

A STUDY OF THE DECAY OF PHOTOCURRENTS AND DISCHARGING DARK CURRENTS IN POLYCRYSTALLINE LAYERS OF *p*-QUARTERPHENYL

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The decay of photocurrents and discharging dark currents in polycrystalline layers of *p*-quaterphenyl (*p*-QPh) equipped with appropriate gold electrodes was studied.

The results were interpreted in terms of release of trapped charge carriers which form a space charge in the dielectric layer. These investigations allow to obtain information on the trap structure of the energy gap in *p*-QPh layers. Densely distributed trap levels were found in the energy gap, suggesting a continuous distribution or one which decreases exponentially with energy and shows definite maxima found by the studies of the photocurrent decay.

1. Introduction

In both organic and inorganic dielectrics and high resistance semiconductors the flow of current is observed after removing the external voltage supply and grounding the electrodes. The current drops to zero and it flows in the opposite direction to that when the external voltage is applied [1-8]. This phenomena, known as the depolarization process, the discharging process or the reverse current has a time constant of the order of seconds, minutes, hours and sometimes even days. It may be associated with various processes. One of such processes is ion displacement in an internal electric field, which results from their separation during the application of the external field, while another is connected with the disappearance of interphase polarization. The reverse current may also be associated with dipole reorientations, after removal of the external field. Another possibility

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is the accumulation of charges injected from the electrodes, in trap levels of the investigated layer, followed by their release. The released holes or electrons will be displaced until they eventually recombine or become retrapped or else they reach one of the electrodes. However, the value of the reverse current and its time constant tend to rule out the possibility of ion displacements especially when the numbers of these ions are small. On the other hand interphase depolarization is likely to play an important role in multicomponent systems or in systems of clearly miscellaneous structure. Dipole reorientation processes, moreover, are likely to be important when considering polar dielectrics. Thus without actually excluding the possibility of the above mechanisms, especially that of dipole reorientation, it seems that the reverse current may be connected with the release from traps of charges — injected from the electrodes. The conjecture that this mechanism is highly probable is supported by the fact that these phenomena occur both in organic [1-4, 8] as well as in inorganic [5, 6] dielectrics. Hence a study of the discharging processes in a dielectric is a direct way of providing some data on its trap structure.

In this work photocurrent decay and discharging dark current in polycrystalline layers of *p*-Q Ph are interpreted in terms of charge release from trapping sites. The carriers can be introduced into the dielectric by injection from the electrodes or by being generated by light.

If light is used for the creation of electron-hole pairs which subsequently take part in electrical conduction then the current, after removal of the light source, decreases with time to a value equal to the dark current. When there are no trapping centers, the photocurrent decreases with time as does the concentration of free carriers, and the observed decay time is equal to the lifetime of the free carriers. If however the investigated substance contains trapping centres and their concentration is comparable with the free carriers concentration, then the process of photocurrent disappearance can be extended by thermal release of the trapped carriers. As a result the observed decay time will be greater than the actual life time of the free carriers as defined by the process of recombination. In the case when the trapped carriers concentration is far greater than the free carrier concentration, the decay time is primarily defined by the rate of trap emptying and subsequent retrapping. In that case recombination rate does not affect the observed decay time [9, 10].

A study of photocurrent decay *i. e.* current decrease with time after the light source generating the carriers has been removed, also provides information about the energy, distribution and the concentration of trap and recombination levels.

2. Theoretical considerations

A) Discharging processes

The discharging current is the result of the transport of thermally released trapped charge carriers while its disappearance is due to a drop in the trapped carrier concentration combined with a change in their spatial and energetical distribution. Let us assume that the space charge, accumulated in the traps during charging occupies different energy levels [8].

The probability β_k of release of trapped carriers from the k -th energy level of energetical depth E_k per time unit is a function of temperature T :

$$\beta_k = \beta_0 \exp \left[-\frac{E_k}{kT} \right] \quad (1)$$

where: β_0 — constant, k — Boltzmann's constant.

The average period of stay of a carrier in a trap is equal to

$$\tau_k = \frac{1}{\beta_k} \quad (2)$$

while the number n_k of trapped carriers at a depth E_k is the following function of time t ,

$$n_k(t) = n_{0k} \exp \left(-\frac{t}{\tau_k} \right)$$

where: n_{0k} is the initial number of trapped carriers. The discharging current i_k resulting from the carriers trapped at a depth E_k can then be written in the form

$$i_k(t) = i_{0k} \exp \left(-\frac{t}{\tau_k} \right)$$

where: i_{0k} is the initial discharging current.

If there are several trap levels, the dependence of the discharging current on time is given by

$$I(t) = \sum_k i_{0k} \exp \left(-\frac{t}{\tau_k} \right). \quad (3)$$

Provided the trap levels are sufficiently far apart, the process, up to a certain moment, of releasing charge carriers trapped at a definite energy depth dominates [8].

Thus the time constant τ_k can be assigned to the specific trap levels dominating at that time. The plot of equation (3) on a semilogarithmic scale is composed of several straight lines of different slopes *i. e.* of different time constants τ_k which define the rate of emptying of specific trap levels. Using experimental values of τ_k , the energy distance between neighbouring trap levels can be found from equations (1) and (2). These may be rewritten in the following form for neighbouring trap levels:

$$\frac{1}{\tau_k} = \beta_0 \exp \left(-\frac{E_k}{kT} \right)$$

$$\frac{1}{\tau_{k+1}} = \beta_0 \exp \left(-\frac{E_{k+1}}{kT} \right)$$

which gives

$$E_{k+1} - E_k = kT \ln \frac{\tau_{k+1}}{\tau_k}. \quad (4)$$

B) Photocurrent decay

Charge carriers generated by light in a dielectric layer form a space charge. This charge is free in the dielectric if there are no traps and it is trapped if there are. If the current is strongly disturbed by the presence of the space charge then the equations governing the dependence of the instantaneous current density on time are complex and can only be solved numerically [11]. Solutions of equations of this kind, presented graphically, can be found amongst others in the works of Papadakis [12]. The maximum current appears after a time $t \approx 0.8 t_r$ where t_r is the time needed for current carriers to cross the layer. By measurements of the instantaneous currents, limited by a space charge, generated by light pulses, the life-time of the charge carriers τ , can be found. For this purpose the crossing time t_r must first be measured. Various theoretical curves of the current density dependence on time for different $\frac{\tau}{t_r}$ ratios can then be compared with experimentally obtained impulse

photograms to find the best fit. Knowing t_r and the ratio $\frac{\tau}{t_r}$, the life-time of the carriers may be easily calculated.

Streetmen [9] showed that if, in a semiconductor, both trapping centres and recombination centres for electrons and holes are assumed to exist in the energy gap, then the high temperature photocurrent decay time τ_f is approximately equal to the recombination time. At high temperature the thermal energy is sufficient to release holes from traps and the photocurrent decay is governed by recombination processes only. The photocurrent decay time may then be written in the form:

$$\tau_f = \frac{N_{\text{eff}}}{S_r V n_0 N_r} \exp\left(-\frac{E_r}{kT}\right).$$

At lower temperatures, the carriers stay longer in the traps and the resultant photocurrent decay may be chiefly related to the time it takes to release thermally the carriers from traps *i. e.* the decay time equals:

$$\tau_f = \frac{1}{S_t V N_{\text{eff}}} \exp\left(\frac{E_t}{kT}\right).$$

The subscripts r and t refer to trapping and recombination processes, respectively, while S_r , S_t are cross-sections of recombination and trapping centres, E_r , E_t — depths of the recombination and trapping energy levels, V — thermal velocity, n_0 — density of free carriers at equilibrium, N_r — state density in the recombination level, N_{eff} — effective density of states in the valence band.

From the plot of $\ln \tau_f$ vs $\frac{1}{T}$ for high and low temperature ranges straight lines are obtained whose slopes are equal to E_t/k and E_r/k , respectively. From the intersection of these lines with the y axis values for $\frac{N_{\text{eff}}}{S_r V n_0 N_r}$ and $\frac{1}{S_t V N_{\text{eff}}}$ can be found.

3. Experimental procedure

Polycrystalline (*p*-quarterphenyl (*p*-Q Ph) layers were chosen as the subject of these investigations since the electrical properties of this substance are reasonably well known, having been studied in detail in our laboratory [13–20]. The specific resistance of the investigated *p*-Q Ph samples was of the order of $10^{17} \Omega \text{ cm}$.

Polycrystalline layers 5–10 μm thick were deposited on an insulating support of mica or quartz. A more detailed account of sample preparation and their shape is given in [13].

In several experiments, which were carried out using different samples with the thicknesses in the above mentioned range, it was found that their variation did not change the character of the observed phenomena influencing only the absolute current values. Vacuum deposited gold electrodes were used, the upper electrode thickness being such as to make it semi-transparent, for photocurrent study purposes. In some papers from our laboratory [13, 19] it was shown that gold is an injecting electrode for *p*-Q Ph layers.

All the results in this paper are based on the measurement of current as a function of time. For long time intervals, an Vakutronik (VAJ-51) electrometer with a dynamic condenser or Keithley model 416 picoammeter were used to measure current intensities. The voltage source was a d. c. current supply composed of a series of galvanic cells. The current as a function of both time and voltage was measured in a standard arrangement consisting of the voltage supply, investigated sample and electrometer all connected in series [22]. For all photocurrent decay studies a mercury lamp type HPW 125 without a filter was set up 30 cm away from the sample providing a constant illumination of the investigated specimens.

Very short (microsecond) photocurrent pulses were measured on the apparatus described in [19–20] and used to measure the drift mobility of charge carriers. For fast decay times the trace on an oscillograph was recorded photographically.

The sample was placed in a metal chamber equipped with a quartz window thus allowing it to be illuminated with UV light. The chamber was constructed so as to maintain a constant temperature between 20° and 150°C.

4. Results

The following types of measurements were performed:

- 1) pulse photocurrent decays for times of from 50 to about 1000 μs ,
- 2) photocurrent decays for times of from 5 to about 2000 s,
- 3) measurement of discharging dark currents for times of from 5 to 2000 s.

In the case of pulse photocurrents, the current carriers were generated using a xenon flash lamp. Measurements were taken at 5 different temperatures between 20 and 70°C at constant light intensity in an electric field of the strength equal to $3.3 \cdot 10^6 \text{ V/m}$. The shape of impulse photocurrent photograms can be analysed when dealing with times of from 50 to 400 μs and even up to 1200 μs depending on the time axis scale of the oscillograms. A typical photogram is shown in Fig. 1.

The measurements of the photocurrent decay processes were carried out at nine different temperatures from 20–125°C with the external electric field strength equal to

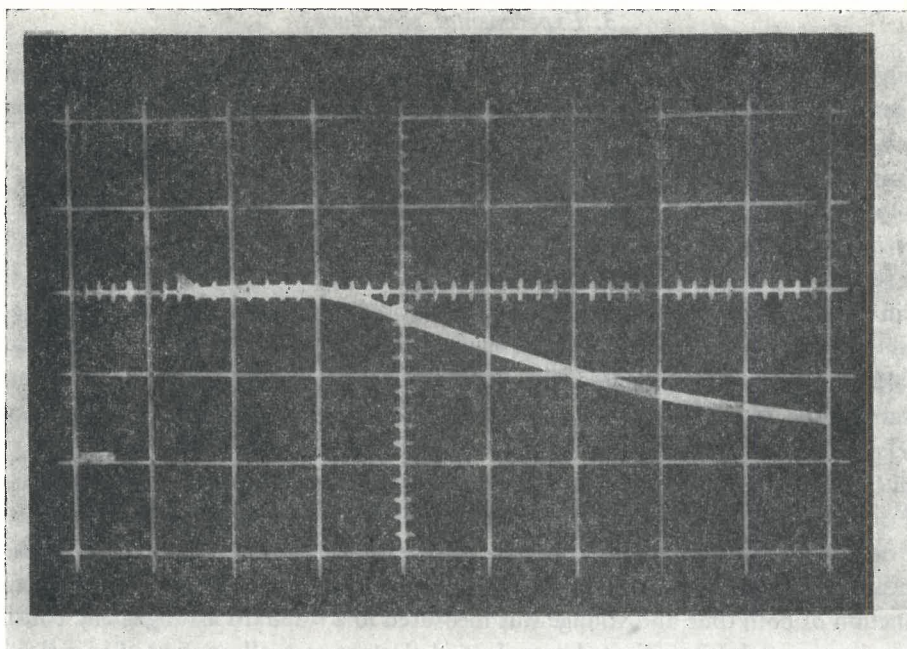


Fig. 1. Pulse photocurrent observed in p - Q Ph layers at 51°C . Electric field strength = $3.3 \cdot 10^4$ V/cm. Time axis scale $50 \mu\text{s}/\text{scale}$

$2 \cdot 10^4$ V/m. A fast drop in current flowing through the layer, is observed when the light source is switched off. It is shown in Fig. 2. The sector A-B on this curve corresponds to the stationary photocurrent. At B the light source was switched off and thus the sector B-C corresponds to the photocurrent decay curve. As can be seen, the photocurrent drops

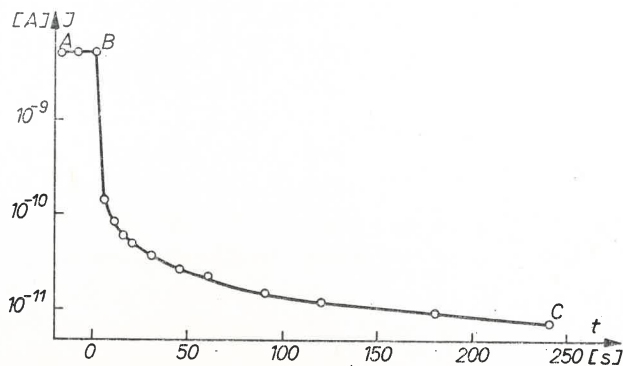


Fig. 2. Plot of current intensity vs time in p - Q Ph layer. AB — photocurrent, BC — photocurrent decay curve

by two orders of magnitude in the first five seconds and a further order in the next few minutes. Typical photocurrent decay curves on a semi logarithmic scale are shown in Fig. 3, in the time period of 5 s to 1500 s beginning from the moment the light was switched off.

Discharging dark currents were measured after the external voltage supply had been removed and both electrodes of the sample grounded. Measurements were taken for various voltages applied to the layer during charging and also for various charging times

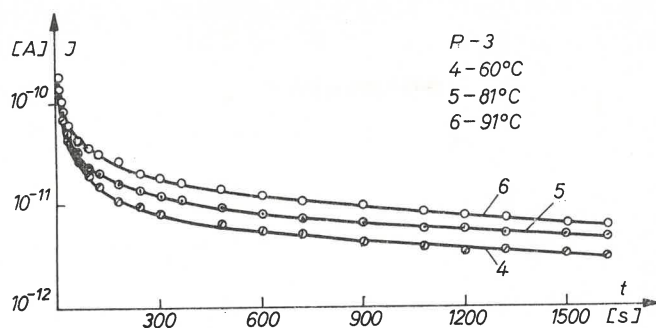


Fig. 3. Photocurrent decay curves in p - Q Ph layers at different temperatures. Electric field strength $= 2 \cdot 10^4$ V/cm. Time $t = 0$ refers to the moment light source was switched off

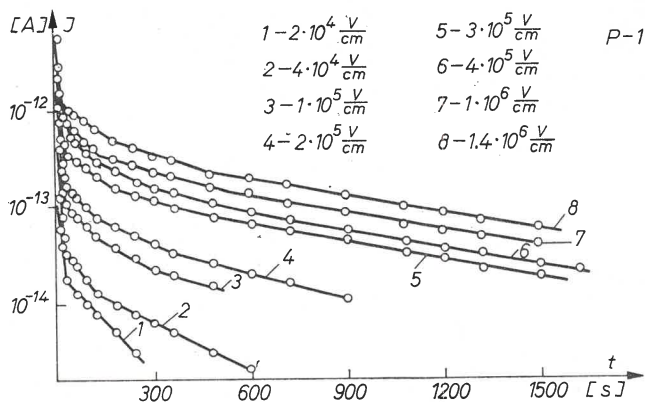


Fig. 4. Discharging curves for $Au-p-Q Ph-Au$ layers obtained for different electric field strengths applied to layer during charging at $22^\circ C$

at constant temperature. Typical discharging curves are shown in Fig. 4. To facilitate interpretation of the discharging processes the discharging curves have been divided into sections, each with a different slope with respect to the time axis. The time $t = 0$ corresponds to the moment at which the external voltage supply was removed and both electrodes grounded.

5. Discussion

In Refs [14] and [19] it was shown that polycrystalline layers of p - Q Ph equipped with gold electrodes display current voltage characteristics that are typical of space charge limited currents. As mentioned earlier in the case of currents limited by a space charge the carrier life-time can be found comparing experimentally obtained photograms of pulse photocurrents with the theoretical curves of Papadakis [12]. An example of such

a comparison is given in Fig. 5. The comparison is made by finding that value of the parameter $\lambda' = \frac{\tau}{t_r}$ which gives the best fit between the theoretical curve and the experimental one, covering the time interval from 0 to $0.8 t_r$. From this type of comparison the life-time τ of the charge carriers in polycrystalline *p*-Q Ph layers was estimated to be about 300 μ s.

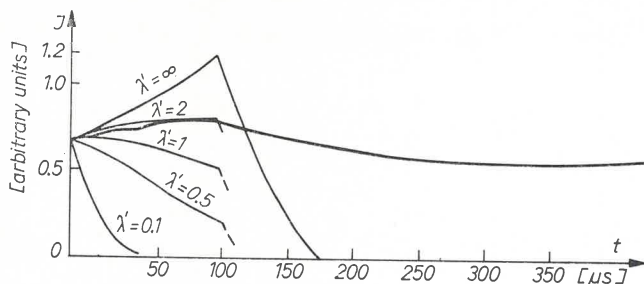


Fig. 5. Comparison of experimentally obtained photocurrent pulse trace with the theoretical curves of Papadakis [12]

Knowing the life-time and mobility, which according to [19] equals $0.6 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$, the mean free path λ of the charge carriers can be calculated from the equation:

$$\lambda = V \cdot \tau = \mu K \cdot \tau$$

where: K — the electric field strength applied to the layer, and V — the velocity of a carrier in the electric field. With $K = 3.33 \cdot 10^6 \text{ V/m}$, $\tau = 300 \mu\text{s}$ and $\mu = 6 \cdot 10^{-5} \text{ cm}^2/\text{Vs}$ one obtains $\lambda = 6 \cdot 10^{-6} \text{ m}$.

If we take into consideration the fact that a molecule of *p*-Q Ph is about 16 Å long then the mean free path will be equivalent to a few thousands of molecular lengths. Measurements of pulse photocurrents decay and slow photocurrent decays render possible the determination of the decay time τ_f . Fig. 6 shows a plot of τ_f vs $\frac{1}{T}$ using the impulse photo-

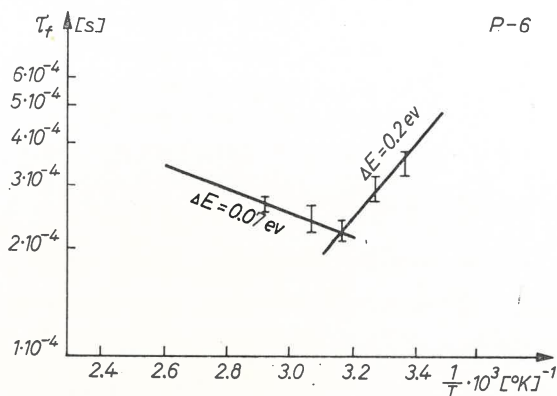


Fig. 6. Dependence of photocurrent decay time on temperature (short decay times)

current studies results. From this graph, trapping centres of depths 0.7 eV and 0.2 eV were found.

From slow photocurrent decay measurements, three values of the decay time could be obtained for every decay curve. From the plot of τ_f against $\frac{1}{T}$ for long time intervals, shown in Fig. 7, trapping centers with depths equal to 0.1, 0.27, 0.45 and 0.62 eV were found. Fig. 7 shows that at low temperatures three different decay times may be singled

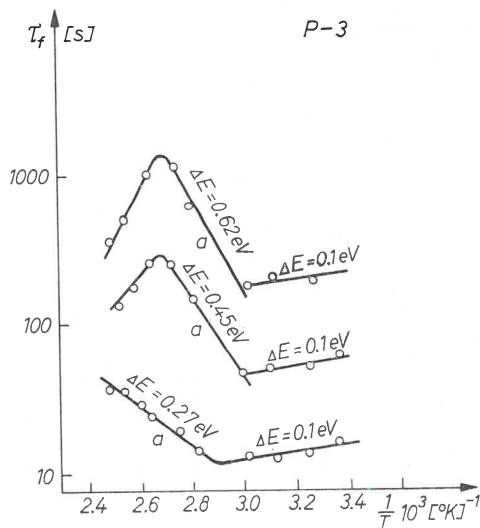


Fig. 7. Dependence of photocurrent decay time on temperature (slow decay times)

out, all corresponding to the same trap level at an energy depth of 0.1 eV. From the intersection of these lines, corresponding to the energy of 0.1 eV, with the ordinate three different values may be obtained for the factor:

$$\frac{1}{S_t V_t N_{\text{eff}}}$$

Since both V_t and N_{eff} are constant, traps of three different cross-sections occur at the energy depth of 0.1 eV. At high temperatures the intersection of the plot of $\ln \tau_f = f\left(\frac{1}{T}\right)$ with the ordinate gives various values for the factor:

$$\frac{N_{\text{eff}}}{S_r V_t n_0 N_r}$$

for curves corresponding to different trap level depths. In this case, however, the cross-section cannot be found since both the free carrier density at equilibrium n_0 and the recombination state density N_r are unknown. One can find the dependence of the product

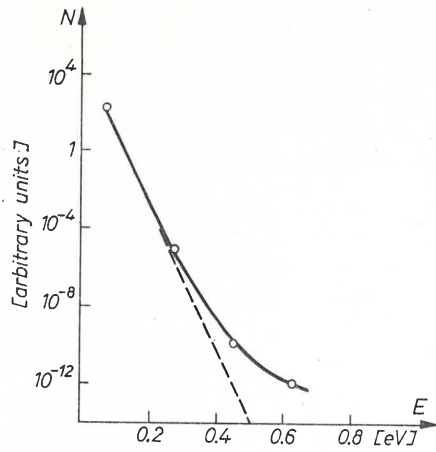


Fig. 8. Dependence of relative density of trapping centres on their energy depth in polycrystalline *p-Q* Ph layers

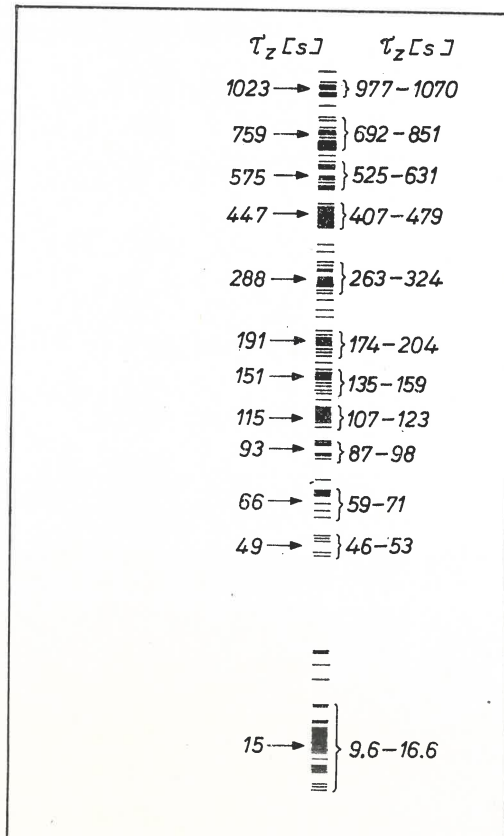


Fig. 9. Distribution of discharging dark decay times in polycrystalline *p-Q* Ph layers

S_r , N_r , or the energy level depth if one assumes $\frac{N_{\text{eff}}}{V_t n_0}$ to be constant and such a relation does not tell us anything about the shape of the trap level density distribution as a function of energy. If, however, one were to assume that all the capture cross-sections are the same — an assumption which cannot be ruled out for trap levels corresponding to single photocurrent decay times — the relative density of levels as a function of their energy depth could be found. Fig. 8 shows the distribution of trap level density reached on the basis of above assumptions. The graph shows that the change in the trapping centres density with energy is slower than exponential. A somewhat similar distribution was proposed earlier in [14] on the basis of analysing space charge limited currents in polycrystalline p -Q Ph layers.

Decay times were determined from the discharging dark current decay curves of Fig. 4. Fig. 9 shows the distribution of the decay times obtained from 48 discharging curves at room temperature. As can be seen the decay times, within experimental error, are grouped around certain values which correspond to definite discrete trap levels. The

TABLE I

Decay times τ_z and the energy distances ($E_{k+1} - E_k$) between neighbouring trap levels for polycrystalline p -Q Ph layers

Decay time τ_z [s]	$E_{k+1} - E_k$ [eV]
$3.5 \cdot 10^{-4}$	0.240
12.9	0.034
49	0.008
66	0.009
93	0.005
115	0.007
151	0.006
191	0.010
288	0.011
447	0.007
575	0.007
759	0.008
1023	

decay times are given in Table I which also includes the energy distance between neighbouring trap levels, calculated from equation (4).

The sum of all the energy level distances calculated from slow discharging current equals 0.112 eV. Thus the energy levels are grouped in a relatively small energy range. Assuming that the nature of discharging decay processes of impulse photocurrents is similar to discharging dark processes, it is possible to determine the energy distance between the trap level affecting the drop in photocurrent between 50–800 μ s and the first level found by studying the slow decay of discharging currents in darkness. Using this method the energy distance between these levels was found to be equal to 0.24 eV. Thus a series of densely distributed trap levels was found to be distributed in a narrow energy range.

From the more exact structure of studying the discharging dark currents, one can state that the distribution of the trap levels in polycrystalline layers of *p*-Q Ph is not discrete. The energy levels, found by the investigation of photocurrent decay constitute maxima on the energy level distribution curve which decreases approximately exponentially with energy.

Similar results have been obtained for single crystals of anthracene [8] and tetracene [21]. The occurrence of densely distributed energy levels has also been found in thin films of copper phthalocyanine [23] as well as in some macromolecular organic dielectrics [22, 24].

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