APPARENT AGEING OF A SEMICONDUCTOR CAUSED BY THE MIGRATION OF DEFECTS

ŠTEFAN LÁNYI*, Bratislava

The effect of migration of mobile defects, acting as donors, on the dark- and photoconductivity of a semiconductor has been analyzed. The proposed model of ageing yields a time dependence of the current $i \sim t^{-n}$ with $n < 0.5$, a sublinear voltampere characteristic at the time t: $i_t \sim U^{1-n}$ and a sublinear luxampere characteristic at the time t: $i_t \sim \varepsilon^{1-n}$. The results are in agreement with the properties of HgI₂ single crystals.

КАЖУЩЕЕСЯ СТАРЕНИЕ ПОЛУПРОВОДНИКА, ОБУСЛОВЛЕННОЕ ПЕРЕМЕЩЕНИЕМ ДЕФЕКТОВ

В работе анализируется влияние перемещения дефектов, действующих как доноры, на электропроводность в темноте и фотопроводимость полупроводника. Предлагаемая модель старения полупроводника приводит к зависимости тока от времени типа $i \sim t^{-n}$ с показателем $n < 0,5$ и к сублинейной вольт-амперной характеристике в момент времени t вида $i_t \sim U^{1-n}$ и сублинейной люкс-амперной характеристике в момент времени t вида $i_t \sim \varepsilon^{1-n}$. Результаты находятся в хорошем согласии со свойствами HgI₂.

I. INTRODUCTION

An apparent polarization effect in HgI₂ single crystals, appearing as a slow fall of the current flowing after switching on a d.c. voltage, has been reported in paper [1]. However, the current following the shorting the sample showed some peculiarities. Its initial magnitude became the smaller the longer the polarization time was and the greater the applied voltage was, if the polarization time was kept constant. The current flowing after the polarity reversal of the voltage applied for some tens of minutes contained no observable transient and its magnitude was the same as before the polarity reversal. Even if we do not consider the unusually slow decay of the charging current $i \sim t^{-(0.4-0.5)}$, the behaviour of the short-circuit and the polarity reversal currents cannot be interpreted in terms of any known polarization mechanism. The phenomenon can be rather considered an apparent ageing in the electric field. We assume its origin to be the migration of ionized defects, which

* Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta, CS-899 30 BRATISLAVA.

causes a local change in electrical conductivity. The measurements of potential distribution support this concept [1].

The assumption widely used in the semiconductor theory that the impurities are immobile, has a limited validity. With the use of semiconducting compounds with greater ionicity of bond the possibility of the occurrence of a similar effect as in HgI₂ arises, first of all in devices which are stressed by an intensive electric field. Therefore the theory of the supposed ageing effect will be outlined and some of its typical consequences will be shown in the present paper.

II. THEORY

II.1. Assumptions

Let us consider a material which may be depending on impurity contents, intrinsic or extrinsic at a given temperature. Impurities with a mobility μ, give rise to a single donor level¹). If an electric field is applied to the sample via two ohmic electrodes, the ionized donors start to migrate. Their concentration in the vicinity of at least one of the electrodes will change, because even if they could leave the sample at the cathode the missing ones cannot be supplied by the anode. Thus we are faced with the problem of a non-steady state transport in the presence of at least three different charge carriers with electrodes differently blocking them and at voltages $U \gg kT/e$. It cannot be solved analytically. Therefore we shall introduce some simplifications: a) neglect of diffusion; b) considering the slowness of migration of the defects, the solution of a quasi-steady state — neglect of displacement current; c) assumption of an oblong concentration profile of donors, i.e. that the doped part of the sample is gradually reduced, while the concentration, which is then independent of the coordinate in this part of the sample, is increased; d) assumption of total blocking of donors at the electrodes, whereas electrons and holes may freely pass the interfaces [2].

A confrontation of results obtained with other concentration profiles (triangular and parabolic ones) has shown that not satisfying item c) does not affect significantly the results. The migration of donors is not hindered by a space charge, as they are neutral as a whole or, let us say the positive charge of ionized donors is screened by electrons. Within a short time after the application of voltage a depletion layer arises near the anode. The conductivity drops in it, the field strength increases and the migration is enhanced. In this manner a layer exhausted of donors will probably arise and broaden with time.

¹) The treatment applies for an acceptor level as well. For simplicity we shall assume the mobility of majority carriers (the concentration of which is increased by the impurity) to exceed that of minority carriers.

II.2. Procedure of solution

The concentration of electrons n_i and holes p_i in the exhaustion layer are equal and the conductivity is

$$\sigma_i = en_i\mu_n + ep_i\mu_p = en_i(\mu_n + \mu_p),$$

where μ_n, μ_p are the mobilities of electrons and of holes, e is the protonic charge. The concentrations in the extrinsic area (Fig. 1a) are

$$n_2 = p_2 + N_D^+ = p_2 + BN_D^{1/2},$$

where N_D^+ denotes the concentration of the ionized donors, N_D the concentration of all donors and

$$B = \left(\frac{m_n}{2\pi\hbar^2}\right)^{3/4}(kT)^{3/4}\exp[-\varepsilon_D/(2kT)] \quad (1)$$

[3], where m_n is the effective mass of electrons, ε_D is the distance of the donor level from the edge of the conduction band, k is the Boltzmann constant and T the temperature. The electrical conductivity is

$$\sigma_2 = en_2\mu_n + ep_2\mu_p + eN_D^+\bar\mu_D \approx eBN_D^{1/2}(\mu_n + \bar\mu_D).$$

The blocking of donors at the electrodes results in an average distance, which they may travel, smaller than the length of the crystal. This may be expressed by a modified mobility $\bar\mu_D$.

$$\bar\mu_D = \mu_D/3$$

in case of the rectangular concentration profile and

$$\bar\mu_D = \mu_D/2$$

in case of the triangular profile. The mobility of impurities is usually thermally activated, which can be expressed as

$$\mu_D = \mu_{D0}\exp[-h_D/(kT)],$$

where h_D is the enthalpy of their migration.

At the moment $t=0$ the voltage

$$U = \int_0^l E(l)\,dl$$

is applied to the electrodes. L is the length of the sample, $E(l)$ is the local field strength. The current $i(t)$ is constant throughout the length of the sample and it is represented by the flux of the corresponding charge carriers. The transference number of the donors in the doped area is

$$t_D^+ = \frac{\bar\mu_D}{\mu_n + \bar\mu_D}.$$

The flux of the ionized donors is identical with the flux of all the donors. The assumed total blocking of donors leads to the equation

$$dN_D(L-l) = N_D\,dl$$

and to the equation governing the shift of the boundary between the intrinsic and extrinsic part of the sample

$$\frac{dl}{dt} = \frac{(L-l)^2}{N_D L}\frac{dN_D}{dt}, \quad (2)$$

caused by the flow of the current

$$\frac{dN_D}{dt} = \frac{i_t t_D^+}{e} \quad (3)$$

$\bar N_D$ is the initial average concentration of the donors.

The current density i_t is given by the applied voltage and the resistance of the sample at the instant t, at which the coordinate of the boundary is l_t.

$$R_t = R_1 = \frac{l}{\sigma_1} + \frac{L-l}{eB[\bar N_D L/(L-l)]^{1/2}(\mu_n + \bar\mu_D)} \quad (4)$$

Substituting (5) into (3) and (3) into (2) and after the integration of Eq. (2), using the boundary condition $t=0$, $l=0$ we have

$$i_t = \frac{U}{L}eB(\bar N_D)^{1/2}\frac{n_1 L^{3/2}}{B(\bar N_D L)^{1/2}l/(\mu_n + \mu_p) + n_1(L-l)^{3/2}/(\mu_n + \bar\mu_D)} \quad (5)$$

$$\frac{eB(\bar N_D)^{3/2}(\mu_n + \bar\mu_D)^2}{n_1\mu_D(\mu_n + \mu_p)}\left[\frac{r}{1-r} + \ln(1-r)\right] + \frac{eN_D}{2}\frac{\mu_n + \bar\mu_D}{\mu_D}[1-(1-r)^{1/2}] = i_0 t, \quad (6)$$

where $i_0 = \frac{U}{L}eB(\bar N_D)^{1/2}(\mu_n + \bar\mu_D)$ and $r = l/L$.

Instead of the complicated and rather clumsy derivation of the explicit $i(t)$ dependence we shall limit ourselves to expressing the dependence $l(t)$ and to the calculation of the time dependence of the current density as a function of the position of the boundary $i = i(l)$, using expression (5).

The result for the triangular concentration profile is obtained using the expression for the resistance

$$R = R_1 = \frac{l}{\sigma_1} + \frac{\sqrt{2}(L-l)}{eB[\bar N_D L/(L-l)]^{1/2}(\mu_n + \bar\mu_D)}. \quad (7)$$

Except for a different effective mobility of the donors and the factor $\sqrt{2}$ the expressions (4) and (7) are identical. However, expression (7) is only approximate, as in the vicinity of l the conditions $p_2 \ll n_2$ and $n_2 \approx N_D^+$ are not fulfilled. This simplification is seen in Fig. 1b. The equation (2) is valid also for the triangular profile.
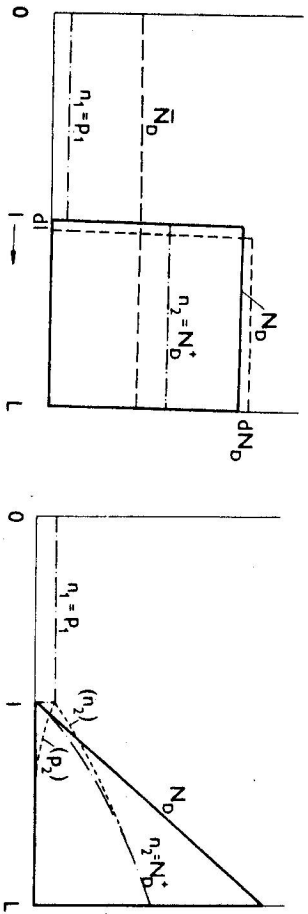

Fig. 1. a) Schematic representation of the sample with oblong profile of concentration of donors. b) Schematic representation of the sample with triangular profile: (n_1), (p_2) are the actual concentrations of electrons and holes, the full line is the employed approximation of electron concentration, the presence of holes in the interval (l, L) is neglected.

The initial magnitude of the current density may be defined in various ways. If we assume a uniform concentration of donors throughout the sample at $t = 0$

$$\frac{i_t}{i_0} = \frac{n_1 L^{3/2}(\mu_n + \mu_p)}{Bl(\bar{N}_D L)^{1/2}(\mu_n + \mu_D) + \sqrt{2}(L-l)^{3/2} n_1(\mu_n + \mu_p)} \qquad (8)$$

while the equations (2) and (7) do not give a picture of the arising of the triangular profile. If we consider the initial profile a triangular one with $l = 0$, we obtain

$$\frac{i_t}{i_0} = \frac{\sqrt{2}\, n_1 L^{3/2}(\mu_n + \mu_p)}{Bl(\bar{N}_D L)^{1/2}(\mu_n + \mu_D) + \sqrt{2}(L-l)^{3/2} n_1(\mu_n + \mu_p)}. \qquad (9)$$

Anyway, such a profile at $t = 0$ is not likely. This problem could be eliminated by relating the current to its final steady value, however, this is not suitable from an experimental point of view.

III. RESULTS

III.1. Dark current

Some time dependences of the current, calculated by means of expressions (5) and (6) for $n_2/n_1 = 10$, 10^2 and 10^3 under the assumption $\mu_p \ll \mu_n$, $\mu_D \ll \mu_n$ are seen in Fig. 2. For great n_2/n_1, a well expressed dependence $i \sim t^{-n}$ with $n < 0.5$ develops.

For n_2/n_1 small the resulting exponent n decreases. The current vs. time dependences for different electric field strengths and $n_2/n_1 = 10^2$, 10^3 are shown in Fig. 3. The dashed — dotted curves correspond to the triangular concentration profile. They were calculated using relations (6) and (8).
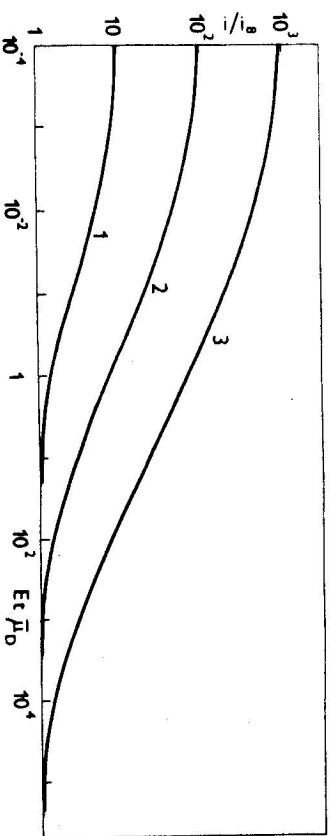

Fig. 2. Current density vs. time dependences calculated for rectangular profile: (1) $n_2/n_1 = 10$, (2) $n_2/n_1 = 10^2$, (3) $n_2/n_1 = 10^3$.
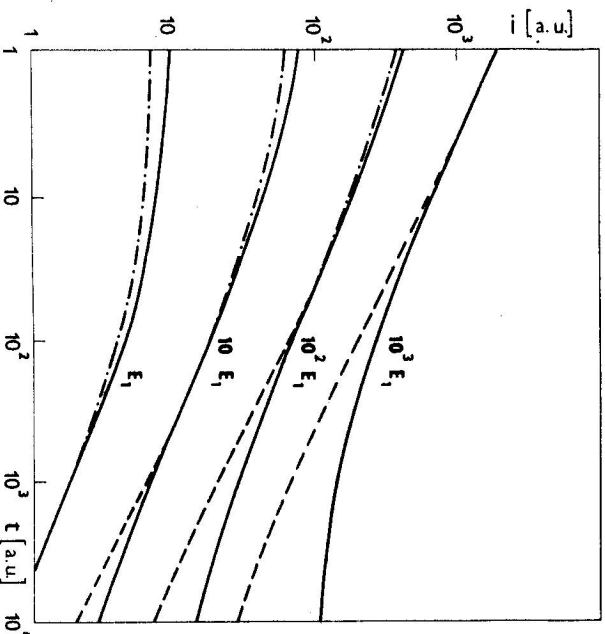

Fig. 3. Current density vs. time at different field strengths. Full lines: $n_2/n_1 = 10^2$, dashed lines: $n_2/n_1 = 10^3$, dashed-dotted lines: triangular profile, $n_2/n_1 = 10^2$, 10^3.

Following from (5) and (6) the VA-characteristics at different time instants after switching on the voltage are shown in Fig. 4. At $t = 0$ and $t \to \infty$ the response of the system is linear, while for an intermediate time a sublinear section $i_t \sim U^m$ with $1 > m > 0.5$ exists. This corresponds to the drop of the current from its initial ohmic to the steady state ohmic value and the relation $m = 1 - n$ is valid.
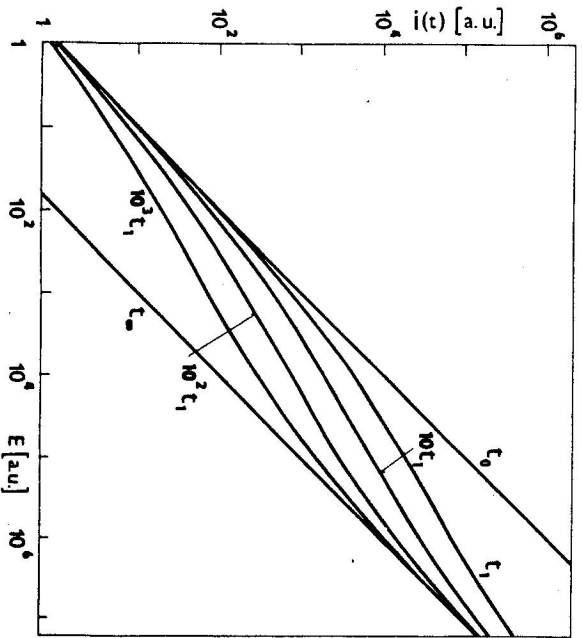

Fig. 4. VA-characteristics at different time instants. $n_2/n_1 = 10^2$

III.2. The effect of illumination

Using expressions (5) and (6) the effect of light on the conductivity of the sample may be deduced. Different effects of radiation of various wavelengths should be expected. The number of all possibilities depends on the properties of the centres present in the crystal. We shall restrict the treatment to properties assumed originally.

a) $hv \geq E_G$, where E_G is the gap of the material. The light of the wavelength needed to excite electrons from the valence band to the conduction band increases n_1, p, and the steady state current density i_∞. At small light intensities there remains $n_2/n_1 > 1$ and the initial current density is not influenced. The character of the time dependence of the current does not change, only its decrease should be slower. At high intensities $n_2/n_1 < 1$ and the current starts to be independent of time.

b) $hv = E_C - E_D = \varepsilon_D$, E_C is the edge of the conduction band, E_D is the energy of the donor level. At this wavelength donors become ionized, n_2 and the initial current increase, whereas the steady state value i_∞ does not change. Any difference between photo- and dark currents appears at short times only, which can be interpreted as a photopolarization.
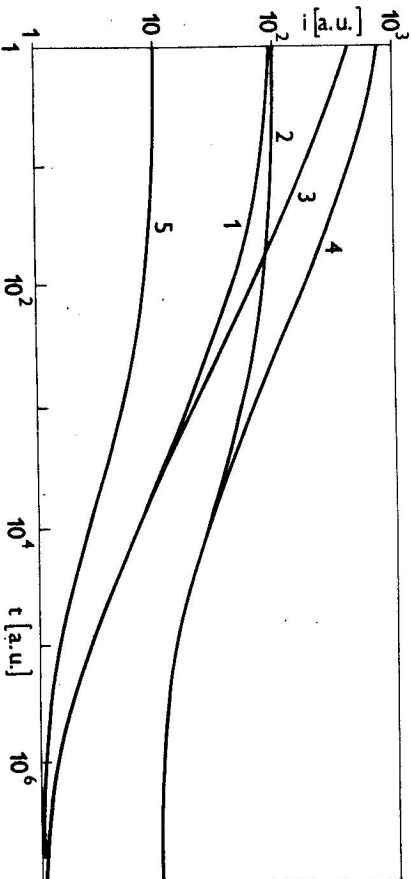

Fig. 5. The effect of light on the time dependence of the current: (1) dark current, $n_2/n_1 = 10^2$, (2) $hv \geq E_G$, (3) $hv = \varepsilon_D$, (4) $hv_1 \geq E_G$, $hv_2 = \varepsilon_D$, (5) $hv = E_D - E_V$.

c) $hv = E_D - E_V$, E_V denotes the valence band edge. At this energy excitation of electrons from the valence band and their capture by ionized donors, which act as acceptors, occur. In this way the concentration of the neutral donors n_2 grows, which in turn tends to increase the concentration of the free electrons n_2. At the same time the concentration of free holes increases in a much higher degree and thus the probability of direct and indirect recombination, hence a shift of quasi-Fermi levels of both electrons and holes towards the valence band and a decrease of n_2 result. Therefore, the irradiation by means of light of this wavelength leads to a decrease of i_0.

d) $hv_1 = E_G$, $hv_2 = \varepsilon_D$. Under simultaneous illumination at both these energies i_0 decreases and i_∞ increases.

The effect of illumination with a light of different wavelengths is seen in Fig. 5. The dark current has been calculated for $n_2/n_1 = 10^2$ and the same parameters as in Fig. 3 and the photocurrent for light intensities causing a tenfold increase (or decrease) of the respective concentrations n_1, n_2.

III.3. Voltage dependence of photocurrent

Since the type of time dependence of the photocurrent remains similar to that of the dark current, the volt-ampere characteristics measured at the time instant t time.

under illumination should have similar properties as those in the dark. The range of time and of voltages, at which a sublinear section with $i_\sim \sim U^m$ exists, depends on the wavelength and on the light intensity.

III.4. Dependence of photocurrent on light intensity

The variety of effects of light of different wavelengths on the current vs. time dependence leads to more types of current vs. light intensity dependences at the time t. Light of low intensity with $h\nu = E_G$ increases i_∞ linearly and does not affect i_0. Within an appreciable range of times $0 < t < \infty$ a sublinear $i_\sim \sim \varepsilon^m$ characteristic with $1 > m > 0.5$ may exist. Here ε denotes the light intensity. At high intensities $n_1 > n_2$ and $i_\sim \sim \varepsilon$. Infrared radiation with $h\nu = \varepsilon_D$ increases i_0 linearly, it has no effect on i_∞, for $0 < t < \infty$ the slope of the luxampere characteristic should continuously vary without the appearance of a section with a defined $m < 1$. At very high intensities the ionization of all donors should cause a saturation of i_0. The light with $h\nu = E_D - E_V$ leads to $i_0 \sim \varepsilon^{-1}$ and does not affect i_∞. For $0 < t < m$ an area with $i_\sim \sim \varepsilon^{-m}$ with $1 > m > 0.5$ may develop. At high light intensities a saturation should occur, when all ionized donors get neutralized by electrons excited from the valence band.

IV. DISCUSSION

As it is seen in Fig. 3, the time dependence of the current would be little affected whether the concentration profile were rectangular or triangular. Some minor differences exist at short times. However, the curves calculated for the triangular profile for $(n_2/n_1)_\triangle = \sqrt{2}(n_2/n_1)_\square$ and $(\mu_D)_\triangle = (\mu_D)_\square/\sqrt{2}$ are in fact indistinguishable from the respective oblong profile curves. The presupposition of the concentration in form of a quadratic parabola yielded a similar result. This suggests that the actual profile has little effect on the time dependence of the current and thus on further consequences following from it. A more serious deficiency is the neglect of the displacement current, although its contribution should be greater at short time intervals, at which also the conduction current is great.

In confrontation of theoretical predictions with experimental results the assumption of ohmic electrodes for electrons and holes and totally blocking ones for donors may be important. In reality ideally ohmic electrodes for both electrons and holes are hardly possible, hence some space charge will arise in the sample, which can affect the results mainly at low voltages. Similarly total blocking for mobile defects acting as donors need not be realized. If the donors leave freely the sample, the expected current vs. time dependence should approach $i \sim t^{-1/3}$. However, such

a system is irreversible, repeated measurements cannot be carried out with it and its treatment was beyond the scope of the present paper.

The assumption of a single donor level in the forbidden gap may be an oversimplification. If the material contains more kinds of defects having the
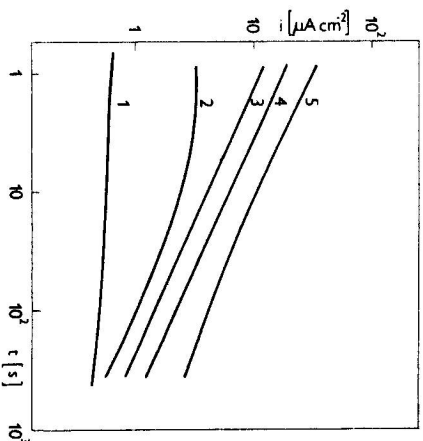
necessary properties but different mobilities, more complicated dependences of current vs. time on voltage are to be expected. The inevitable presence of a small concentration of acceptors modifies the meaning of the quantity B and of the activation energy in expression (1) [2].

The consequences of the proposed model may be compared with some results obtained on HgI2 single crystals [1]. Fig. 6 shows the time dependence of the dark current at different voltages and Fig. 7 the current-voltage characteristics, measured at different time instants using increasing voltage pulses. Their slope is smaller than expected, although otherwise their behaviour corresponds to the theoretical curves from Figs. 3 and 4. The discrepancies originate in experimental difficulties, since, as it is demonstrated by the dashed lines in Fig. 7, the measurements are affected by previous polarization. The time of short-circuiting between two runs (ca 100 min.) was insufficient to restore the initial conditions in the sample. Fig. 8 shows a series of photocurrent vs. time dependences under illumination by orange light of 2000 lx with the maximum of intensity at 600 nm. The relatively small change in the current density, corresponding to the employed high intensity of irradiation causes that the slope of current-voltage characteristics exceeds the theoretical minimum. Bube [4] found voltampere and luxampere characteristics with an exponent close to 0.5, which is in far better accord with the present theory. Similar results were obtained by Chepur [5]. However, Fig. 8 shows the expected fall of the photocurrent to be slower then that of the dark

Fig. 6. Current density vs. time in HgI2 single crystals with graphite electrodes. $L = 1$ mm, $T = 368$ K. (1) $U = 1$ V, (2) 3 V, (3) 10 V, (4) 30 V, (5) 100 V.

current. The dark current (dashed) and the photocurrent at 5 V get close at short times. In paper [6] the a.c. dark and photocurrent met at high frequencies. The slower decrease of the photocurrent with respect to the dark one may be formally interpreted as an increase of the capacity of the sample, i.e. as a photodielectric
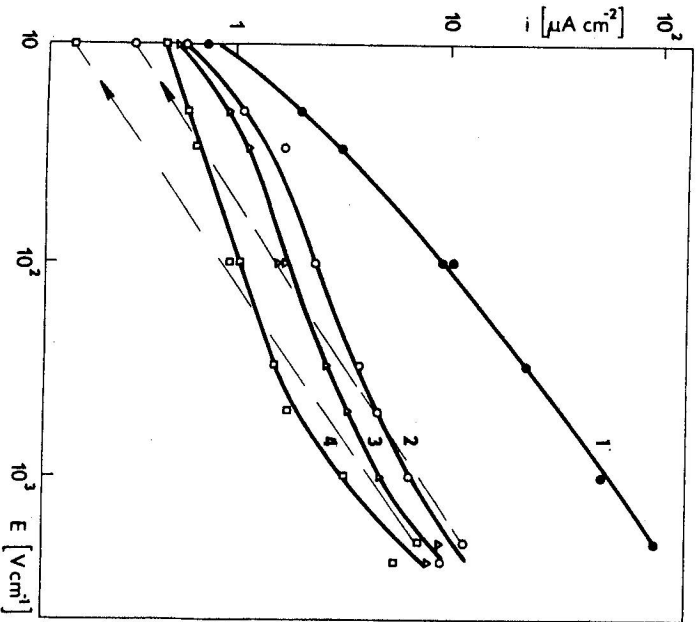
effect, observed in [6]. Owing to the lack of published experimental details it is not possible to decide whether, e.g. the photopolarization and the infrared quenching of the photoconductivity, reported in [7] can be interpreted in terms of the present model or not.

The derived consequences of the apparent ageing resemble the results of [8] obtained on GaP light emitting diodes. The usual interpretation of photocurrents decreasing in time by the trapping of charge carriers [9] is associated with superlinear voltage dependence of both initial and steady state currents, which seems to be the most marked difference compared to the results of the present model. Besides, it may explain a considerable number of effects, the interpretation of which within the framework of a single model is scarcely possible.

Fig. 7. VA-characteristics of HgI$_2$. $L = 1$ mm, $T = 368$ K. (1) $t = 0.5$ s, (2) 30 s, (3) 60 s, (4) 240 s.

Fig. 8. Time dependence of dark current and photocurrent in HgI$_2$. Full lines: photocurrent, $\varepsilon = 2000$ lx, maximum of intensity at 600 nm, dashed line: dark current. $L = 1$ mm, $T = 300$ K. (1) $U = 1$ V, (2) 2 V, (3) 5 V, (4) 15 V, (5) 50 V, (6) 150 V, (7) 5 V.
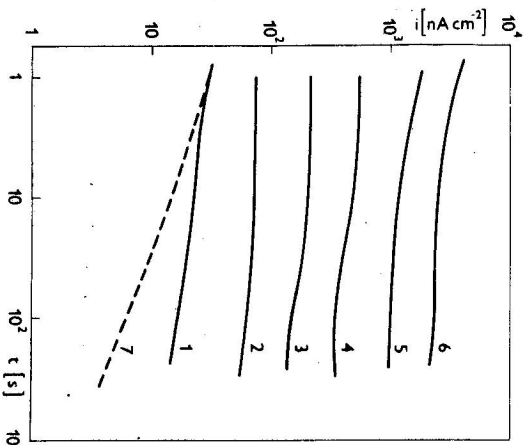
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