

Thermally Stimulated Currents in the Range of Unity Gain Factor

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Dedicated to Professor Dr. N. Riehl on his 70th birthday

Thermally stimulated current-curves in CdS platelets with slit electrodes change their character when the photoelectric gain-factor increases above one. Here the photocurrent remains essentially frozen-in up to temperatures at which marked thermal quenching sets in. A positive space charge region is assumed to be responsible for the frozen-in photocurrent. A reliable TSC-analysis of the trap distribution can be conducted only for gain factors considerably below one.

1. Introduction

Thermally stimulated currents are conveniently used to obtain information on trap distribution¹⁻³ in photoconductors. For this, the crystal is illuminated while cooling (filling repulsive traps) or at low temperature (filling of neutral or attractive traps), the optical excitation is then terminated and the crystal is heated with a heating rate in excess of a critical value (Ref. ²) — typically ~ 0.2 deg/sec — while in the dark. Typically the current decreases several orders of magnitude (decay of the photocurrent) before it starts to increase again as a result of the thermal ionization of traps.

At high current densities, however, the photocurrent can be “frozen-in” at low temperatures without any appreciable decay over extended periods of time. Here the qualitative behavior of the TSC-curves changes and does not resemble the curves obtained after marked decay of the photocurrent. It is the purpose of this paper to analyze this transition.

2. Experimental Set-up

Undoped photoconductive CdS single-crystal platelets were used, which were grown in an N_2/H_2S (98%/2%) atmosphere near 1000 °C by sublimation from high purity CdS powder and cooled in the same atmo-

sphere to room temperature, resulting in Class I (GROSS-NOVIKOV⁴) crystals. An essentially striation-free crystal with the *c*-direction parallel to the applied field is used. Ohmic Ti/Al electrodes⁵ in slit arrangement were evaporated, leaving a 3 mm gap. The cross section of the crystal normal to the current is 0.1×3 mm². 30 V are applied.

The crystal is kept on a copper block surrounded by a copper heat shield in a metal-ultra-high-vacuum system at $p \cong 10^{-9}$ Torr. It can be cooled to liquid nitrogen temperature or heated with ~ 0.1 deg/s through a metal cooling finger. The crystal can be illuminated through a glass window and a glass covered hole in the heat shield.

Monochromatic irradiation is produced by a Jarrel Ash-grating monochromator, the higher order diffraction is filtered out with a CS-369 Corning Glass filter for wavelengths above 550 mμ. The optical excitation density increases from 2×10^{14} to 1.5×10^{15} photons/cm² s for wavelengths changing from 4000 to 5500 Å. For TSC-irradiation a wavelength of 4600 Å with 5×10^{14} photons/cm² s is used.

The current through the crystal is measured with a Type 409 Keithley micro-micro-ammeter.

3. Experimental Results

The photoconductive behavior of CdS-platelets of Class I can be changed⁶⁻⁸ in value by many orders of magnitude via heat treatment between 100 and 270 °C. As a result of this treatment oxygen is desorbed from the surface^{6,7}, the spacial dis-

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tribution of native defects changes⁶ (homogenizing effect), and possibly new defects are created in the surface-near region. This causes the spectral distribution of the photocurrent to shift towards higher currents and to change from a typical Class I behavior to a Class II behavior^{4, 6, 7} with successive heat treatments (see Fig. 1).

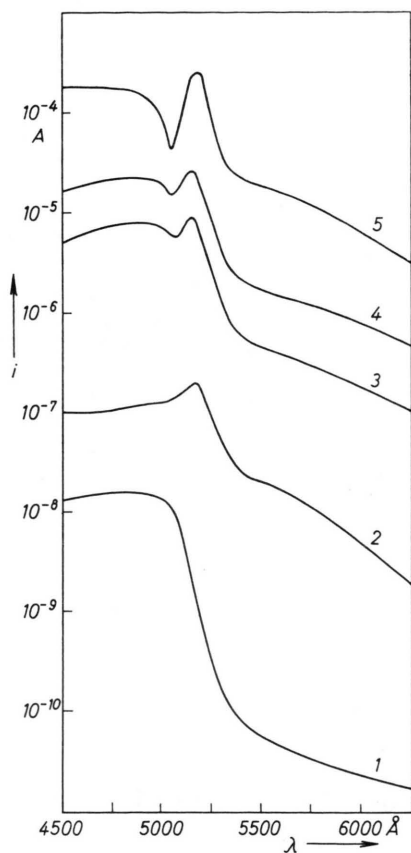


Fig. 1. Spectral distribution of the photocurrent of a CdS crystal, measured at room temperature. Curve 1 after 5 min heat treatment at 120 °C, Curve 2 after 5 min heat treatment at 210 °C, Curve 3 after 5 min heat treatment at 240 °C, Curve 4 after 10 min heat treatment at 240 °C and Curve 5 after 5 min heat treatment at 270 °C.

Frozen-in photocurrents can be observed after treatment above 240 °C and with intrinsic optical excitation. Fig. 2 shows the photocurrent at 4600 Å excitation as function of the temperature after the same heat treatments as used as family parameter in Fig. 1. These curves were taken while cooling the crystal at a rate of ~ 0.1 deg/s.

In Fig. 3 a family of thermally stimulated currents (TSC) is shown as observed adjacent to each of the curves in Fig. 2. After treatment at 120 °C

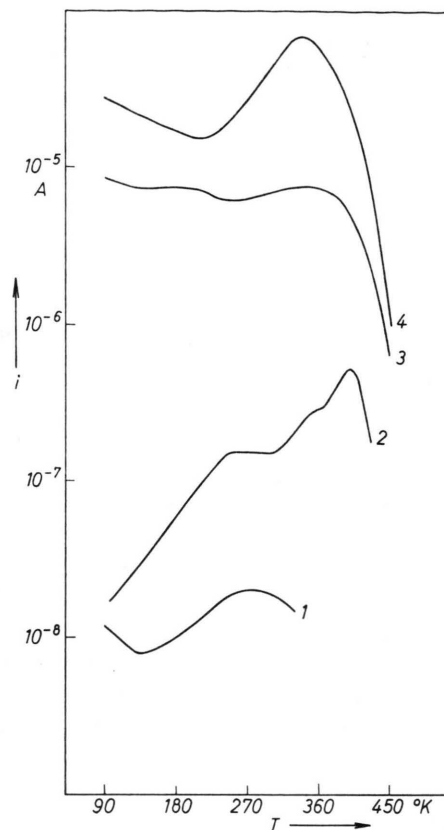


Fig. 2. Photocurrent (excited with 5×10^{14} photons/cm² at 4600 Å) as a function of temperature (measured while cooling down) after heat treatments as given for Fig. 1 and corresponding curves.

a well structured TSC-curve is observed. After treatment at 210 °C at least three new peaks have grown while two (low temperature-) peaks become invisible. After the 240 °C heat treatments the low-temperature part of the TSC curve increases dramatically. The curve becomes less structured. Finally, after the 270 °C treatment, the TSC curve has completely changed its character: The photocurrent does not decay markedly after switching-off the optical excitation at 90 °K. As the temperature increases, the current decreases monotonically, first slowly, and as T reaches ~ 350 °K very rapidly by almost four orders of magnitude.

This behavior is restricted to excitation in the intrinsic range. TSC curves taken after band-edge excitation (causing a more homogeneous optical excitation at lower excitation densities) behave largely normal and look similar to curve 2 in Fig. 3. Since the intrinsic light is absorbed in a surface

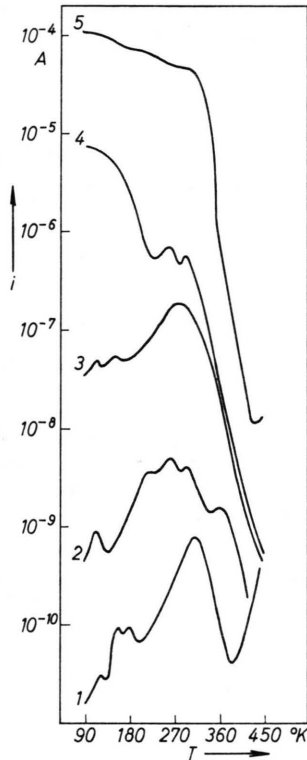


Fig. 3. Thermally stimulated currents starting directly after the corresponding curves of Fig. 2 were taken.

near region of about 10^{-5} cm thickness, the optical excitation rate in this layer is $\sim 5 \times 10^{19}$ cm $^{-3}$, while with band-edge (50% absorption) irradiation the excitation rate for the crystal bulk is $\sim 5 \times 10^{16}$ cm $^{-3}$.

4. Discussion

The current, i , is commonly used as a direct measure of the released carriers from traps during a TSC-curve. The density of these carriers, i. e. the density of the emptied traps, can be estimated by

$$\int_{E_1}^{E_2} N_t(E) dE \cong \frac{\int_{T_1}^{T_2} i(t) dt}{e G V_0} \simeq \frac{a}{i_0} \int_{T_1}^{T_2} i(t) dt \quad (1)$$

with V_0 the volume of the crystal, a the optical excitation density and i_0 the photocurrent at excitation a and at a temperature in the TSC-peak range ($T_1 < T < T_2$). The energy of the trap may be estimated by

$$E_c - E_t \cong k T \ln(N_c/n), \quad (2)$$

with E_c , the energy of the lower edge of the conduction band and $N_c = 2 (m_{\text{eff}} k T / 2 \pi \hbar^2)^{3/2}$, with m_{eff} , the effective mass of electrons (of density n).

The gain factor is given by

$$G \cong \tau_n \mu V / L^2 = i_0 / e a q L, \quad (3)$$

with τ_n the lifetime of a photogenerated electron, L , the distance between the electrodes, q , the crystal cross section, μ , the mobility of electrons and V the applied voltage. For the investigated crystal and the optical excitation density used for the TSC-curves in Fig. 3, the gain factor is given by

$$G \cong 1.2 \times 10^5 i. \quad (3a)$$

Hence the gain factor becomes unity when the current is about 10^{-5} A. This coincides with the transition from an essentially normal TSC curve below 10^{-5} A to a "frozen-in" photocurrent behavior (curves 4 and 5 in Fig. 3).

It is therefore suggested that at high current densities when G becomes larger than one, the "TSC" current is little influenced by ionization of electron traps and largely determined by a positive space charge close to the cathode, produced by optical excitation and depletion of majority carriers close to the cathode in an external field. The current therefore stays essentially constant with increasing temperature until, at high enough temperatures, this space charge is annihilated, probably by thermal ionization of hole traps.

However, for the current to be continuous, one must assume that the lifetime of trapped holes along a continuous path from cathode to anode is sufficiently large to maintain a frozen-in photocurrent after termination of the optical excitation. For this it is of interest to analyze this primitive model in somewhat more detail in respect to the spacial position of the positive space charge, its originating mechanism, and which levels in the band gap are involved to store this space charge. Since the used electrode-geometry as well as the specific optical excitation mode seems to be important (with other arrangements such TSC transition has not yet been observed) it is helpful to analyze the specific geometry of the current transport (Fig. 4).

In the optical excitation range of a thickness of the order of the reciprocal absorption constant ($K^{-1} \sim 10^{-5}$ cm) between the two electrodes, electron-hole pairs are produced. Electrons and holes can diffuse into the deeper part of the crystal bulk.

If the two carriers diffuse together, there is primarily no space charge layer produced. The thickness of such layer is determined by the random walk length of the less "mobile" carrier (here holes)

$$A_p = \sqrt{\lambda_p v_p \tau_p} \quad (4)$$

with λ_p the mean free path, v_p the thermal velocity, and τ_p the lifetime of holes in the valence band. This length is probably of the order of (or smaller than) 10^{-5} cm (Fig. 4).

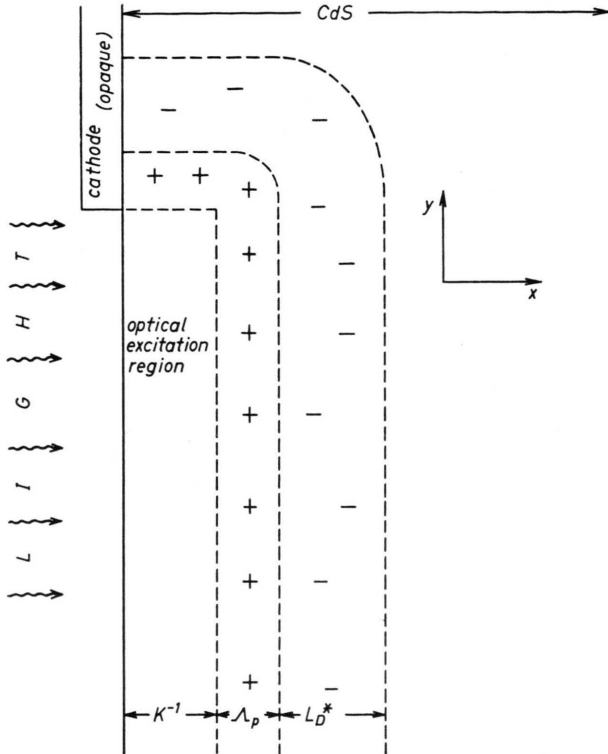


Fig. 4. Optical excitation with intrinsic light and space charge creation in the adjacent (dark) bulk region.

The more mobile carrier, however, will diffuse further into the crystal bulk, creating a space charge double layer (the region into which electrons are diffusing alone becomes negatively charged, leaving a positively charged region behind where electrons and holes originally were together with equal densities). The geometry of this double layer is depicted in Fig. 4. The field created by this double layer counteracts the diffusion and — in stationarity — causes the current normal to this double layer to vanish. The thickness of this double layer is of the order of a few Debye-screening lengths L_D . The

thickness of the negative space charge layer can easily be estimated:

$$L_D^* \cong \frac{E_{Fn} - E_F}{kT} L_D \quad (5)$$

with E_{Fn} the quasi-Fermi-level for electrons, E_F the "dark"-Fermi-level, and

$$L_D \cong \sqrt{\frac{\epsilon \epsilon_0 k T}{E_{Fn} e^2 \int_{E_F} N_t(E) dE}} \quad (5a)$$

With a level density of about 10^{16} cm $^{-3}$ the thickness of the double layer again is of the order of 10^{-5} cm.

When an external voltage is applied, electrons are carried from the region near the cathode toward the anode, leaving a positive space charge close to the cathode (Fig. 5).

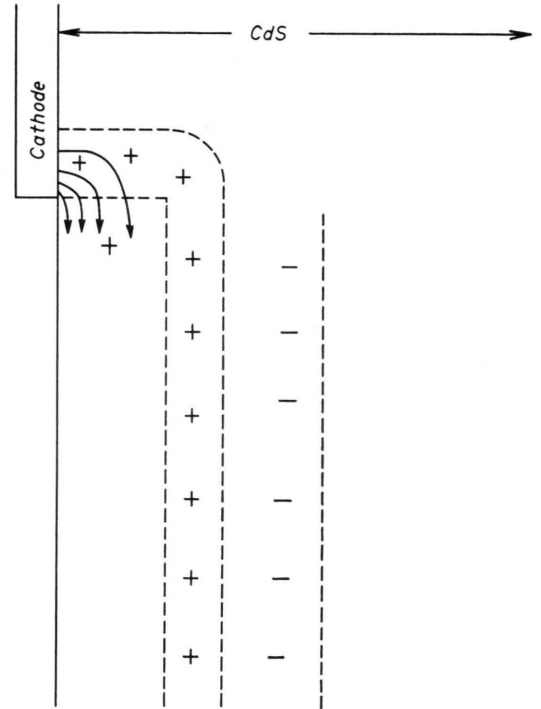


Fig. 5. Space charge distribution during the frozen-in photocurrent state.

It is conceivable that the life time of trapped holes in the positive space charge region of the double layer (Fig. 5) is considerably larger than in the neutral region where electrons and holes were created in equal numbers. A considerable increase in life time of carriers seems to be necessary for the

frozen-in current since an injection of majority carriers can supply only a transient current during the dielectric relaxation time and the field is not high enough for marked double injection. It needs a careful analysis to determine whether the space charge region is sufficient for sustaining the current through the crystal.

However, since the electrical properties near the electrode and in the space region connecting both electrodes are not well enough known, it seems too early to analyze this space charge behavior in more detail. It may suffice to say that it is known that positive space charge can be stored in slow recombination centers. This space charge should then become annihilated (via thermal ionization and recombination) as thermal quenching sets in. This agrees well with the experimental observation of the similar decrease of the photo- and the TSC-current for temperature above 350 °K (compare curve 4, Fig. 2 and curve 5, Fig. 3).

It is therefore indicated that TSC-curves give a useful tool for analysis of the trap distribution only as long as the photoelectric gain factor is much smaller than one. For gain factors above one the crystal seems to act essentially as a lead with a current determined by a positive space charge region with markedly increased carrier life time. The space charge density is determined by the previously applied optical excitation density. Probably a recombination annihilation of this space charge is retarded because of the specific geometry, forcing electrons drifting from the cathode toward the anode to avoid partially the space charge region. This creates a frozen-in photocurrent, which starts to decay rapidly only at temperatures at which thermal quenching becomes marked.

Acknowledgement

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