PHOTOTRANSPORT EFFECTS IN POLYACETYLENE, (CH)$_x$

T. Tani,* P.M. Grant, W.D. Gill, G.B. Street and T.C. Clarke

IBM Research Laboratory, San Jose, CA 95193, U.S.A.

We have made the first comprehensive measurements of the photovoltaic
and photoconductivity effects in polyacetylene in that we have extended
the spectral range originally covered by Matsui and Nakamura [17] to
include the visible region as well. The photovoltaic experiments were
done on Schottky barrier junctions formed between AsF$_5$ lightly-doped
p-type $trans$-(CH)$_x$ and a low work function metal, the first junctions of
this type to be produced in semiconducting polyacetylene. The observation
of a photovoltaic response threshold at 1.48 eV provides the first definitive
measurement of the single-particle band gap in $trans$-(CH)$_x$. In addition, we
have found the existence of a peak at 1.35 eV in the photoconductivity
spectrum of undoped $trans$-(CH)$_x$ which may be due either to extrinsic
sources or to thermal dissociation of a weakly bound Wannier exciton.

DOPED POLYACETYLENE, (CH)$_x$, because of its
unusual transport properties, has attracted the increasing
attention of both polymer chemists and solid state
physicists. The success in synthesizing [1] high quality
films and controlling [2] their $cis/trans$ content by
Shirakawa and co-workers has led to intensive efforts in
the investigation of their electronic properties. Most of
the recent work has concentrated on highly doped
specimens which display the metallic behavior of a
degenerate semiconductor [3–8]. For the undoped and
lightly doped material, however, some very fundamen-
tal parameters, such as the value of the single-particle
energy gap, have not yet been decisively elucidated. In
order to produce some quantitative answers to this
question, we report in this paper our studies of the
photovoltaic (PV) and photoconductivity (PC) effects
in semiconducting $trans$-(CH)$_x$ at room temperature.
In general, the photovoltaic effect is sensitive mainly
to the change in the concentration of minority carriers
due to interband excitation under illumination. There-
fore, it may provide a more definitive way to identify
the free electron–hole band gap of the material
than other alternatives such as optical absorption or
the photoconductivity effect. We believe our observation
of a 1.48 eV threshold in the photovoltaic response of
$trans$-(CH)$_x$ yields the first definitive measurements of
the intrinsic free electron–hole band gap in this
material. Furthermore, the detection of this threshold
at an energy below the first peak in the absorption
spectrum, opposite to that found for other polymeric

semiconductors such as polydiacetylene [9], suggests
that strongly bound excitons are not present in (CH)$_x$ at
elevated temperatures.

Our sample configurations are shown in Fig. 1. The
A configuration was employed for both photoconduc-
tivity and photovoltaic measurements. All samples were
deposited on sapphire substrates. Metal layers 1 and 2
were formed by thermal evaporation. In configuration A,
layer 1 was made thin enough to function as a light
transmitting electrode, and layer 2 thick enough to
secure electrical conductance on the rough surface of the
(CH)$_x$ film. Our (CH)$_x$ samples were synthesized at
$-77°$C [1] with subsequent thermal isomerization [2]
into completely $trans$ material. Two major considerations
enter into the fabrication of a sample suitable for
observation of the photovoltaic effect. The first is the
use of a low work function metal as the light trans-
mitting electrode in order to form a good rectifying con-
tact with p-type (CH)$_x$. The second requires moderate
doping of (CH)$_x$ with AsF$_5$ to produce a depletion layer
of appropriate depth (i.e. comparable to the optical
penetration depth) at the light transmitting contact.
For this contact, a low work function is desirable in
order to form a Schottky barrier within the p-type
(CH)$_x$, whereas the back contact, metal 2, should have
higher work function so that an ohmic contact will be
obtained. In the photovoltaic measurements, we used
indium ($\phi_m = 4.12$ eV) [10] for metal 1 and gold
($\phi_m = 5.1$ eV) [10] for metal 2. Our current–voltage
characteristics confirmed the existence of a rectifying
contact at metal 1. Detailed electrical characteristics of
these junctions will be reported elsewhere [11].

Most of the sample handling was carried out in the
argon or helium atmosphere of a chemical dry box. The

* Permanent address: IBM Japan World Trade Fellow,
  Department of Applied Physics, Faculty of
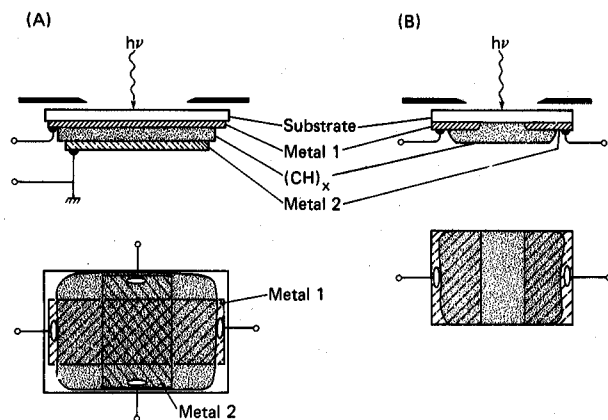 Engineering, University of Tokyo, Tokyo, Japan.

Fig. 1. Sample configurations adopted in our experiment: (A) the sandwich type, and (B) the surface electrode type. Light is incident through the substrate and metal layer 1 in (A) and through the substrate in (B). The illuminated area in configuration (A) was about 1 mm^2 and in configuration (B) about 0.5 cm^2. The film thicknesses were typically 15–20 μm.
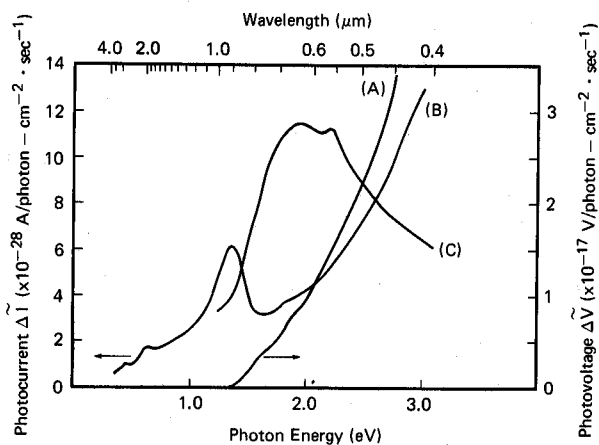

Fig. 2. (A) Open-circuit photovoltaic response normalized to the incident photon flux density and the transmittance of the In contact (metal 1 in Fig. 1) with sapphire substrate; (B) photoconductivity response similarly normalized; (C) absorbance spectrum of undoped trans-(CH)$_x$, measured at room temperature.

only exposure to air occured during mounting of the sample in the vacuum metallization chamber for the deposition of metal 2 after which the sample was returned to the dry box for mounting in an enclosed holder that was kept evacuated for the duration of the measurements. Thus total exposure to air was only perhaps 1 or 2 min at most and we believe this minimal amount had negligible effect on our phototransport results. A Bausch and Lomb high intensity monochromator with a 45 W tungsten quartz/halogen source was used to illuminate the sample in the photon energy range from 0.35 to 4.7 eV. The incident light

was chopped at 150 Hz and the resulting phototransport signal detected by lock-in methods. Bandpass optical filters were employed for order separation and all data were normalized to incident photon density as measured by a calibrated thermopile.

Figure 2 shows a typical example of the open-circuit PV response of trans-(CH)$_x$ lightly dopes with AsF$_5$. The data were corrected to account for the transmittance of the semitransparent indium contact. The conductivity of the sample was measured to be $5.7 \times 10^{-3} \, \Omega^{-1} \, cm^{-1}$, which probably corresponds to a doping level of about 0.6% [4], and the thickness of the depletion region was estimated at 100–600 Å from capacitance–voltage measurements [11]. As can be seen, the photovoltaic response has a distinctive threshold at 1.48 eV and continues to increase in the higher energy region. Transposed with these data in Fig. 2 is an absorbance spectrum of a thin film of undoped (CH)$_x$ [12]. Close coincidence between the absorption edge and the onset of the photovoltage is observed. Of particular note is the fact that the PV threshold is well below the peak in absorption. To our knowledge, this is the first observation of such an effect in an organic semiconductor. We have also measured the PV response of several other samples with conductivities in the range $2.6 \times 10^{-4} - 4.0 \, \Omega^{-1} \, cm^{-1}$. The results were essentially the same as shown in Fig. 2; thus the PV threshold is independent of doping level in the range of conductivities above, reinforcing our belief that 1.48 eV represents the single-particle band gap in trans-(CH)$_x$. We must caution that photoinjection over the Schottky barrier cannot be completely ruled out as the source of the observed threshold. On the other hand, a plot of the square of the PV response vs photon energy, whose interpretation we will duscuss further below, was far more linear than a Fowler plot of the same data (i.e. (PV)$^{1/2}$ vs $h\nu$, which, under conditions of photoinjection results in a straight line).

For low illumination intensities, the PV response should depend linearly on the density of the free electron–hole pairs generated by the absorption of photons, which should be directly related to the interband absorption coefficient [13]. We measured the response as a function of intensity at 2.21 eV, the energy of maximum output, in the sample yielding the greatest PV signal. We observed a distinct proportionality to incident light intensity over the range $1.11 \, \mu W \, cm^{-2} - 1.53 \, mW \, cm^{-2}$ (1.23 mW cm^{-2} was actually used to obtain the spectrum shown in Fig. 2). The PV response should ideally follow on the absorption; however, this dependence can be skewed by surface recombination effects in the region of high absorption thus giving the appearance of a steeply rising phototransport amplitude well beyond the maximum in
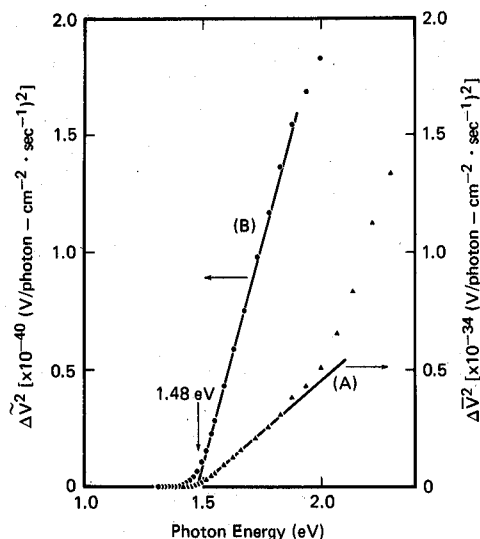
Fig. 3. (A) Energy dependence of the square of the photovoltaic response shown in Fig. 2(A), and (B) that of the same data without the correction for the transmittance of the In contact in the vicinity of the threshold.

optical absorption. More recent measurements indicate that the photoresponse peaks at 3 eV and decreases thereafter.

On the other hand, near the PV threshold it is reasonable to expect that the closest direct dependence on absorption will exist. In Fig. 3, we plot the square of the photovoltage vs photon energy for two different ways of correcting for incident light effects. One, curve (B), shows normalization to the incident photon flux only, and the other (A) includes the In film absorption as well. As can be seen, any energy dependence of the In absorption scarcely affects the determination of the PV threshold energy. The straight line result in both cases indicates $\alpha \propto (E - E_{th})^{1/2}$ as would be expected for optical excitations into a 3D-like continuum, where α is the absorption coefficient, E is the incident photon energy and E_{th} is the threshold energy, respectively. Such a result could arise from sufficient interchain interaction to suppress the expected square-root singularity in the joint density of states, as indicated by the calculation of Grant and Batra on 3D cis-(CH)$_x$ [14], or by the quenching of the $E^{-1/2}$ singularity in 1D into the weaker $E^{1/2}$ by Wannier exciton borrowing of oscillator strength from the 1D continuum [15]. The 1.48 eV threshold is in fair agreement with the energy gap in the 1D band structure calculation of Grant and Batra for trans-(CH)$_x$ [14] which yielded a value of 0.9 eV for bond lengths chosen from β-carotene. They found the value of the gap to be very sensitive to the degree of bond alternation and obtained a gap as large as 2.3 eV for completely conjugated bonds. It is evident

that the bond alternation is somewhere intermediate between uniformity and complete conjugation. The PV threshold is also considerably smaller than the 2.3 eV correlation gap inferred by Ovchinnikov et al. [16], from the spectral convergence of finite length polyenes to the infinite chain limit.

In Fig. 2, we also show the result of the PC response of undoped trans-(CH)$_x$ in the low illumination intensity limit. Measurements were performed in both configurations A and B using Au electrodes for all metal layers thus assuming ohmic contact. Nearly identical results were obtained from each configuration. The bias potential was roughly 50 V and the sample resistance usually around 35 MΩ. The photocurrent was detected by measuring the voltage drop across a 1 MΩ load resistor in series with the sample. The illumination and lock-in methods were as previously described. Typical photocurrents near threshold (1.35 eV) were 9×10^{-12} A above a dark current background of 1.2×10^{-6} A. The photocurrent/dark current ratio was then approximately 8×10^{-6}. The quantum yield, or photoconductive gain, and the $\mu\tau$ product were calculated as follows. For the geometry of configuration (B), under conditions where the photon penetration depth is much less than the sample thickness, the total photocurrent, I_{pc}, is expressed by [20]

$$I_{pc} = 2\mu\tau e V_s N W / L, \qquad (1)$$

where μ is the carrier mobility (assumed equal for holes and electrons, see [14]), τ the inverse trapping rate, V_s the voltage drop across the sample, N the incident photon flux density in photons cm^{-2} sec^{-1}, W the width of the illuminated area, and L its length between electrodes. It is assumed that each photon absorbed with energy greater than the band gap results in a free hole and electron pair. We define the quantum yield by normalizing the photocurrent to unit electronic charge and the total photon flux, obtaining,

$$G = \frac{I_{pc}}{eNWL} = 2\mu\tau V_s / L^2. \qquad (2)$$

Using $N = 8 \times 10^{15}$ photons cm^{-2} sec^{-1} as measured at 1.35 eV with a calibrated thermopile, and the area for configuration (B) from Fig. 1, we find $G \approx 3 \times 10^{-8}$ carriers/absorbed photon from the second term of equation (2) when the incident flux is corrected for transmission losses through the substrate. We note that this definition of the photoresponse figure of merit depends on sample geometry and external circuit conditions. A more satisfactory photoresponse measure is the $\mu\tau$ product contained in the third term of equation (2). Solving for this quantity results in $\mu\tau = 2 \times 10^{-10}$ cm^2 V^{-1} as the value characterizing undoped trans-(CH)$_x$.

Typical values for well-known photoconductors are $10^{-5}\,\mathrm{cm^2\,V^{-1}}$ for CdS and unity for Si. We remark that the quantity we call the quantum yield, or photoconductive gain, is not to be confused with the so-called solar cell efficiency.

The PC response displays three distinct features. One prominent feature is the peak at 1.35 eV which is not observed in the PV spectrum of lightly doped samples; another is the steep increase in the high energy region similar to the PV response. A third is the relatively large background which appears to be proportional to the incident photon energy (when the response data are normalized to the incident photon flux) and which is not related to the d.c. dark current mentioned above. The source of this background is probably the thermal modulation of the sample resistance by the incident light, which, in the near infrared, approaches a power density of around $0.01\,\mathrm{W\,cm^{-2}}$. The temperature dependence of the resistivity of undoped trans-(CH)$_x$ at 300 K is significant [4] and we estimate from the background magnitude that the mean temperature rise is roughly $3 \times 10^{-5}\,\mathrm{K}$. Extrapolation of the steep part of the PC response to the background yields a threshold of about 1.5 eV, in very good agreement with the PV finding.

The most notable difference between the PC and PV response spectra is the appearance of the 1.35 eV peak in the former. The source of this structure is presently unknown; it may in fact arise from some extrinsic electronic state. We note that early photoconductivity measurements of Matsui and Nakamura [17] terminated at an energy corresponding to the leading edge of this peak. It is also interesting to observe that a similar peak appears in the PC spectrum of polydiacetylene [9]. On the other hand, we never saw the 1.35 eV peak in the PV or PC spectrum of any lightly doped trans-(CH)$_x$ samples, yet it did appear in the PV response of the only sample of undoped material in which we measured photovoltage. In this latter case, we used the A configuration of Fig. 1 with Au and Al ($\phi_m = 4.28\,\mathrm{eV}$) [10] for metal layers 1 and 2, respectively. This sample gave a comparatively strong peak at exactly 1.35 eV with a width nearly the same as the PC signal. One explanation for the presence of this peak, which we offer as an alternative to the extrinsic picture, is that it represents dissociation of a weakly bound exciton either thermally or through collision with surface states. In the lightly doped material, the coloumbic forces binding these excitons would be screened by carriers, and, indeed, we did not detect any signal at 1.35 eV in the phototransport response in any of these samples. It is well known that photoconductive can be much more sensitive than optical absorption in detecting the existence of weak transitions which eventually result in current-carrying particles. Interestingly, a very small absorption peak has in fact been observed in thick films of trans-(CH)$_x$ near 1.35 eV at 4.2 K by Bludau et al. [18]. Further studies on the temperature dependence of the phototransport and absorption properties of this structure would seem to be in order.

In conclusion, we have made the first comprehensive measurements of the phototransport properties of polyacetylene. For the photovoltaic response, this required the first fabrication of metal–semiconductor barriers in semiconducting (CH)$_x$ [19]. The PV threshold observed at 1.48 eV for lightly-doped trans-(CH)$_x$ yields a definitive value for the single-particle energy gap in this material. Unlike other organic insulators, this threshold occurs below the first maximum in optical absorption implying that strongly bound Frenkel-like excitons are not responsible for the optical properties of trans-(CH)$_x$ in the spectral region up to 3 eV. The energy dependence of the PV threshold is consistent either with a $3D$ joint density-of-states or with a $1D$ model of a continuum from which Wannier excitons have been split. In support of the latter notion is the observation of a peak in the photoresponse of undoped trans-(CH)$_x$ at 1.35 eV which may be the signature of dissociated weakly-bound Wannier excitons.

Finally, we will make some brief remarks about (CH)$_x$ as a useful photovoltaic device. We have obtained peak photovoltages of 80 mV under illumination with a collimated 18 W tungsten lamp filtered to remove i.r. radiation at wavelengths greater than $1\,\mu\mathrm{m}$ in spite of the poor transmittance of the In film ($\lesssim 0.1\%$). Thus efficiencies are presently quite low as can also be seen from the quantum yield and $\mu\tau$-product stated above. In fact, a rough estimate of the solar cell efficiency from these numbers yields roughly 0.002% under 1 sun (air mass 1) illumination. Nonetheless, the band gap of (CH)$_x$, and thus the absorption, matches the solar spectrum quite well. Given the low cost of the material, the fact that it can be produced by a low energy-intensive technology, that it could be easily fabricated in wide-area film form, and that we made no special effort to optimize junction properties, improvements in both material preparation and junction formation may bring nearer the possible use of (CH)$_x$ in solar applications.

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