Investigation of Organic Semiconductor
for Photovoltaic Application

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13. ABSTRACT

1) Based on photovoltaic current-voltage measurement, cells of tetracene with a TCNQ layer are found to have 50 times improved efficiency. Further improvement can be made by reducing the shunt conductivity.
2) Transient photovoltaic effect shows a decay under a continuous photoexcitation as well as a repeated excitation indicating an exhaustion of the photoionization centers.
3) Transient effect under different wavelength light in-dicates a simultaneous presence of positive and negative currents. The magnitudes of these currents are almost equal at a given wavelength. Therefore, the net differ-ence, i.e. the steady state signal, is more than one order of magnitude smaller than the individual current.
4) Two new solar cell configurations are porposed—(i) to use flexible substrate and to use an evaporated silicon oxide layer on the top of the cell for light entrance; (ii) According to (3), major current is from the surface recom-bination, therefore, a cell with repeated layer structure is suggested.

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Abstract

Four problems are discussed concerning the photovoltaic properties of tetracene and other organic material solar cells:

(1)   Based on photovoltaic current-voltage measurement, cells of tetracene with a TCNQ layer are found to have about 50 times improved efficiency. This mixed layer type cell has a shunt conductance and further improvement can be made by reducing the conductivity.

(2)   Transient photovoltaic effect has been measured which shows a decay under continuous photoexcitation. This current also decreases under a repeated excitation and indicates an exhaustion of the photoionization centers.

(3)   Transient effect measured with different wavelength light indicates a simultaneous presence of both positive and negative currents. The magnitudes of these currents are almost equal at each wavelength---independent of the wavelengths. Therefore, the resultant net difference, which gives the steady state signal, is more than one order of magnitude smaller than the individual current.

(4)   Two solar cell configurations are proposed: (i), to use flexible substrate and to replace the quartz window light entrance by silicon oxide on the opposite side of the substrate; (ii), according to (3), a major current is contributed by the surface recombination, therefore, a cell with repeated layer structure is suggested.

Index

Abstract

List of Figures

I. Introduction

The objective of this research is three-fold:

(1) To perform measurements associated with the photo-
voltaic properties of solar cells made with organic
semiconductor materials,

(2) to analyze the measured results in terms of physical
process involved in the production of the photo-
voltaic current, and

(3) to utilize the analyzed results to design methods
for an improvement of the energy conversion effi-
ciency of the solar cells.

Most of the experimental work and the theoretical analysis in
this investigation have been concentrated on tetracene, some new
materials have been studied only in a cursory manner. However,
the methods developed for the present investigation are equally
applicable to most other organic semiconductors

In Section II of this report, a new photovoltaic current-
voltage measurement system is used to evaluate three types of
solar cells of different organic semiconductor configurations.
In Section III, transient photovoltaic current of organic solar
cells under white light is investigated. The same current under
a selected wavelength of light is investigated in Section IV.
Finally, in Section V, some new organic solar cell configurations
are proposed.

II. Photovoltaic Current-Voltage Curve

(1) Experimental Results

In the previous reprot[1] we have described a system for the
photovoltaic current-voltage (i-v) measurement. Organic semi-
conductors have generally very high impedance (~ 10 to $100^M\Omega$)
and a long relaxation time (in the order of seconds) to reach a
steady state. Therefore, we have had to take data at discrete
points: to wait at each point until a steady state is reached
before proceeding to the next point.

Through the theoretical studies, which will be presented in
Part B, we found that the relaxation time is dependent on the
condition of light excitation: the condition to reach the steady
state is faster if the variation of excitation condition is
gradual. This result suggests that we build a slow motor driv-
ing system to vary continuously a variable voltage source. This
voltage is used to compensate for the pnotovoltaic voltage of the
specimen in variable load conditions. In this way a continuous
i-v curve is obtained. The time it takes to measure an i-v
curve is about 9 minutes.

With the above arrangement three types of specimens are
measured:

Type (A), tetracene with Al as one electrode, adjacent
to the glass substrate, and Au as the other electrode.

Type (B1), double layer consists of 1.5μ of TCNO and
600-700 Å of tetracene, with Au for both electrodes and the
order of layers are glass Au tetracene-TCNQ-Au.

Type (B2), same as (B1) in organic semiconductor, but
with different electrodes, the order of layers are, glass-
Al-tetracene-TCNQ-Au.

The respective i-v curves are shown in Fig. 1. The curves
have rather unique characteristics, for example, (B1) specimen
has almost a straight line while (A) and (B2) curves are concave,
an opposite of an ideal photovoltaic i-v curve which should be
convex and approaching a rectangular shape.

(2) Analysis

In Fig. 1., (B1), being a straight line and situated between
a concave and an ideal convex curve, is consequently the better
of the three types of specimen.

A drastic difference is the short circuit current: (B1)
and (B2) have about 50 times higher value than (A), the overall
efficiency is increased by about 30 times. This demonstrates
most drastically the importance of the idea of using two types
of organic semiconductor layers.

The appearance of the curve (B1) has a simple explanation:
when a solar cell is shunted by a parallel resistor with resis-
tivity value lower than that of the solar cell, the i-v curve
gradually becomes linear when the resistivity is reduced. This
situation is illustrated in Fig. 2, where a good silicon solar
cell is shunted with resistors of various resistance. One cause
of the shunt conductivity could be due to the inhomogeneity of
the specimen and some TCNQ forms a short circuit linkage between
the electrodes. One possible method to verify this mechanism is

to use a microscope with strong light source to delineate if there are separate TCNQ regions besides the intended (TCNQ) + (tetracene) region.

The explanation of the appearance of curves (A) and (B2) is more complex. We list two situations where such curves are observed: (1) In heavily radiation-damaged silicon solar cells of p or n configuration with lithium in the n-region, after the cessation of the radiation, instead of a spontaneous recovery as in the case of lightly radiation-damaged case, spontaneous dam age is observed and the i-v curve in this case bears a similarity to that observed in the present case.[2] The cause was interpreted as due to a large reduction of the carrier generation center and a high concentration of the trapping center. But there is no direct experimental verification. (2) Another possibility is due to the inexistence of a strong junction to separate the positive and negative change carriers into distinct regions, such as n- or p- regions in the ordinary silicon solar cells. This point will be discussed again in Section IV of this report.

III. Transient Photovoltaic Effect in Tetracene

While tetracene solar cell so far has not shown the utility of a photovoltaic energy conversion device, the effect of the reversal of photovoltaic current polarity as a function of the wavelength of the illuminated light is a rather novel phenomenon[3] and it is conceivable to be of practical interest, for example,

for detection of optical informations. In order to proceed
along this direction, one important aspect is to investigate the
dynamic characteristics of the photovoltaic current. As will
be discussed in Section IV, dynamic data also provides informa-
tion which allows to separate the positive and the negative
current, therefore to aid in the basic quantitative analysis.

(1) Experimental Arrangement

In our previous work, to measure the transient response, the
light pulse was controlled directly by the electrical circuit
switch. This arrangement gives a light pulse as shown in Fig.
(3a). It has two undesirable aspects. First, the electrical
signal from the switch already triggers the oscilloscope before
the actual light signal appears. Second, the time to reach a
steady state is about 200 nsec. To overcome this defect, we
decided to leave the lamp in steady operation, and use a camera
shutter to turn on or off the light. In this way, we have a
light source nearer to a square pulse.[3b] The rise time is reduced
to about 70 msec, and the transient response is triggered by the
light signal. A silicon solar cell is used to detect the light
signal. The response of this solar cell is less than 1 msec.
In the measurement of organic solar cells, therefore, we will
always use S_i solar cells to monitor the shape of light pulse as
well as the light intensity.

The camera shutter is operated by an electrical solenoid
operated on 120 volts a.c. source. We hope to replace it by
a d.c. source in the future and, by adjusting the mechanical

spring, an improvement will be made on the shape and the duration of the pulse.

(2) Experimental Results

Fig. 4 shows two curves. Curve (a) is the reference signal obtained with Si cell. The shape is nearly rectangular in 2 sec/scale picture. Curve (b) is the terminal voltage, measured at 1 megaohm shunt of the oscilloscope of a tetracene-TCNQ cell. The vertical scale is 0.05 V/scale. The light intensity, calibrated from curve (a), is about 110 mw/cm^2. The effective area of the organic cell is slightly larger than 1 cm^2.

At t_o, the light is switched on and curve (a) reaches a steady state almost instantly. On the other hand, curve (b) reaches a maximum first, then slowly decays and reaches a steady state only after a time longer than 10 sec. The ratio between the maximum and the final value, just before the time marker t_1, is less than 1/20. That is, in a steady state operation, the photovoltaic voltage is only about one-twentieth of the maximum voltage obtainable from the organic cell.

Next, at t_1, which is about 6 sec after the light is on, the light is turned off. Curve (a) returns to the zero level immediately. On the other hand, curve (b) first shows a sharp increasing spike, then decays at a time rate of about 0.5 sec. That is, there is a residual photovoltaic voltage even though there is no more light illumination. Furthermore, this residual voltage does not return to zero, instead, it becomes a signal with opposite polarity.

Fig. (5) shows two new effects. The vertical scale is the same as in Fig. 4, but the time scale now becomes 2 sec/scale. First, looking at the tail of curve (b) of Fig. 4, this curve, after crossing zero level, went to the opposite polarity. Fig. (5) shows this curve reaches a new maximum, and eventually decays to zero level in a time of about 10 sec.

Second, by comparing Figs. (4) and (5), we note that while the vertical magnitude of curve (a) remains constant, that of curve (b) has been decreased. This is especially prominent in the two maxima at the opposite sides of zero line. Thus, there is a sign of fatigue. This effect is shown in Fig. 6. Curve (0) is taken for a specimen which has been kept in the dark overnight. Curve (1) is taken at 20 sec after t_1 where the light is turned off. Curve (2) is taken at 20 sec after curve (1) is completed. The steady state signal of organic cell is the distance separated from o-line; the value is 0.02 volts. On the other hand, the value at maximum of curve (o) is estimated to be 0.5 volts.

The detailed structure of the maximum is hsown in Fig. 7. As always, curve (a) refers to Si solar cell and curve (b) to organic solar cell. At t_0, light is injected. From the time scale of .1 sec/scale, we can estimate the breadth of the peak. But the most interesting observation is that, using curve (a) as a reference, it is known that Si solar cell has a linear response to the light intensity. Therefore, curve (b) shows that the organic solar cell has non-linear response· at weak light (before the shutter is fully opened to reach a maximum light inten-

the sharp corner of curve (a)), curve (b) already shows a .... within the accuracy of measurement, the maximum of curve (b) seems to coincide with the maximum of the light intensity.

Our next measurement is to investigate the rate of the recovery of the decayed photovoltaic activities of Fig. 6. This is shown in Fig. 8. Following the descending order from the top, the first curve was taken after the organic solar cell is exposed to the light for a full two minutes. After that , light is turned off by the shutter for 5 sec. And then light is turned on again and this first curve is obtained. This curve has a barely noticeable maxiuum. After a one minute (time counted at the beginning of the light pulse) interruption, the second curve is taken. The consecutive curves correspond to 3 10 and 20 minutes. A datum is also taken at 60 minutes, although not shown in Fig. 8. The result is plotted in Fig. 9, curve (I). The curve (II) is for 1-V/Vm, where Vm is an extrapolated value of V as the time approaches infinity. We took a value of Vm=0.3 volts and (II) is a reasonable good straight line. That means the recovery of follows first order kinetic with a recovery rate of 12.4 minutes.

All above measurements were made with 1 MΩ shunt of the oscilloscope. If a parallel 6K resister is introduced, we obtain the result of Fig. 10. The vertical scale in this ase is 0.005 volts. We see that photovoltaic current reaches a steady state much faster in comparison with the photovoltaic voltage data of Fig. 5. Otherwise, all the characteristics of Fig. 5 are preserved· the fast maximum, the spike as light is

turned off, and the reversal of the polarity after the light is turned off.

Our last experimental result, Fig. 11, is for the "pyrazine 101"-TCNQ cell. In the similarity aspect, (1) we observe the maximum, (2) when light is turned off, there is a spike, but somewhat less pronounced, (3) decay follows to zero as the light is turned off, and there is no reversal in the voltage. The most interesting difference is that the decay at repeated pulse still exists, but much less noticeably. The vertical scale for both reference Si cell and organic cells are the same as before, thus the maximum voltage in "pyrazine 101"-TCNQ is somewhat less than that of tetracene=TCNQ cell, but the decay after the maximum is very much reduced.

In conclusion, we observe a wealth of new phenomena as almost each figure in this report shows some unusual characteristics. During this period, some new publications have appeared which, although in different fields, are obviously interrelated with our work:

(1) One drastic difference in the solar cell structure of A. Glubovic used in this experiment is that the mixture type consists of two organic materials. An existence of interaction, either in the form of charge transfer or some new interaction process, is evident. Some of this aspect has been reported by Ishihara and Nakada on the anthracene-tetracene mixture.

(2) Queisser et al,[5] pointed out the importance of p-n junction structure in semiconductor where the dielectric relaxation time is larger than the carrier recombination lifetime.

Their experiment was performed on complex compensated gallium arsenide. It seems that the organic semiconductors fall automatically also into this category and a study in parallel to the work of Queisser et al. would be interesting.

(3) In organic semiconductors, the role of bulk and surface combination has not been clarified.[6] In this regard, the recent theoretical treatment of Silver et al.[7] and the calculation of Eer Nisse[8] is most interesting.

The experimental results suggest two conclusions: (1) a drastic ahange in the performance of the organic solar cells can be obtained, and (2) a defect structure is inherent in some organic semiconductors either as an intrinsic property or as a result of processing. The fact that an undesirable decay in tetracene-TCNQ is minimized by a substitution of "pyrazine 101" is most encouraging in this respect. (2) From the present data, as indicated in Figs. 6 and 9, one can separate the effect due to either photoionization of traps or surface recombination. This point will be discussed in the following section.

IV Spectral Response of Transient Photovoltaic Current

In a previous work[3] experimental results and theoretical analysis were presented concerning the dependence of the steady state photoboltaic current of tetracene on the wavelength of injected photons. Present work extends to the dynamic case where the time dependence at several selected wavelengths is investigated. The previous work has been emphasized on the transport

equation, and in the original version, two different lengths--
one for optical absorption and attenuation, and the other for
carrier diffusion--are introduced. There are some criticisms[9]
and a considerable revision was made by changing the boundary
conditions of the diffusion equation. Essentially the same re-
sults are obtained. This revised version is included in this
report as an Appendix I.

In the subsequent work[10] we attempted to interpret the
results by the same transport equation which was used in Ref. 3,
extended to the time dependent case. The result was not success-
ful: when we carried out numerical calculation, the transient
response curve was found to be a monotonic curve to approach
either a steady positive or a steady negative

state. This is not consistent with the experimental data
which show a positive maximum, and the negative state is reached
from an initially positive value.

From the above results we are led to an interpretation that
the transient current is responsible for the simultaneous presence
of a positive and a negative current. Therefore, an entirely
different approach is used based on the superposition of two
currents. The result, in the form of a complete paper, is pre-
sented in Appendix II. We draw here only one important result:
according to our analysis, the photovoltaic current generated
in tetracene is more than an order of magnitude of the observed
steady state current which is the net difference of a positive
and a negative current. The magnitude of the currents is

almost equal and the consequent net difference indeed is very
small. Furthermore, by an examination of the literature[6] we
conclude that this small difference is mainly due to the surface
recombination and a photovoltaic process based on this effect
would have a severe limitation on the photovoltaic efficiencies.

V Solar Cell Configurations

Two alterations of the presently adapted solar cell con-
figuration are proposed in the following:

(1) The presently adapted configuration uses glass (quartz)
substrate and electrodes and the organic material are evaporated
on it. The photovoltaic efficiency is higher when light enters
from the glass side of the solar cell. The explanation is an
over-all optical index matching between air and the specimen.
Another utility of glass substrate is to protect the Al electrode
from atmospheric oxidation. It will not be conceivable that if the
organic semiconductor device becomes practical, one still retains
such a bulky and brittle structure.

We propose to use plastic substrate similar to that used
in Cds solar cells. This will give flexibility and lighter
weight. Since the plastic does not have a good uv transparency,
the light will not enter through the plastic. Instead, a
silicon oxide layer of sufficient thickness is evaporated on
the top electrode. This will basically replace the functions
of quartz glass. In the new system, therefore, both electrodes
are protected. A configuration of protected electrodes has the

advantage that the thickness of the electrode could be consider-
ably reduced and yet to have an equivalent conductibity of
thicker ones, and an increase in the optical transparency.

(2) In the organic solar cell, net contributions to photo-
voltaic current are not the carriers generated deep in the mater-
ials far away from electrodes. This is caused by several factors--
by the higher concentration of traps, short diffusion lengths
of minority carriers, and the inefficient charge separations.
Therefore, in spite of the fact that a thicker specimen would
absorb more photons and consequently create larger numbers of
minority carriers, the observed net photovoltaic current is
reduced. On the other hand, thinner specimen would waste the
photons. We have done the following experiment: a complete
tetracene solar cell is placed upon a second complete cell and
the photovoltaic i-v curve of the second cell is measured. A
still appreciable photovoltaic effect, corresponding to about
30% of the cell without being observed by the top solar cell
(Fig.12) is observed. If one can improve the intimate contact
between different layers and optimize the thickness of electrodes
and the specimen, one should be able to introduce more layers of
solar cells and improve the efficiency of conversion per unit
area several times.

References

1. P. H. Fang, M. Hirata and M. Hirata, "Investigation of Organic Semiconductor for Photovoltaic Application", Final Report, AFCRL Contract F 19628-70-C-0263. 1 July, 1970-31 Oct., 1970.

2. P. H. Fang and Y. M. Liu, "Interaction of Lithium with Impurities and Defects in Silicon", Appl. Phys. Lett. $\underline{9}$, 364 (1966).

3. P. H. Fang. A. Glubovic and Noreen A. Dimond, "Photovoltaic current anomaly in tetracene" (Submitted for publication).

4. Y. Ishihara and I. Nakada, "On the energy gap of Anthracene" J. Phys. Soc. Japan $\underline{28}$, 667 (1970), also comments by J. Scvorakowshi, ibid, $\underline{29}$, 1390 (1970).

5. H. J. Queisser, H. C. Casey, Jr. and W. van Roosbroeck, "Carrier transport and potential distribution for a semiconductor p-n junction in the relaxation region," Phys. Rev. Lett. $\underline{26}$, 551 (1971).

6. N. Geacintov, M. Pope and H. Kallmann, "Photogeneration of charge carriers in tetracene," J. Chem. Phys. $\underline{45}$, 2639 (1966).

7. M. Silver, K. S. Dy and I. L. Huang, "Monte Carlo calculation of the transient photo-current in low-carrier-mobility materials," Phys. Rev. Lett. $\underline{27}$, 21 (1971).

8. E. P. Eer Nisse, "Accurate capacitance calculations for p-n junctions containing traps," Appl. Phys. Lett. $\underline{18}$, 183 (1971).

9. Reference of J. Chem. Phys.

10. P. H. Fang, First Quarterly Report (1971) of the present contract.

Contributing Personnel

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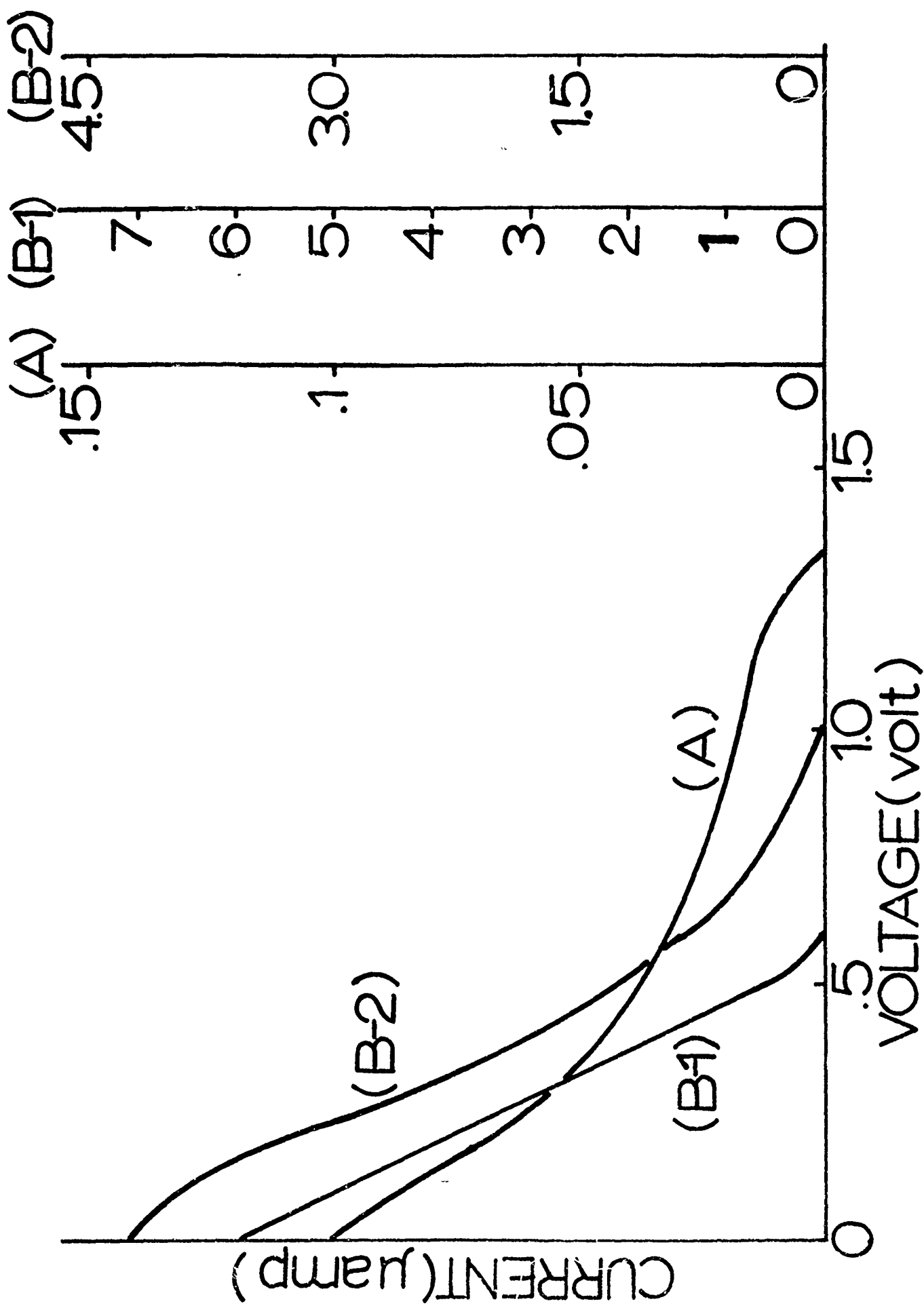
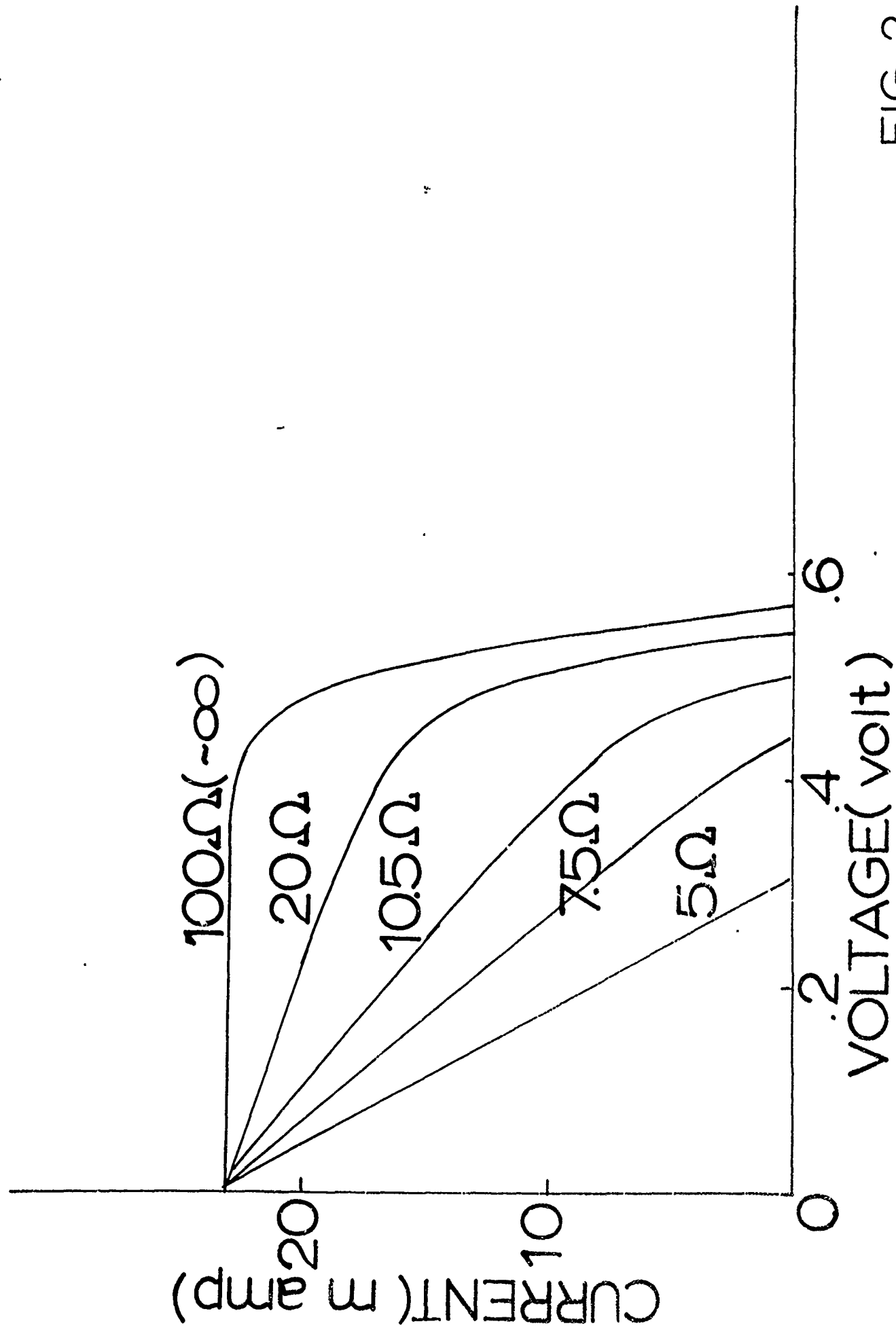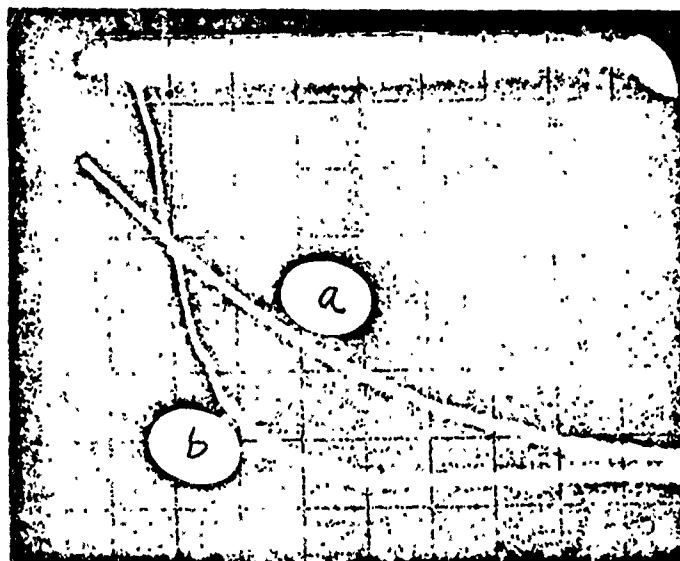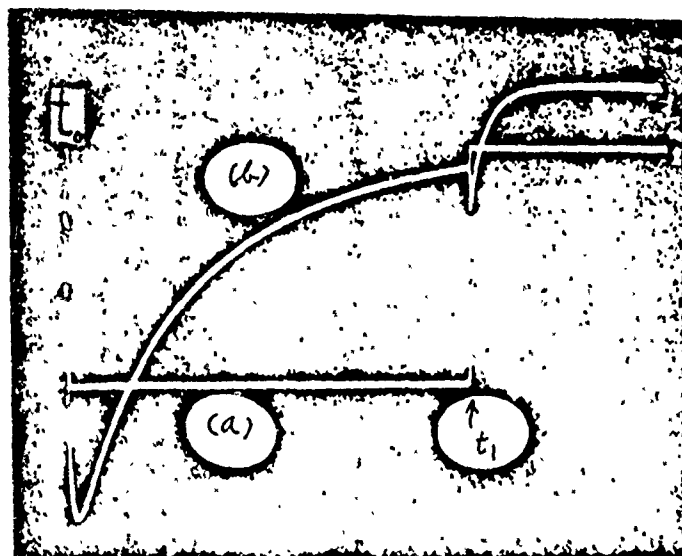Mr. Shyh-Shyong Hsu - Research Assistant

FIG.1

16

FIG. 2

17

FIG. 3

TIME(20msec./scale)

O(volt/scale)

81

FIG. 4

TIME(1sec./scale)

O

FIG. 5

TIME (2 sec./scale)

FIG. 6

TIME(1 sec./scale)

19
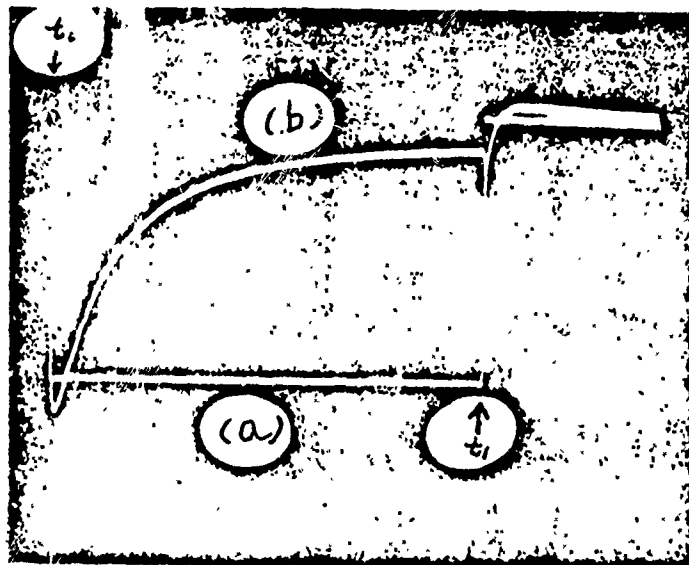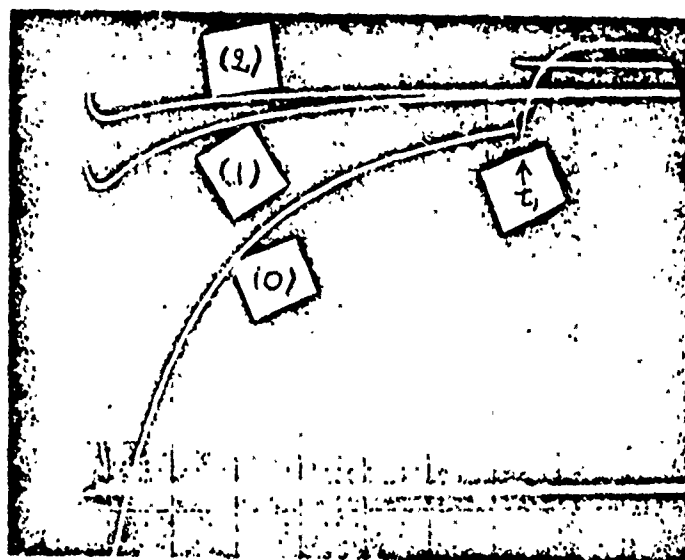
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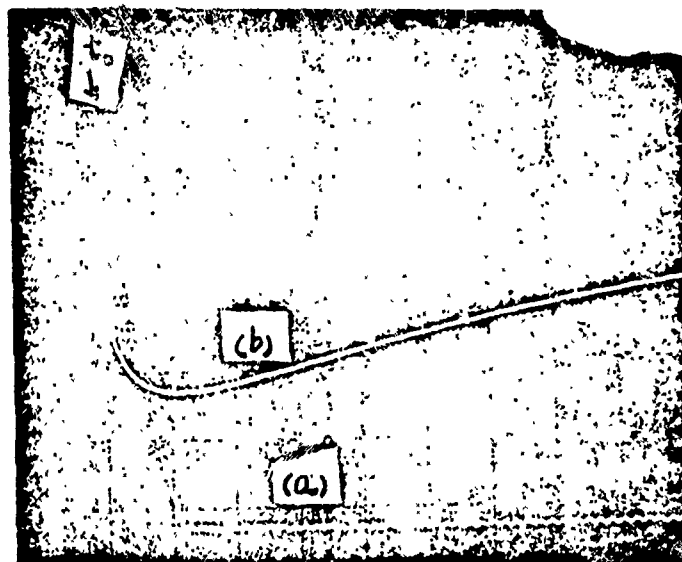
TIME(.1 sec./scale)

FIG. 8

TIME(2 sec./scale)

FIG. 9

FIG. 10
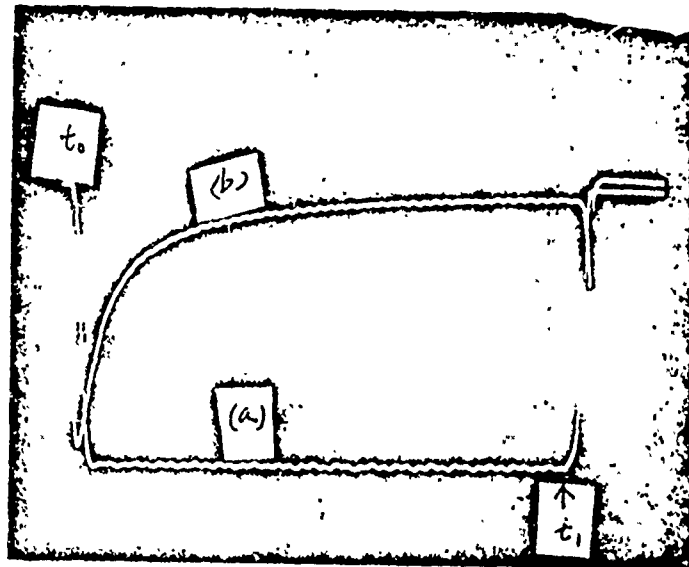
TIME(.1sec./scale)

FIG. 11

TIME(.5sec./scale)

FIG.12

(B-2)CELL

open

covered

CURRENT(μamp)

VOLTAGE(volt)

30

15

0

5

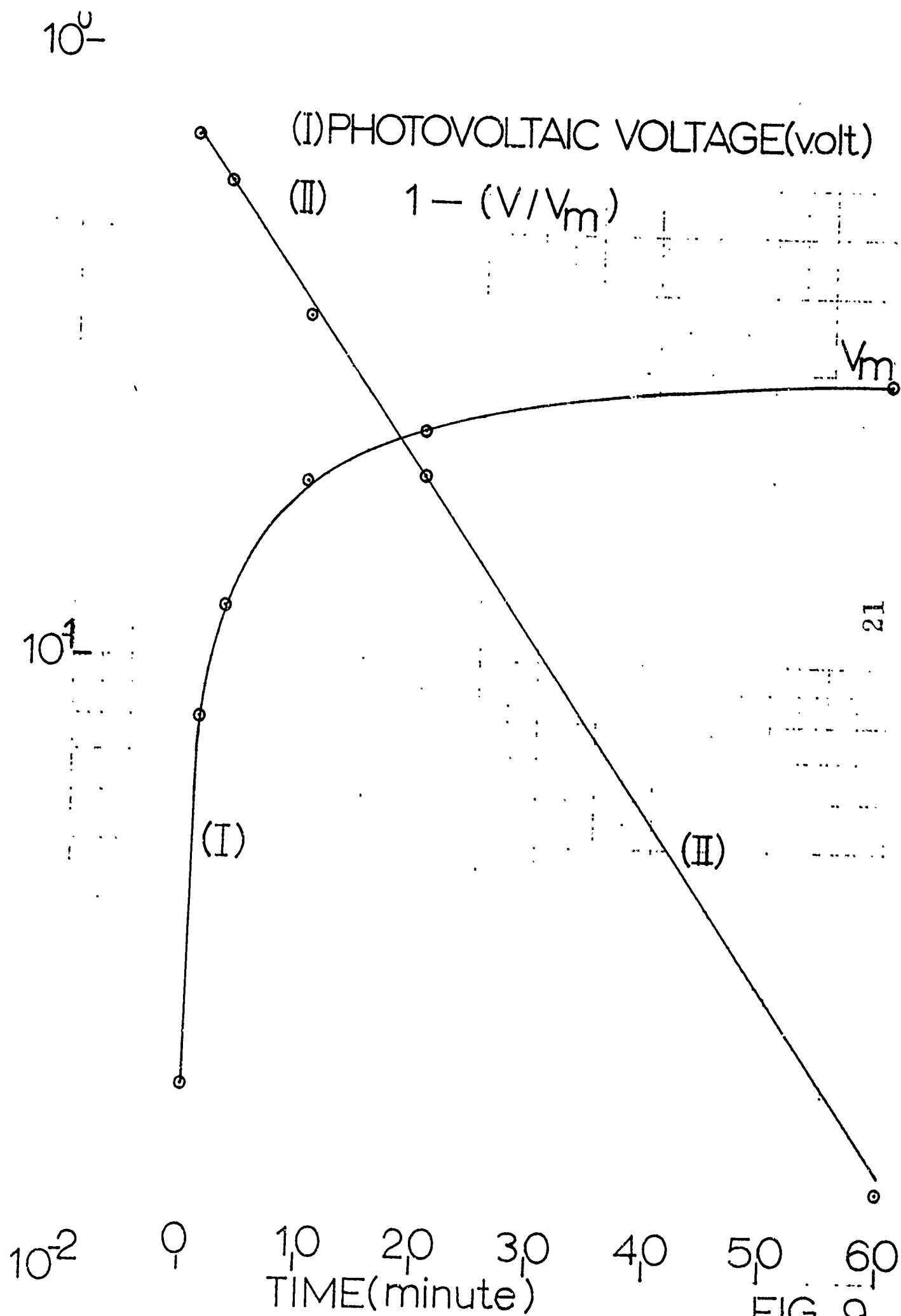10

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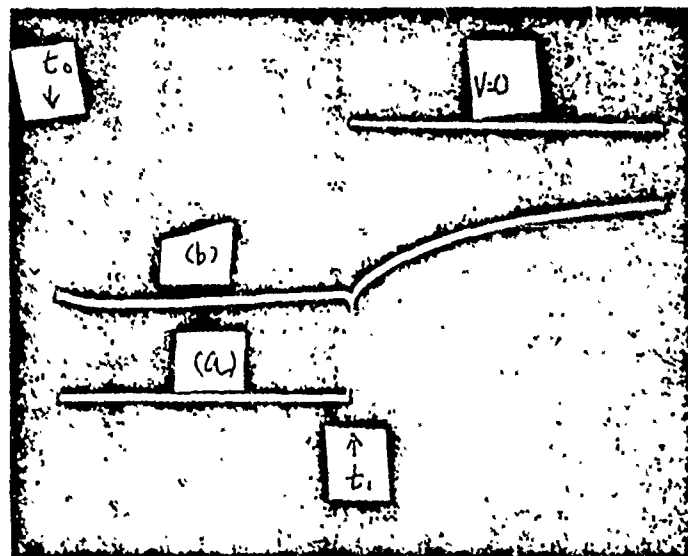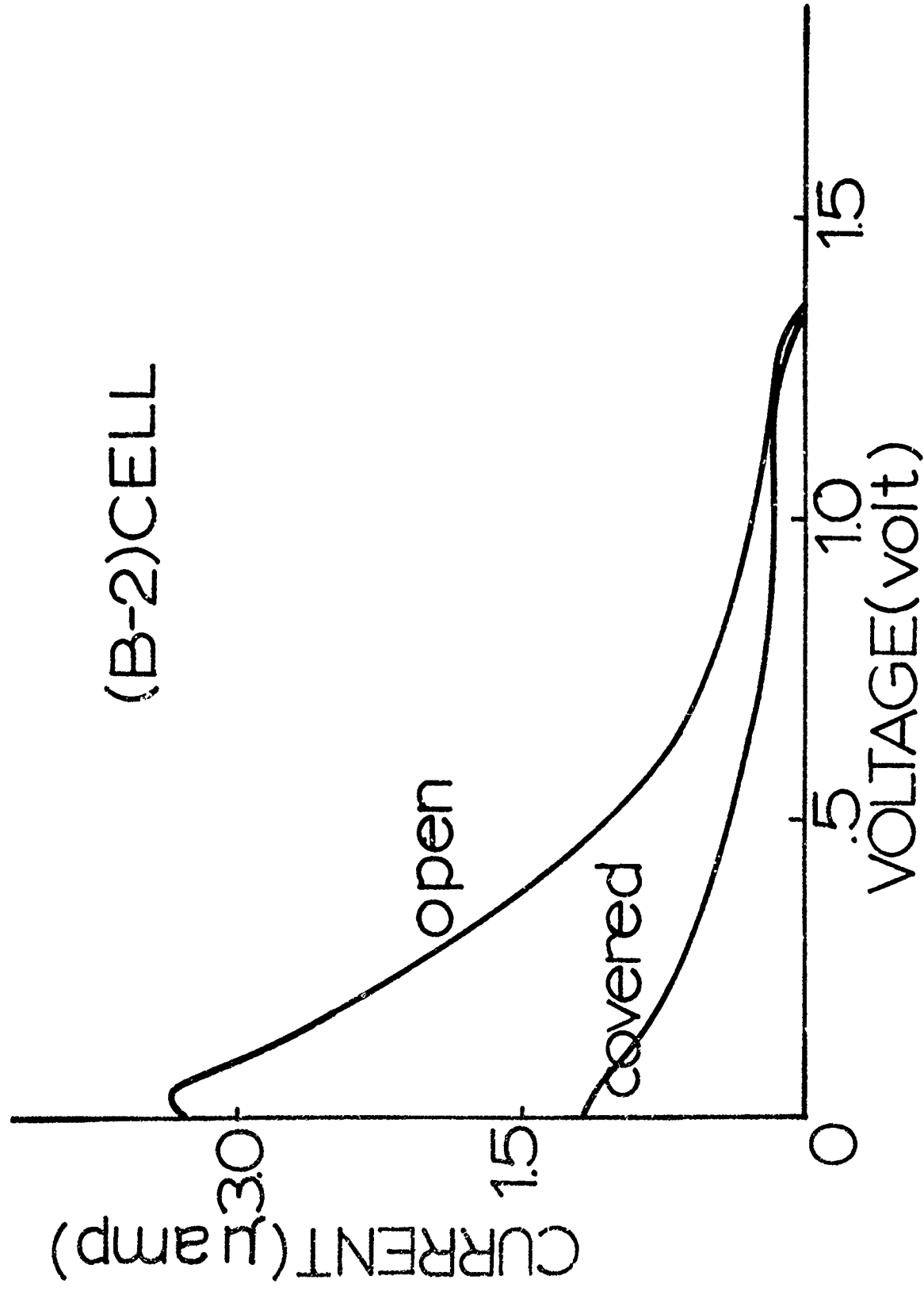
Appendix I

Photovoltaic Current Anomaly in Tetracene

Photovoltaic Current Anomaly in Tetracene*

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Abstract

A reversal of the polarity of photovoltaic current in tetracene
at some wavelength region is observed. This effect is inter-
preted as the consequence of the photovoltaic transport equation.
The observational data implies that either there is a very large
surface recombination rate, or the major annihilation of the
excitons instead of on the surface in the interior of the crystal.

I. Introduction

In this paper, we would like to analyze the wavelength
dependence of the photovoltaic current observed in tetracene,
an organic semiconductor. Our particular interest is an obser-
vation that at a certain wavelength region, the polarity of the
photovoltaic current is reversed, as shown in Fig. 1. We pro-
pose to explain this phenomenon by a diffusion equation employed
by Geacintov, Pope and Kallmann (GPK)[1] in the investigaiton of
similar material. However, in the work of GPK, some approxima-
tions are used which we will show to be not valid, and their
result does not show a reversal of the polarity in the whole
wavelength region.

The specimen of tetracene for the photovoltaic experiment
consists of a thin layer (~1μ) of tetracene sandwiched between
two semi-optically transparent and electrically conductive film
of gold electrodes.[2] Monochromatic light from a grating spect-
rometer is projected to a strip of about 2 mm width of the speci-
men of approximately 1x1 cm^2 in dimension. In view of a somewhat
similar observation in Sns due to partial illumination of the
specimen,[3] we have also tried to have light projected on the
complete specimen and we found in our case, the result is inde-
pendent of the area coverage of the illumination.

II. Transport Equation

We would like to investigate the spectral dependence of the
photovoltaic current, especially in the reversal of the polarity

26

of the photovoltaic current. In the work of GPK, origins of
this current are explained in terms of different excited states
in tetracene, and the surface trapping effect. It is important
to recognize that the polarity of the photovoltaic current is
not only dependent on the sign of the charge carriers, but also
on the direction of the charge flow between the electrodes. In
fact, we propose that this reversal has a natural explanation
in the transport equation. The fact that the diffusion current
could have positive as well as negative signs does not seem to
be recognized in the litereture[1] and in the following we will
discuss this problem.

Under a steady state, the equation of photovoltaic carrier,
n, can be written, [1,4]

$$D\frac{d^2n}{dx^2} - \frac{1}{\tau}n = -\epsilon I_o e^{-\epsilon x}, \qquad (1)$$

where D is the diffusion coefficient and τ is the lifetime of
the carrier in tetracene, ϵ is the optical absorption coefficient
of tetracene, x is the distance travelled by the carrier to the
site of collection, and I_o is the light intensity at the surface
of tetracene where light enters, and I_o is dependent on the wave-
length λ. In our experiment, constant energy, instead of constant
number of photons, is used for I_o. Since the experiment is
carried out in a continuous but confined wavelength region of
0.3 to 0.6 μ, we do not expect a great difference in the spectral
response cures.

Since the diffusion length $c=\sqrt{D\tau}$, with $x=\ell\xi$, $\epsilon l=\beta$, Eq. (1)
becomes,

$$\frac{d^2n}{d\xi^2} - n = -\frac{\tau}{\ell} I_o \beta e^{-\beta\xi}. \qquad (2)$$

A particular solution of n is that

$$n_p = \frac{\tau}{\ell} I_o \frac{\beta}{1-\beta^2} e^{-\beta\xi}. \qquad (3)$$

For the general solution, from the homogeneous part of Eq. (2), we have,

$$n_1 = a_1 e^{\xi} + a_2 e^{-\xi} \qquad (4)$$

therefore,

$$n = n_1 + n_p. \qquad (5)$$

The coeffecients a_1 and a_2 are determined from the two following boundary conditions: In the surface recombination, with a surface recombination velocity k,

$$kn(o) = \frac{D}{\ell} [\frac{dn}{d\xi}]_{\xi} = o. \qquad (6)$$

The optical density of the specimen is ϵd, where d is the thickness of the specimen. Since our specimen is polycrystal with multiple grain boundaries, there is a spatial distribution of distance where the recombination and capture takes place. Therefore, we have two different coordinates for . In optical transmission and absorption,

$$\epsilon d = \epsilon\ell \frac{d}{\ell}$$
$$= \beta\xi_1 \qquad , \qquad (7\cdot)$$

on the other hand, ξ in Eq. (4) becomes independent of x=d, $\xi \to \xi_2$ with

$$\eta = \xi_2/\xi_1 < 1, \qquad (8)$$

and the second boundary condition is that

$$a_1 e^{\eta\xi_1} + a_2 e^{-\eta\xi_1} + \frac{\tau}{\ell} I_o \frac{\beta}{1-\beta^2} e^{-\beta\xi_1} = 0 \qquad (9)$$

From Eqs. (6) and (9), we can solve for a_1 and a_2, and the final solution for $n(o)$ is now,

$$n(o) = I_o \frac{\tau}{\ell} \cdot \frac{\beta}{\ell - \beta^2}(\cosh \eta\xi_1 - e^{-\beta\xi_1} - \beta\sinh \eta\xi_1)/(\alpha\sinh \eta\xi_1 + \cosh \eta\xi_1)$$

(10)

where $\alpha = k\ell/D$.[5]

The photovoltaic current, which is our central interest, is obtained from Eq. (10) with a simple multiplier constant,

$$i = e\frac{\ell}{\tau}\frac{d\mu}{\partial\xi}\Big|_{\xi=0}$$

$$= e\gamma\kappa n(o),$$

(11)

where γ is the fraction of photovoltaic carriers collected and e is the electronic charge.

When ξ_1 and $\beta\xi_1 \gg 1$, $n(o)$ becomes approximately,

$$n(o) = I_o \frac{\tau}{\ell(1+\alpha)}\frac{\beta}{1+\beta} \cdot$$

(12)

This is the same equation given by GPK. Since $\beta > 0$, $n(o)$ is always positive and in this case, the polarity of the photovoltaic current would not have a reversal for all β, therefore, for the whole wavelength range. We will see later that $\beta\xi_1$ is not necessary $\gg 1$ for some wavelength regions, and in these regions the polarity of the photovoltaic current in fact shows a reversal.

III. Analysis of Experiment

Fig. 1 shows the spectral response of the photovoltaic current of specimen with three thicknesses. In the case of thick specimens, photovoltaic current bears a resemblance to the absorption spectrum (Fig. 2). When crystal becomes thinner, in

the spectral regions where the optical density has minima, the polarity of i changes from positive to negative and to positive again.

Fig. 2 gives the spectrum of ρ for three specimen thicknesses. We should note that, while in the inorganic semiconductors for photovoltaic application, there is only a single transition to the major absorption, in the organic semiconductor as in the present case, there are several major absorption peaks corresponding to multiple transition processes.

From Eq. (10), for given values of ξ and η we can calculate $n(o)$ as a function of ρ. The values of ρ are based on the experimental data of Fig. 2 which relates ρ to the wavelength λ. Therefore, $n(o)$, consequently, the photovoltaic current i, as a function of λ is obtained. Fig. 3 is the result where the numerical value of the parameters are,

$$\epsilon \kappa \gamma \tau I_o / \ell = 7.8 \times 10^{-9},$$

$$\eta = .30,$$

$$\xi_1 = d/\ell = 6 \times 10^{-5} cm = 3$$

$$\beta \xi_1 = 2.3o3\rho \tag{13}$$

These parameters are determined in the following manner:

The value of ℓ is given by GPK. Therefore, for given d, ξ_1 is determined, and from given ϵ, β is determined. The only remaining parameter is η. We observed from Figs. 1 and 2 that at 4650 $\overset{o}{A}$, i=o and ρ=1.8. The only way for Eq. (10) to become zero is that

$$\cosh \eta \xi_1 - e^{-\beta \xi_1} - \beta \sinh \eta \xi_1 = o. \tag{14}$$

Substituting for the values of β and ξ, a value of 0.30 is obtained for η.

The general agreement between the theoretical curve and the experimental data, over several decades of logarithmic scale, is

remarkably satisfactory. Appreciable differences occur in the two ends of the spectrum, and the two negative peaks on each side. One source of deviations could be contributed by the experimental limitations: the theoretical calculation is based on the mono-chromatic wavelength. In the experiment, the grating has a finite dispersion and the specimen always sees a band of wave-lengths; consequently, β does not have a single value at each point along the curves of Fig. (1) and (2).

Another conceivable source of deviations is that in a more exact description, ξ' and η should have ranges of values and each has a distribution in the range. However, to reformulate our problem by taking into account the distribution functions, it will unduly complicate the mathematical problem without yielding additional physical insights. Therefore, we have decided not to expand our work in this direction.

We believe our theoretical interpretation proposed in this paper is not confined to tetracene since the result is a direct consequence of the solution of a general transport equation for photovoltaic carrier generation. Therefore, similar observation of the reversal of the polarity of the photovoltaic current is expected in silicon. In this case, since the diffusion length is in the order of 0.05 to .2 cm,[4] at the wavelength near the absorption edge where the absorption coefficient ε becomes com-patible with the reciprocal of the diffusion length, this anomaly should be observed.

References

1. N. Geacintov, M. Pope and H. Kallmann, J. Chem. Phys. 45,
    2639 (1966).

2. A. Golubovic, Organic Photovoltaic Devices, Proc. OAR Res.
    Appl. Conference March, 1967

3. O. Cheroff and S. P. Keller, Phys. Rev. III, 98 (1958).

4. R. L. Cummerow, Phys. Rev. 95, 16 (1964).

5. An essentially similar result cna be obtained by a system
    consisting of layers of different crystals, but the analy-
    tical result is very complicated and is not presented here.

Illustrations

Fig. 1. Spectral response of the photovoltaic current of tetra-
cene of different thickness; (-.-), .6 µ; (---), 1.0 µ;
(___), 1.6 µ.

Fig. 2. Optical density of tetracene specimen of Fig. 1, with
some thickness designation.

Fig. 3. Spectral response of photovoltaic current:
(---), experimental data of tetracene of 0.6 µ thick;
(-o-), theoretical result from Eq. (5) and (6) with
numerical parameters given in the text.
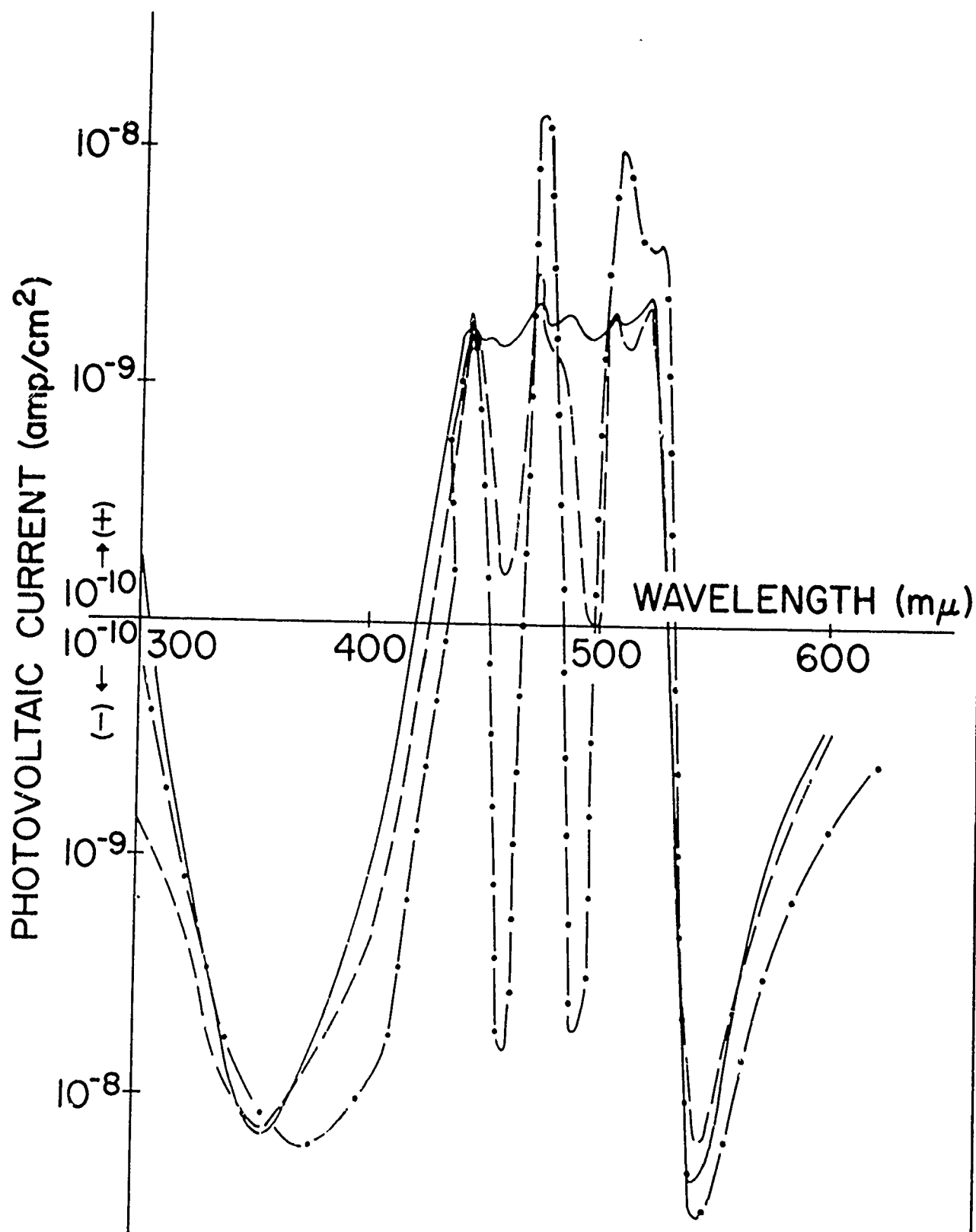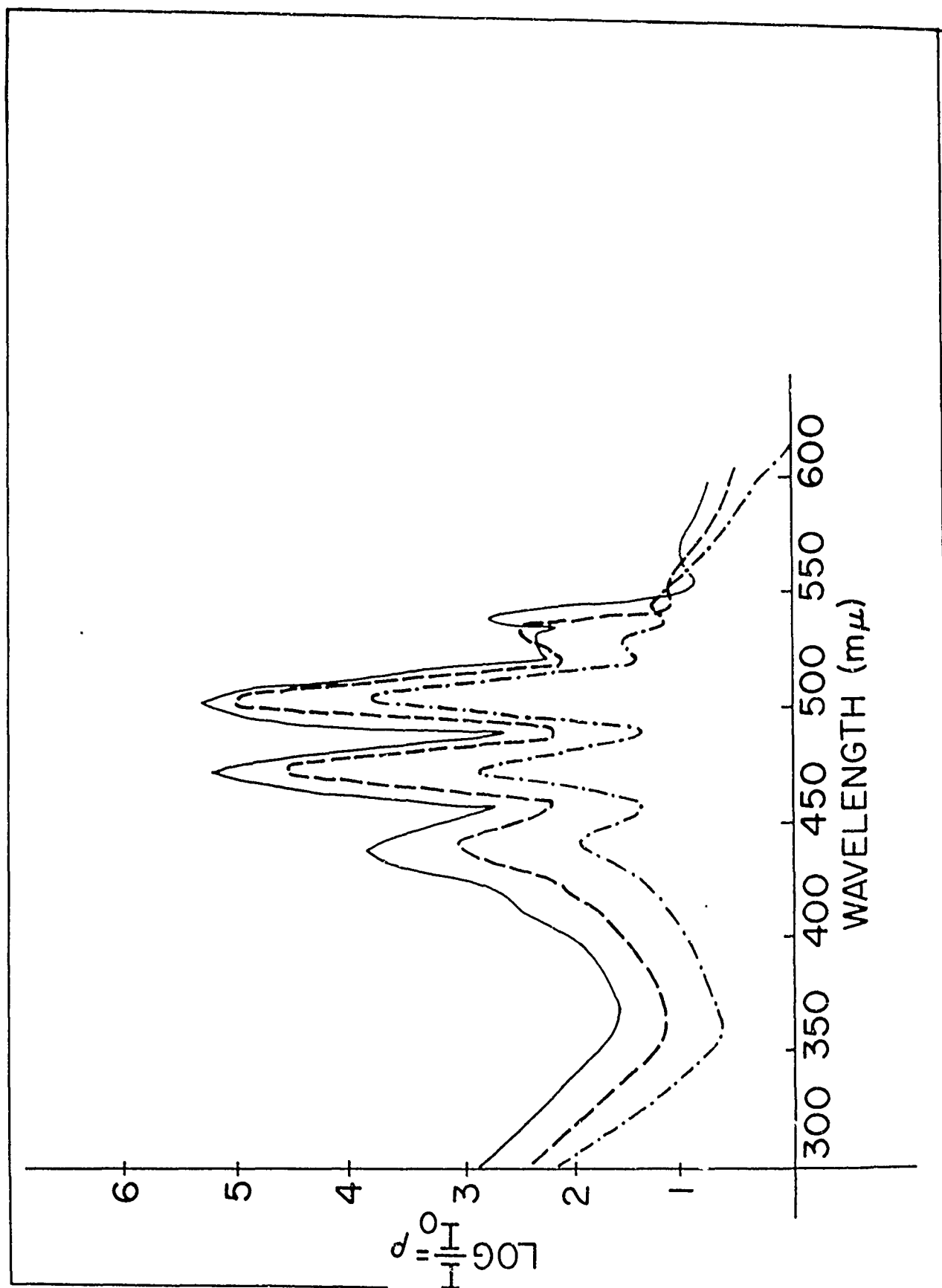
Appendix II

Transient Photovoltaic Current in Tetracene

Transient Photovoltaic Current in Tetracene

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Abstract

In order to analyze the positive and negative charge current
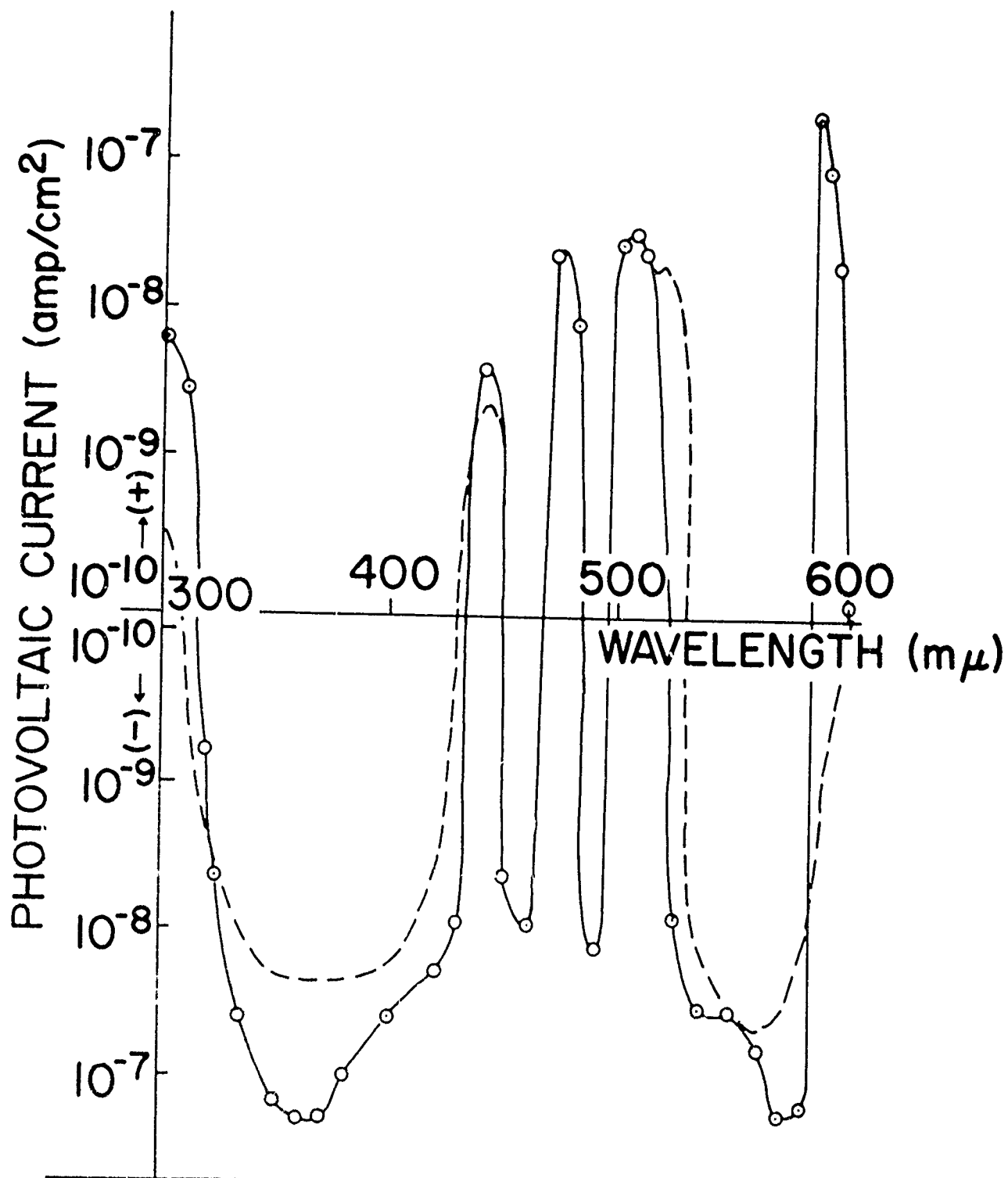in the organic semiconductor, tetracene, we measured the transient
photovoltaic current. From the rate equations for the relaxation
of these two currents, the magnitude and the relaxation time of
these currents are evaluated. The magnitude of the steady state
value of these two currents are almost equal, and they are more
than one order of magnitude larger than their net difference.
This difference is the usual photovoltaic current refered to in
the characterization of the photovoltaic efficiency of tetracene.

I. Introduction

In a previous paper by Fang, Golubovic and Dimond (FGD)[1], we presented experimental results and theoretical analysis of the dependence of the steady state photovoltaic current in tetracene on the wavelength of injected photons. The present work extends to the transient case where the time dependence is also investigated. In the previous work, we found the polarity of the photovoltaic current is dependent on the energy of the excitation photons. In the present work, we would like to investigate the same dependence for the transient photovoltaic current. Reucroft, Kronick and Hillman[2] have reported some anomalous behavior of this current. Their time scale is rather coarse (in the unit of minutes). We have observed down to a fraction of a second. We will show that the result at the region of fraction of a second gives most direct information on the composition of these currents.

In this paper, in Section II, we would like to present the experimental results. In Section III, theoretical analysis based on the superposition of one positive component and one negative component of the photovoltaic current is made. This model is based on the experimental observation of the non-linear dependence of the photoconductivity on the light intensity[3], and the non-symmetry of the rise and the decay when a pulsed light is used for the excitations.[4]

II. Experimental Results

The specimen configuration has been described in the work of FGD. The transient photovoltaic current is recorded by an x-y recorder with x on time base, and y-import is triggered by the fast light signal. The rise time of this signal is 70 msec. The reslut is given in Fig. 1.

When light is injected to the specimen, through different band pass filters, there is a finite relaxation time for response and the photovoltaic current reaches a maximum in the order of 0.2 sec. After this over-shooting, there is a gradual decrease. This decrease follows one of two courses depending on the wavelength of the injected photon: either to reach a stable value with the same polarity as the initial response current, or a continuous decrease goes to the opposite polarity before a stable value is reached. In a closer examination, we found that these two courses are closely related to the photovoltaic anomaly:[1] with our arrangement which assigns negative polarity on the side of electrode where light is illuminated, we found that in the case of positive current, there is no reversal in the polarity of the transient photovoltaic current; in the case of negative current, there is a reversal. Fig. 1 shows two curves; in the curve with 5000Å (100 Å band width) illumination, there is no alteration of the polarity. In the case of 3100-4000 Å illumination, obviously, the current polarity is reversed. Although in the case of short wavelength, the bandwidth of the filter is 900Å, our light source does not have appreciable emission at wavelength

shorter than 3500Å. Therefore, effectively, the wavelength in this case is 4200 ± 200Å.

In comparison of those two curves, we also noted that the relaxation time to reach saturation in the case where there is no polarity reversal is faster. This characterization is true for all wavelengths although the result is not presented here.

III. Two Component Model

In a study of the light intensity dependence of the photoconductivity current, Golubovic and Dimond[4] observed that, under pulsed light excitation, the rise time is faster than the decay time, and the decay follows a second order kinetics. The implication is that there are two relaxation times in the operative. From the characteristic of the transient photovoltaic current as shown in Fig. 1, it is implied mathematically that these two relaxation processes have opposite polarities. Therefore, the transient current is analyzed with one component which follows the first order kinetics and another component which follows one second order kinetics. The relative sign of those two components is determined, in the present work, from the fitting of the experimental data by the proposed model; that is,

$$i(t) = i_1(t) + i_2(t), \tag{1}$$

where the transient current $i_1(t)$ and $J_2(t)$ are given by Eqs. (A6) and (A6) in the Appendix, respectively. Eqs. (1) has four unknown parameters, αI, τ, βI and k, which are to be determined from the experimental data. To evaluate these parameters,

instead of a more complicated least square approach, we simply
selected four arbitrary data points from which the vaules are
found. The result is given in the following table:

wavelength	$\alpha I \tau$	τ(sec)	$\beta I/k$	$(2\beta Ik)^{-1}$(sec)	$i(t=\infty)$
4200Å	-133.7	.139	+128.7	.0785	-5
5200Å	-36.1	.151	+39.1	.0910	+3

The units of $\alpha I \tau$ and $\beta I/k$ have the same arbitrary unit as in
Fig. 1 and of $i(t-\infty)$: i.e., the steady state value of i in
the above table.

Substituting the values of parameters of the above table to
Eq. (1), $i(t)$ can be computed for different vaules of t, and the
result is hsown in Fig. 1. The fit is generally staisfactory,
except at some intermediate time intervals. An improvement can
be made in the fitting by using mixed first nad second order
kinetics as discussed in the photo-induced current in polyvinyl-
carbazole[5] or b· a different combination of reaction kinetics.
However, we founa that there is no basic alteration of the values
of the preceeding table.

Several points are noted from the table:

(1) The current component following the first order kinetics
is negative, and the component following the second order kinetics
is positive.

(2) The difference in the relaxation time of the negative
component at the two wavelengths is 6%. Within the accuracy of
evaluation, this difference is practically null. The difference

in the case of positive component cannot be made because of a diffuculty in calibrating the light inennsity values at present.

(3) The magnitude of the two components, that is; the value of $\alpha I \tau$ and $\beta I/k$ are, for a given wavelength, practically the same.

(4) From a practical point of view, the steady state current, because of (3), is more than an order of magnitude smaller than that of individual component. This effect evidently is a major cause for the smallness of the photovoltaic efficiency observed in tetracene.

IV. Discussion

A basic photovoltaic problem of the organic semiconductor is the origin of the positive charge current and the negative charge current. There are several experimental observations and qualitative descriptions. Since, in the experimental data as illustrated in the present paper, these currents occur simultaneously, a quantitative method to evaluate these two currents separately, as described in the present work, would be useful.

Frankevich and Balabanov found that gold, for example, forms a good hole injection contact and exhibits negative potential.[6] However, when gold is used for both electrodes, the gold electrode deposited on the glass substrate forms positive potential relative to the gold electrode deposited on the semiconductor.[4] These currents are also affected by the energy of photons: since there is no evidence of multiple carrier generation, this effect is interpreted as due to the strength of the absorption coefficient.

In a weak absorption case, a photoionization of trapped electrons
gives a negative current. In the case of strong absorption,
excitons are recombined near the surface and a positive current
is resulted.[7,8] This origin or this effect must be different
from that observed by Golubovic and Dimond; in the case of gold
electrodes on both sides of the semiconductor, independent of the
side of light injection, the gold electrode deposited on the
semiconductor is always negative. Finally, Geacintov et al.[9]
discussed a negative current which is independent of the electrodes
and depends only on the absorption coefficient at specific values
of photon energy where transitions to excited states are observed.

From the result of the present work, we conclude on two
grounds that the process of Geacintov et al.[9] is dominent in
tetracene: (1) for a given wavelength, the magnitude of the
positive and the negative currents are almost equal, therefore,
the current carriers are dominently generated in the bulk and
(2) the small difference of these two currents, which gives the
steady state current as observed in most experiments, is origina-
ted at the side of surface recombination, therefore, a small
effect due to the electrode is observed.

In conclusion, transient current measurements provide a
method to evaluate quantitatively the opposite charge current
observed in tetracene, and similar methods should be useful in
the investigation of other organic semiconductors. By repeated
transient measurements at specific time intervals, we have also
observed a change in the transient current. From the data,
one can measure quantitatively the photoionization of trapped

charges. This problem is currently under investigation.

We would like to thank Dr. V. Yannoni for his advice and Dr. A. Golubovic for many helpful discussions. Miss Susan LeVangie is most helpful in the preparation of this paper.

Appendix

We present here the kinetic equation of first and second order kinetics, for a pulsed light and a continuous light injection separately.

For a pulsed light, only the decay is observed, and the kinetic equation is,

$$\frac{di_1}{dt} = \frac{i_1}{\tau} \qquad\qquad\qquad\qquad (A-1)$$

for the first order kinetics, and

$$\frac{di_2}{dt} = -k^2 v_2^2 \qquad\qquad\qquad (A-2)$$

for the second order kinetics. With i_o as the initial current, i.e., the current at the value of $i(t)$ when the light pulse is dropped to zero, we have, for Eq. A-1,

$$i_1 = i_o e^{-t/\tau} \qquad\qquad\qquad (A-3)$$

For Eq. (2),

$$i_2 = i_o/(1+k^2 i_0 t) \qquad\qquad (A-4)$$

Therefore, for i_1, the relaxation time is independent of the light intensity; for i_2, the relaxation time depends on the light intensity as well as on the pulse length where i_o is reached.

In the case of continuous light injection, a source term should be included. Thus,

$$\frac{di_1}{dt} = -\frac{i_1}{I} \qquad \text{for } t<0$$
$$= -\frac{i_1}{\tau} + \alpha I \qquad \text{for } t>0 \qquad (A-5)$$

where I is the light intensity and α is the current generation

rate. The solution of (A-5) is that, with the initial condition i=o at t≤o, i.e.at I=o,

$$i_1 = \alpha I \tau (1-e^{-t/\tau}). \qquad (A-6)$$

For second order kinetics,

$$\frac{di_2}{dt} = -k^2 i_2^2 \qquad \text{for } t<o,$$

$$= -k^2 i_2^2 + \beta^2 I^2 \qquad \text{for } t>o, \qquad (A-7)$$

with the same initial condition as (A-5)

$$i_2 = \frac{\beta I}{k} [1 - \frac{2}{1+\exp(2\beta Ikt)}] \qquad (A-8)$$

We note that, while the relaxation function and the relaxation time of (A-6) are the same as those of the pulsed decay case, those of (A-8) are different from those of (A-4). Furthermore, qualitatively, in the pulsed case, the decay rate of second order kinetics is slower that that of the first order case. The opposite is the result for the case of continuous injection.

Finally, the transient current, i(t), of two component models is the sum of (A-6) and (A-8).

List of Figures

References

1. P. H. Fang, A. Golubovic and N. A. Dimond, "Photovoltaic
   Current Anomaly in Tetracene (submitted for publication).

2. P. J. Rencraft, P. L. Kronick and E. E. Hillman, Mol. Cryst.
   and Liquid Cryst. $\underline{6}$, 247 (1969).

3. N. Almeleh and S. E. Harrison, J. Phys. Chem. Solids, $\underline{26}$,
   1571 (1965).

4. A. Golubovic and N. Dimond (to be published)

5. J. E. Carnes and P. J. Warter, Phys. Rev. $\underline{5}$ B 1557 (1972).

6. E. L. Frankevich and E. I. Balabanov, Phys. Stat. Sol. $\underline{14}$,
   523 (1966).

7. L. E. Lyons and O. M. G. Newman, Aust. J. Chem. $\underline{24}$, 13 (1971).

8. V. V. Vladimirov, M. V. Kurik and O. Yu. P. Piryatinskii,
   Doke. Akad. Nauk SSSR, $\underline{181}$, 1365 (1968) (Transl. Soviet Phys.
   Dakl. $\underline{13}$, 739, 1969).

9. N. Geacintov, M. Pope and H. Kallamnn, J. Chem. Phys. $\underline{45}$, 2639
   (1966).

51