levels of the slow recombination centres II lie in the forbidden band closer to the valence band than the levels of the fast recombination centres I. In the darkness, the centres I and II are occupied by holes, and the hole traps are partly occupied by electrons. In this work we introduce to the recombination model (Fig.1) two classes of hole traps (acceptors) taking into account the experimental results of Hall effect measurements [3]. We also assume that the thermal excitations of electrons from the centres I and II to the conduction band are possible.

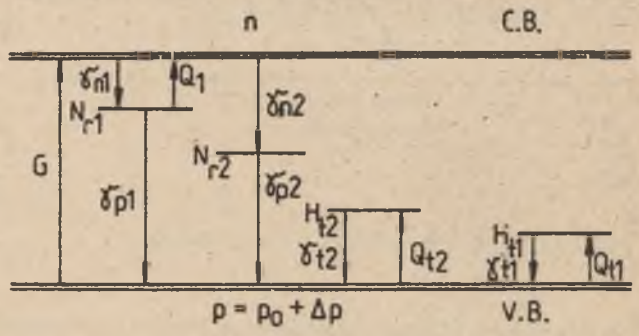

Fig. 1. Energy level scheme and electronic transitions forming the recombination model of photo-excited p-type semiconductor

When in such a semiconductor are photo-generated electron-hole pairs at the rate G, then in the steady-state, the following equations describe the model:

$$G - p\, n_{r1}\, \gamma_{n1} - p\, n_{r2}\, \gamma_{p2} = 0, \tag{1}$$

$$p\,(H_{t1} - p_{t1})\, \gamma_{t1} - p_{t1}\, \gamma_{t1}\, Q_{t1} = 0, \tag{2}$$

$$p\,(H_{t2} - p_{t2})\, \gamma_{t2} - p_{t2}\, \gamma_{t2}\, Q_{t2} = 0, \tag{3}$$

$$n\,(N_{r1} - n_{r1})\, \gamma_{n1} - p\, n_{r1}\, \gamma_{p1} - n_{r1}\, \gamma_{n1}\, Q_{r1} = 0, \tag{4}$$

$$n\,(N_{r2} - n_{r2})\, \gamma_{n2} - p\, n_{r2}\, \gamma_{p2} - n_{r2}\, \gamma_{n2}\, Q_{r2} = 0, \tag{5}$$

$$n + n_{r1} + n_{r2} =$$

$$= p + p_{t1} + p_{t2} + N_{r1} + N_{r2} - H_{t1} - H_{t2}, \tag{6}$$

where $p = p_0 + \Delta p$ and $n = n_0 + \Delta n$ are respectively concentrations of free holes and electrons, Δp and Δn are respectively concentrations of photo-generated free holes and electrons , N_{ri} concentration of the i-th class of recombination centres $(i = 1,2)$, H_{ti} concentration of the i-th class of hole traps,

$\gamma_{n(p)i}$ recombination coefficient of the i-th class centre for electron(hole), γ_{ti} trapping coefficient of the i-th class of hole trap, $Q_{ri} = N_c \exp(-E_{ri}/k\,T)$, $Q_{ti} = N_v \exp(-E_{ti}/k\,T)$, N_c and N_v are respectively the effective densities of states in the conduction and valence bands, E_{ri} and E_{ti} are energy ionization of the i-th class recombination centres and the i-th class hole traps, n_{ri} concentration of electrons in the i-th class recombination centres, p_{ti} concentration of holes in the i-th class of hole traps, T temperature, and k the Boltzmann constant.

The set of equations (1) to (6) was numerically solved and the values of $p(G,T)$, $n(G,T)$, $n_{r1}(G,T)$, $n_{r2}(G,T)$, $p_{t1}(G,T)$ and $p_{t2}(G,T)$ were calculated using a PC 1512 Amstrad computer. Fig. 2 shows the calculated dependences $\Delta p(1/T)_{G=const}$ and $\Delta n(1/T)_{G=const}$.

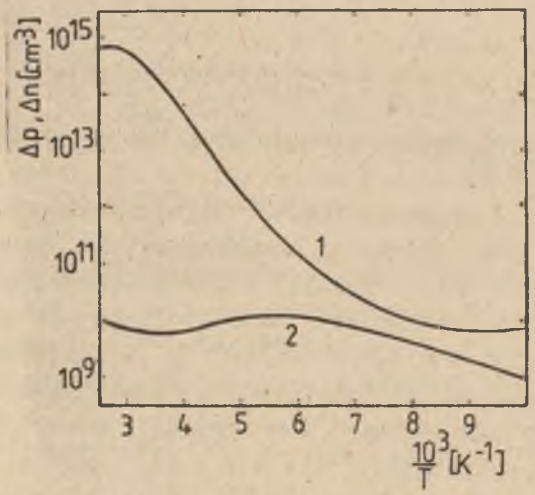

Fig. 2. Calculated temperature dependences of concentrations of photo-generated free holes (1) and electrons (2). For the calculations the following parameters were used : $N_{r1} = 2.8 \times 10^{17}$ cm^{-3}, $N_{r2} = 2 \times 10^{16}$ cm^{-3}, $E_{r1} = 0.2$ eV, $E_{r2} = 0.6$ eV, $N_{t1} = 1.1 \times 10^{17}$ cm^{-3}, $N_{t2} = 2 \times 10^{17}$ cm^{-3}, $E_{t1} = 0.14$ eV, $E_{t2} = 0.24$ eV, $\gamma_{n1} = 10^{-7}$ cm^3 s^{-1}, $\gamma_{n2} = 10^{-8}$ cm^3 s^{-1}, $\gamma_{p1} = 10^{-8}$ cm^3 s^{-1}, $\gamma_{p2} = 10^{-14}$ cm^3 s^{-1}, $N_c = 2.9 \times 10^{17}$ cm^{-3}, $N_v = 6.7 \times 10^{18}$ cm^{-3}

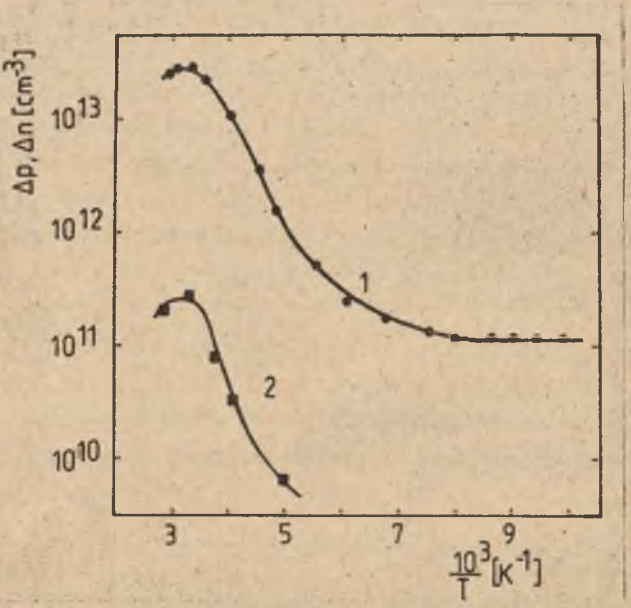

Fig. 3. Measured temperature dependences of concentrations of photo-generated holes (1) and electrons (2) in the p-$CuInS_2$ crystal. The values of Δp are found on the basis of the results of measurements of photoconduction [4] and Hall effect [3]. The photoconduction was excited with the weakly absorbed light ($h\nu$ = 1.36 eV) of intensity F = 3.6 x 10^{16} cm^{-2} s^{-1}. The values of Δn are determined from the study of photomagnetoelectrical effect excited with the strongly absorbed light ($h\nu$ = 1.91 eV) of intensity F = 1.7 x 10^{16} cm^{-2} s^{-1}, and by using a method described in [5]

For the calculated $\Delta p(1/T)$ dependence a good qualitative agreement with the experimental one (Fig. 3) for the p-$CuInS_2$ crystal is observed. In particular, at T > 120 K a thermal stimulation region of calculated Δp is found. As can be seen from Fig. 2 the calculated Δn is weakly dependent on temperature in contrast to the experimental result of $\Delta n(1/T)$ based on the measurements of photomagnetoelectrical effect in the p-$CuInS_2$ crystal (Fig. 3) . The shapes of the calculated and measured

$\Delta n\,(1/T)$ dependences are also different. These differences may be resulted from the fact that the calculated $\Delta n\,(1/T)$ relates to the bulk of the crystal, whereas the measured $\Delta n\,(1/T)$ is found for the thin layer at the crystal surface. In fact, the surface recombination is not included in the recombination model used for the calculations.

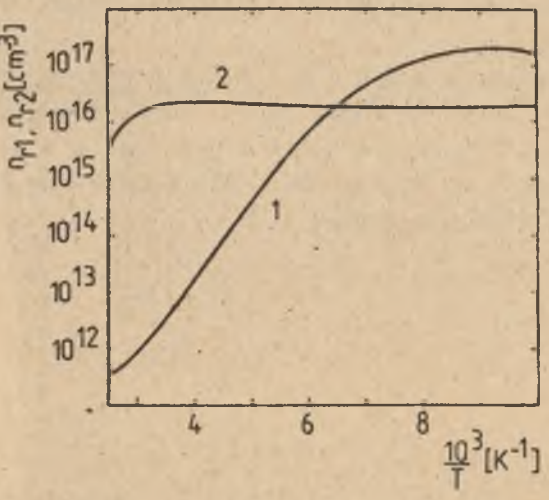

Fig. 4. Calculated temperature dependences of concentrations of photo-generated electrons captured by the recombination centres I (1) and II (2). The parameters used for calculations are presented in the caption of Fig. 2

Fig. 4 shows the calculated temperature dependences of the electron occupancies of the recombination centres I and II. From this figure it is seen that the thermal stimulation of Δp (Fig. 2) appears when the concentration of electrons in the recombination centres I strongly decreases. On the other hand, the electron concentration in the centres II is nearly constant in this temperature range (Fig. 4).

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