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PHOTOCONDUCTIVITY IN TRANS $(CH)_x$

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Abstract A photogenerated electron-hole pair is supposed to evolve within 10^{-13}s into a soliton-antisoliton pair[1] and then, as deduced from photoinduced absorption measurements[2], to form either two neutral spin 1/2 SSH solitons or to separate into two charged solitons on neighbouring chains by interchain charge transfer. The efficiency of the interchain charge transfer and therefore the generation of charged solitons was determined to be $\leq 10^{-2}$. Since $(CH)_x$ shows light induced conductivity and since the charged solitons are the only species which move in the electric field we have tried to use photoconductivity techniques to complement the photoinduced absorption measurements by determining the quantum efficiency and also by trying to obtain information on the lifetime and mobility of the photoexcited species. The quantum efficiency as determined by photoconduction gives the fraction of excited electron-hole pairs which goes into conducting states and thus also the fraction which is left in bound states and/or subject to geminate recombination. Using ohmic contacts we found that the light induced currents were predominantly due to heating of the samples, whereas photocurrents were undoubtedly measurable with blocking contacts which allowed us to determine the quantum efficiency. The results on quantum efficiency will be discussed in view of the geminate recombination model and put in context with the results on photoinduced absorption.

INTRODUCTION

Comparison with theoretical models and information about the nature of electronic excitations in the photo-typical material $(CH)_x$ is essentially based on results of photoinduced absorption measurements. Photoinduced absorption gives results on those photoexcitations which are accompanied with a measurable change in absorption. In experiments on trans$(CH)_x$ two metastable gap

states have been found to appear under illumination at 1.4 eV and at 0.4 eV [3-7]. Both these states are only observable below ~150K and are quenched at room temperature[8]. The state of 0.4 eV has been interpreted as being due to weakly pinned solitons[3-5]. The pinning has been explained[9] by assuming that the solitons are bound at an equilibrium separation R_0 and the dissociation energy of the bound pair has been calculated to be consistent with the temperature of ~150 K observed for the onset of photoconductivity. The charged soliton, the only species which can be responsible for photoconduction, is generated with an efficiency of $\lesssim 10^{-2}$ [3]. The state at 1.4 eV has been argued to be due to a bound state of two neutral spin 1/2 SSH solitons[2]. Alternatively, it has been shown by computer simulation that the separating solitons leave behind a well-localized oscillatory "breather" excitation[10], which should show up in optical absorption as an absorption line below the continuum band edge. The presence of the photoinduced absorption at 1.4 eV is thus also in agreement with the notion that the photoexcited electron-hole pairs decay into charged solitons and breathers. Since the signature of the photogenerated charged soliton, pinned or unpinned, is the "midgap" absorption at ~0.4 eV and within the framework of the aforementioned theories also the absorption band at 1.4 eV and since the observation of these states is restricted to low temperatures the quenching of the photoinduced absorption raises the following questions: Is the efficiency for soliton generation (charged and/or bound solitons) reduced at room temperature due to an increase of geminate recombination? Why is at room temperature photoconductivity but no photoinduced absorption observable[11] if charged solitons are the only charge carriers?

It is the purpose of this work to reexamine the photogeneration of charge carriers in trans$(CH)_x$ by determining the relevant parameters from photoconductivity measurements and thus to complement the results obtainable by photoinduced absorption. Photoconductivity with ohmic contacts has been measured by various

authors[12-14] and used to determine the $\eta\mu\tau$ -product (η = quantum efficiency, μ = mobility, τ = lifetime). $\eta\mu\tau$ varied between 2.10^{-10} - 8.10^{-14} cm^2/V. Blocking contacts were used to construct solar cells[15-17] and an interpretation of the sub-bandgap response of the photovoltaic effect has been given by Galuzzi and Schwartz[18] in terms of geminate recombination, competing with soliton formation, whereas Weinberger[19] questions that the photovoltaic response can be explained in terms of solitons.

In this paper we will report on our experimental results which we have obtained at room temperature. An analysis of time dependent photocurrents allows, in principle, to obtain drift mobility and lifetime of the photoexcited species. Using blocking contacts, the quantum efficiency η can be determined. Since the quantum efficiency is the key parameter, we will focus our attention in this paper on η . Further details and results, in particular on the temperature dependence of the photoconductive process and on the determination of the depletion layer width and of the space charge density of the Schottky barrier from the time response of the photocurrents will be reported elsewhere.

EXPERIMENTS

Cis-rich $(CH)_x$ films were synthesized at -78°C with the Luttinger catalyst system. The film thickness ranged between 10 and 20 μm. Fully converted trans samples were made by heating cis-films at 180°C for 5 minutes. Ohmic and blocking contacts were prepared by evaporation of Au and Al, respectively. For semitransparent contacts in sandwich cells care was taken to have sufficient lateral conductivity of the contacts on the $(CH)_x$ in order to be sure of having a coherent metal film. The film thickness as well as the lateral conductivity were monitored during evaporation. The Al contacts had a thickness usually between 25-30 nm which resulted in a lateral resistance of $5\text{-}10 \cdot 10^2 \Omega$. The optical transmission of Al films ranged between 5.10^{-3} and 10^{-2} at λ = 630 nm. The

transmission of the Al films was usually measured between 200 nm $\leq \lambda \leq$ 800 nm so that appropriate corrections for the light intensity incident on the $(CH)_x$ could be made. The light sources were a Xe flash lamp for light pulses of 20 μs duration and a mercury high pressure lamp for light pulses of $\geq$ 5 ms duration produced with a shutter. A monochromator allowed to cover the wavelength range between 0.2 and 1.2 μm. Special care was taken for calibrating the light intensity with various calibrated detectors. It was found that the accuracy of light can only be given within 10% to 20% due to differences obtained with the different calibration detectors.

Photocurrents with ohmic contacts were measured in both, gap cells and sandwich cells. Since the photocurrents were only a small fraction of the dark current the question of heating of the samples and falsifying the results was pertinent. We found that the time constant of our gap cells decreased from 10^{-1} s to 10^{-3} s whenever the pressure of the sample chamber was increased from 10^{-6} Torr to atmospheric pressure by admission of nitrogen or when the thermal contact to the substrate was improved by glueing the $(CH)_x$ film directly to the sample holder. In order to be able to distinguish between heat and photoinduced changes of conductivity we decided to use sandwich cells with one semi-transparent electrode. If the heat is predominantly causing our signal, then a decrease of the transmission of the electrode should not affect the magnitude of the current induced by illumination. Otherwise it should decrease with decreasing transmission. We found (Figure 1) that decreasing the transmission of the electrode did not affect the magnitude of the current induced by light. Therefore, our results give only an upper limit to the $\eta\mu\tau$ -product which must be $\eta\mu\tau \leq 2.10^{-11}$ cm^2/V.

The photocurrents obtained with blocking Al-contacts[16, 17]

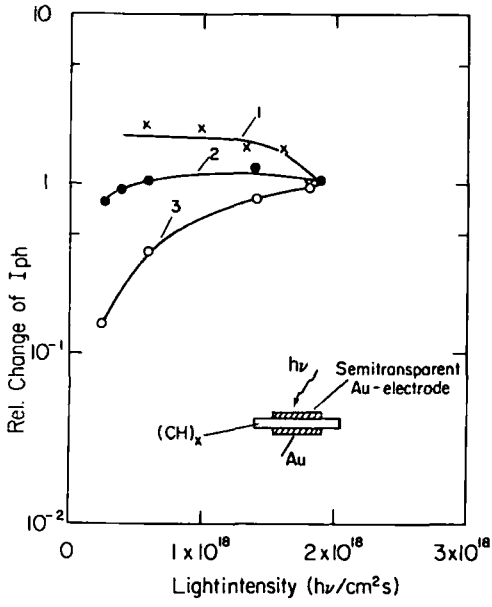

Fig. 1. Light induced current of two sandwich cells as a function of transmission of the semitransparent electrode. Both contacts are ohmic Au contacts. Curve (1) refers to a sample of 7.10^{-8}S/cm with a light induced current of $2.5 \cdot 10^{-10}$ A/V, curve (2) to a sample with $1.2 \cdot 10^{-6}$ S/cm and a light-induced current of 1.10^{-8} A/V. The light induced current is practically independent of the transmission of the semi-transparent electrode. Curve (3) was calculated assuming a linear relationship between photocurrent and transmitted light intensity.

were measured as a function of light intensity with voltage as parameter and as a function of voltage with the wavelength of the light as parameter. The photocurrents depend linearly on intensity at low light levels and tend to level off at high intensities (Figure 2). Measurements of the I_{ph}-V- characteristics and in particular the determination of the quantum efficiency as a function of the wavelength were made at light intensities at which the linear relationship between photocurrent and light intensity was valid.

The shape of the J_{ph}-V-characteristics is independent of the wavelength of the light. In Fig. 3 the peak photocurrent is plotted as a function of voltage at $h\nu$ = 1.96 eV for light pulses of 6 ms duration. The change-over from a square-root behaviour to a voltage independent saturation current occurs at approximately 2-3 V. From the relaxation time of the photosignal easily measurable with 20 μs light pulses the

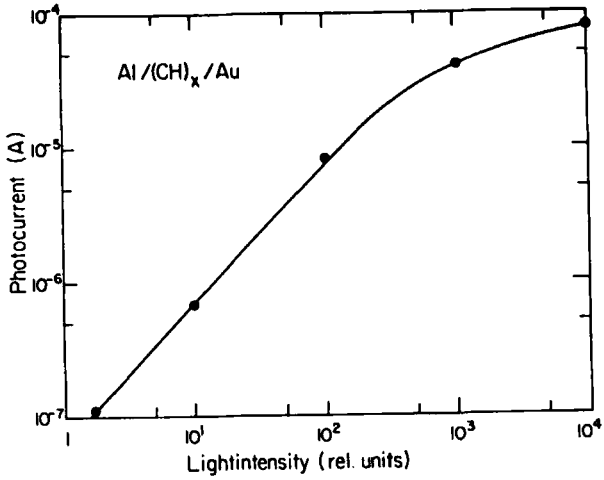

Fig. 2. Photocurrent as a function of light intensity of a sandwich cell. The semitransparent Al electrode forms a blocking contact to the $(CH)_x$. Applied voltage: 3V, electrode area: 7.1 mm^2, Light source: Xe Flash lamp.

density of charged states in the Schottky barrier can be calculated and hence the width w of the barrier as well as the electric field in the depletion region. It is found that w corresponds to the penetration depth of the light at the change-over voltage V_c of the I-V-characteristics, so that it can be safely assumed that in the saturation regime of the current all photons absorbed by the $(CH)_x$ are absorbed within the high-field region of the depletion layer. Thus, knowing the incident light intensity and the transmission of the Al electrode, the quantum efficiency η can be calculated without any further assumptions. Taking into account the width of the depletion layer at voltages below the voltage V_c we find that also there the quantum efficiency remains constant and equal to that determined in the saturation regime. From the voltage and the space charge density in the depletion region we can calculate the electric field and thus we find that the quantum

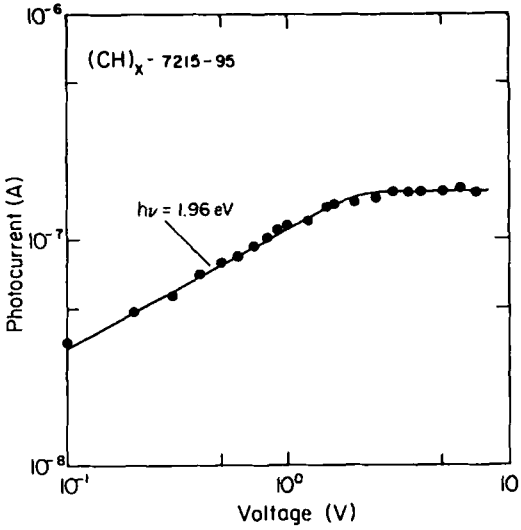

Fig. 3. Photocurrent as a function of voltage with a semitransparent blocking Al contact of area 7.1 mm^2. Light intensity $B_L = 2.3 \cdot 10^{-3}$ W, photon energy $E_{ph} = 1.96$ eV. The light intensity is attenuated by filters, windows and Al electrode to $2.8 \cdot 10^{12}$ photons/sec. The quantum efficiency obtained is $\eta = 0.35$. This value represents a lower limit, the upper limit being $\eta = 0.43$.

efficiency is independent of the electric field above 7.10^4 V/cm, this value representing the arithmetic average of the field across the depletion region.

The quantum efficiency as a function of photon energy is shown in Fig. 4. The quantum efficiency has a value of about 0.6 to 0.3 between 1.8 eV and 3.6 eV and drops to significantly lower values between 3.8 eV and 5 eV.

DISCUSSION

Our measurements on the quantum efficiency indicate a discrepancy with the results reported with PA in the "book keeping" of the photoexcited carriers though one has to keep in mind that our results refer to room temperature and those of PA to temperatures below 150 K, and furthermore that PA measurements are made without applied electric field. The question arises, therefore, whether the Onsager or Poole-Frenkel theory as discussed in Ref. 17 and 18 resp. might reconcile the differences. The quantum efficiency is in the Onsager theory composed of two terms and may be written as

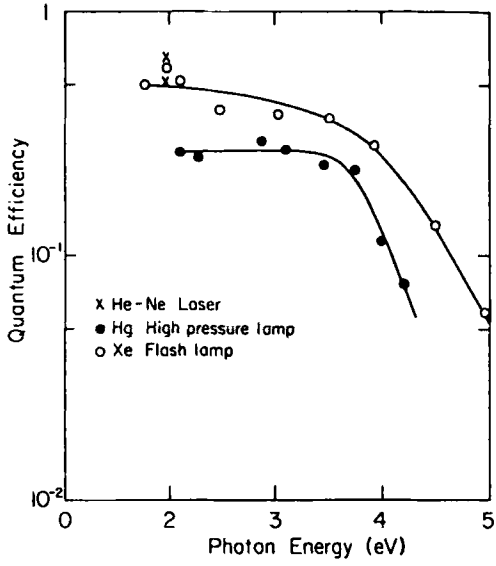

Fig. 4. Quantum efficiency as a function of photon energy. Results obtained from two cells. The differences are probably due to calibration errors.

$\eta = \eta_0 \cdot f(r,E)$ where η_0 is the yield of electrons/holes per photon transferred from bound states into the continuum states whereas f(r,E) is the efficiency of a thermalized pair at separation r for overcoming the mutual Coulomb attraction and for being separated in the electric field E. The thermalization radius r increases with increasing photon energy. Usually it is assumed that η_0 is independent of the electric field whereas $f(r,E) \ll 1$ and field independent for small electric fields and $f(r,E) \sim 1$ at high fields. Within the framework of this model the generation of charged solitons and of two neutral spin 1/2 SSH solitons could be enhanced at high fields at the expense of geminate recombination. Though an increase of the quantum efficiency was never observed with increasing field nor with increasing photon energy it cannot be excluded that the limiting value of the quantum efficiency η_0 is reached already at the lowest field of $\sim 5.10^4$ V/cm at which the measurements were taken. As a consequence, quantum efficiency should strongly decrease with decreasing field to a value significantly below 10^{-2}, and, vice versa, the photoinduced absorption peak at 0.4 eV should become strongly enhanced at fields $> 5.10^4$ V/cm, and become easily visible at room temperature. Since

however, to the best of our knowledge simultaneous observation of photoconduction and of photoinduced absorption has not been possible up to now, conventional semiconductor models cannot be excluded for explaining the phenomena.

The decrease of quantum efficiency is within the Onsager theory related to a change of η_0. Since η_0 decreases with increasing photon energy above ~3.5 eV, photo-excitation would lead to bound states (rather than into a continuum of states) with small probability of auto-ionization and thermalization of the electron-hole pair.

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