INFLUENCE OF SAMPLE THICKNESS, TEMPERATURE AND ELECTRIC FIELD STRENGTH ON MODULATED PHOTOCURRENTS IN POLY(N-VINYLCARBAZOLE)

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INTRODUCTION

One of the useful tools for determining the energetic density of states (DOS) in forbidden gap of amorphous solids is the analysis of sinusoidally modulated photocurrent (MPC). The photocurrent is due to carrier generation in the sample by modulated light beam and measured as function of modulation frequency. The technique has originally been used in experiments in coplanar sample configuration. Its theoretical description has been given by Oheda [1] and extended by Longeaud and Kleider [2,3]. Alternative formulae for determining the DOS have been proposed by Brüggemann *et al* [4] as well as by Hattori *et al* [5].

Later on, the MPC method has been adopted by Schumm and Bauer [6] for experiments in sandwich (time-of-flight, TOF) sample configuration in order to determine the DOS in well-photoconducting amorphous solids, particularly in hydrogenated silicon (*a*-Si:H). The analogous measurements were also performed by other autors, e.g. Amato *et al* [7] and Cohen and Zhong [8]. Results of more detailed theoretical investigations of the MPCs have been given by Tomaszewicz [9], Hattori *et al* [10] and Grygiel and Tomaszewicz [11]. Influence of some physical factors (the intensity of steady-state component of sample illumination, the light absorption depth in the sample, the effect of carrier diffusion) on MPCs has been examined by Grygiel *et al* [12] and Grygiel [13] . In this paper, the MPC theory is verified by measurements on poly(N-vinylcarbazole) (PVK). On the basis of the experimental results, energetic hole trap distributions in PVK has been determined.

THEORY

Expressions for the MPC

Theoretical description of the MPC has been developed in terms of the usual multiple-trapping model, under following assumptions: a) the photocurrent is due to transport of one-sign carriers, e.g. electrons, b) the density of carriers thermally generated in the sample can be neglected, which is the case of an insulating solid, c) the applied field is high enough to ignore the space-charge effect in the sample, d) the electrodes do not inject carriers into solid, and quickly neutralize the carriers of opposite sign arriving at them, e) the possible energy dependence of carrier capture coefficient and frequency factor are ignored. The set of carrier transport equations consists of continuity equation and equation describing the carrier trapping/detrapping kinetics. Considering linear sample response to the excitation (the case of shallow light modulation), assuming that the carriers are generated in a thin sample layer adjacent to the electrode and neglecting the carrier diffusion effects, one can write the following formula for the MPC oscillating term in the measuring circuit:
with the Fourier transform of the carrier-release distribution function

$$\Delta I(\omega) = \Delta I_0 \frac{1-\exp\left\{-i t_T \omega\left[1+\tilde{\Phi}(\omega)\right]\right\}}{i t_T \omega\left[1+\tilde{\Phi}(\omega)\right]}, \quad \Delta I_0 = \lim_{\omega\to 0} \Delta I(\omega) \tag{1}$$

$$\tilde{\Phi}(\omega) = C_t \int_0^\infty \frac{N_t(\varepsilon)\,d\varepsilon}{\left[1+C_t n_0 \tau_r(\varepsilon)\right]\left[i\omega + C_t n_0 + 1/\tau_r(\varepsilon)\right]} \tag{2}$$

[9,11]. Here, ε is the energy variable (ε is measured from the edge of conduction band), ω - the light modulation frequency, C_t - the carrier capture coefficient, $N_t(\varepsilon)$ - the trap density per energy unit. The remaining notations are as follows: n_0 is the dc-component of free carrier density, $\tau_r(\varepsilon) = \nu_0^{-1}\exp(\varepsilon/kT)$ is the mean carrier dwell-time in the trap (ν_0 denotes the frequency factor, k the Boltzmann constant and T the sample temperature), $t_T = L/\mu_0 E$ stands for the free-carrier time of flight with L - sample thickness, E – electric field strengh, μ_0 – the microscopic carrier mobility. The photocurrent (1) induced in the measuring circuit can be written in the form of

$$\Delta I(\omega) = \Delta I_m(\omega)\exp\left[-i\varphi_I(\omega)\right] \tag{3}$$

where $\Delta I_m(\omega)$ and $\varphi_I(\omega)$ stand for the MPC amplitude and phase shift, measured in the experiment. Thus, both changes of sample thickness,

sample temperature and/or field strength should affect the time t_T and, therefore, the course of the MPC amplitude and phase shift curves.

Determining the DOS from the MPC measurements

In order to obtain the information about the DOS one has to calculate the complex function (2) by comparison of equations (1) and (3). In the following, we shall adopt the notation [9]:

$$\varphi(\omega) = \omega t_T \, \mathrm{Re}\, \tilde{\Phi}(\omega), \tag{4}$$

$$\gamma(\omega) = -\omega t_T \, \mathrm{Im}\tilde{\Phi}(\omega). \tag{5}$$

For the case of surface carrier generation the functions $\varphi(\omega)$ and $\gamma(\omega)$ represent the phase shift and damping coefficient of the free carrier density wave propagating in the sample (cf. [11,12]). We shall also recall the definitions of demarcation energy and quasi-Fermi levels, given respectively by [1]

$$\varepsilon_0(\omega) = kT \ln(\nu_0/\omega), \tag{6}$$

$$\varepsilon_{f0} = kT \ln(\nu_0/\omega_f), \quad \omega_f = C_t n_0. \tag{7}$$

As it can be seen from equation (6), the mean release time of the carrier from the demarcation level equals to $\tau_t[\varepsilon_0(\omega)] = 1/\omega$. The quasi-Fermi level (7) separates the traps, almost completely filled ($\varepsilon > \varepsilon_{f0}$) and nearly empty ($\varepsilon < \varepsilon_{f0}$). Then, for a wide distribution of localized states, varying slowly in kT -energy range, the two ranges of modulation frequency can be distinguished with the following approaches valid.

$$\varphi(\omega) \approx \frac{\pi}{2} \tau_0 C_t kT N_t[\varepsilon_0(\omega)], \tag{8}$$

$$\gamma(\omega) \approx \tau_0 C_t \int_{\varepsilon_0(\omega)}^{\varepsilon_{f0}} N_t(\varepsilon) d\varepsilon. \tag{9}$$

For the frequencies $\omega >> \omega_f$, corresponding to $\varepsilon_0(\omega) < \varepsilon_{f0}$ one gets [9,10] Therefore, the shape of function $N_t(\varepsilon)$ can be directly determined using equations (8) and (9).

In the case of frequencies $\omega << \omega_f$, that is for $\varepsilon_0(\omega) > \varepsilon_{f0}$ one obtains [13]

$$\varphi(\omega) \approx \tau_0 C_t kT N_t(\varepsilon_{f0}) \frac{\omega}{\omega_f}, \tag{10}$$

$$\gamma(\omega) \approx \frac{1}{2} \tau_0 C_t kT N_t(\varepsilon_{f0} + kT \ln 2) \left(\frac{\omega}{\omega_f} \right)^2. \tag{11}$$

From equations (8) - (11) it is seen that the functions $\varphi(\omega)$ and $\gamma(\omega)$ change their form in vicinity of the frequency ω_f. Therefore, from the experimental data obtained for sufficiently high dc-intensity of excitation light, the value of the frequency ω_f, given by equation (7), can be

determined. This make it possible to calculate the value of the ratio C_t/μ_0, according to the formula

$$\frac{C_t}{\mu_0} = \frac{e\omega_r}{\sigma_0} \tag{12}$$

where $\sigma_0 = e\mu_0 n_0$ is the sample dc-specific photoconductance. In this way, the absolute values of the DOS can be obtained. The functions $\varphi(\omega)$ and $\gamma(\omega)$ can be determined by means of numerical methods from the overall courses of the measured MPCs. In certain modulation frequency ranges, the expressions relating functions $\varphi(\omega)$ and $\gamma(\omega)$ to the MPC phase shift and amplitude, $\varphi_1(\omega)$ and $\Delta I_m(\omega)$, simplify considerably. The corresponding formulae read as follows [9,10].

In the case of low modulation frequencies yielding $\varphi(\omega)$, $\gamma(\omega) << 1$ (weak damping of the carrier density wave) one can obtain from (1) - (5):

$$\varphi(\omega) \approx 2\varphi_1(\omega). \tag{13}$$

In the high frequency domain when $\gamma(\omega) > 1$ from (1) - (5) one gets:

$$\varphi(\omega) \approx \frac{\Delta I_0 \sin\varphi_1(\omega)}{\Delta I_m(\omega)} \tag{14}$$

and

$$\gamma(\omega) \approx \frac{\Delta I_0 \cos\varphi_1(\omega)}{\Delta I_m(\omega)}. \tag{15}$$

In the intermediate frequency range the MPC phase shift exhibits oscillatory behaviour. In the case of weakly dispersive transport, when $\varphi(\omega)/\gamma(\omega) \cong 1$, the maxima of $\varphi_1(\omega)$ occur for the values of carrier density phase given by [11,13]

$$\varphi(\omega_n) \approx (2n-1/2)\pi, \quad n = 1,2,3,.... \tag{16}$$

As mentioned in section 2.1, theoretical description of the experiment concerns the case of weakly photoconductive solid and neglected space-charge effects in the sample. This means that during the measurements the following criteria should be fulfilled:

criterion for omitting the carrier relaxation [9,11,13]

$$\omega >> 1/\tau_M \tag{17}$$

where

$$\tau_M = \kappa\kappa_0/\sigma_0 \tag{18}$$

stands for the Maxwell relaxation time (κ is the dielectric constant, κ_0 – the permittivity of free space),

criterion for neglecting the space-carrier effect in the sample

$$\frac{\sigma_0 L^2 S}{\kappa\kappa_0 e\mu} << V_0 \tag{19}$$

with S – the sample area, μ - the allowed-band carrier mobility ($\mu \geq 0.1$ V/cm^{2}s), e – the elementary charge, V_0 - the applied sample voltage. Moreover, the MPC formula (1) becomes much more complicated for significantly diffusive carrier transport. The influence of diffusion effect on MPCs can be neglected provided that [9,13]

$$\varphi(\omega), \gamma(\omega) << \frac{eV_0}{kT} \tag{20}$$

where $\varphi(\omega)$ and $\gamma(\omega)$ are experimentally established values of density-of-state functions (8)-(11).

In figure 1 exemplary courses of the MPCs phase shift and amplitude are shown, obtained for the case of exponential trap distribution given by expression

$$N_t(\varepsilon) = \frac{N_{tot}}{kT_c} \exp\left(-\frac{\varepsilon}{kT_c}\right) \tag{21}$$

where N_{tot} is the total trap density and T_c the characteristic temperature. The curves have been calculated for four values of dc-illumination, i.e. for four positions of the quasi-Fermi level below the mobility edge. As can be seen, the MPC phase shift increases monotonically in the low modulation frequency range. In the intermediate frequency domain the phase curves exhibit oscillations being more and more strongly damped with the increase of ω. In the same frequency range one can recognize some anomalies in behaviour of the MPC amplitude curves. For limiting cases of low- and high-modulation frequencies the MPC phase shift does not significantly depend on the dc-illumination intensity. With the increase of dc-component of the illumination the oscillations of $\varphi(\omega)$ become more and more distinct and their maxima shift towards higher frequencies. Figure 1b indicates that the MPC amplitude decreases monotonically with modulation frequency. In the low-frequency range the ratio $\Delta I_m/\Delta I_0 = 1$ for sufficiently high dc-illumination level which makes it possible to determine the value of ΔI_0 from experimental data. The presented results have been obtained for relatively high value of the dispersion parameter $T/T_c = 0.8$, that is for the case of weakly dispersive transport. With decreasing T/T_c, the MPC phase oscillations become less and less distinct.

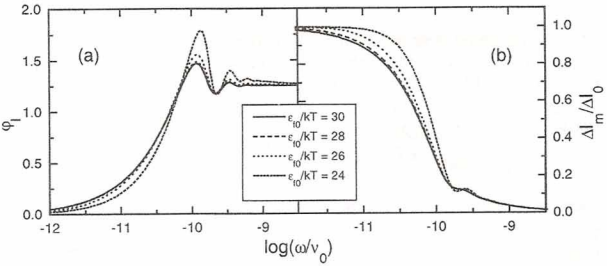

Figure 1. MPC phase shift (a) and amplitude (b) for exponential trap distribution and different positions of the quasi-Fermi level, determined by the values of ε_{f0}/kT. The calculations have been carried out for $T/T_c = 0.8$, $\tau_0\nu_0 = 10^{-5}$ and $C_t N_{tot} = 10^{13}$

EXPERIMENTAL RESULTS

MPCs in poly(N-vinylcarbazole)

Below we give exemplary results of MPCs measurements obtained for 7.0 μm, 14.5 μm and 23.2 μm thick PVK layers sandwiched between 9 mm^2 gold electrodes. The film thicknesses have been determined from capacitance measurements ($\kappa = 3.5$). The photocurrent was due to hole photoemission into PVK from the front semitransparent electrode, illuminated by red light of high-emission LEDs. Sample preparation as well as experimental set-up are described in [12] and [13]. The MPC measurements have been made at sample temperatures ranging from 293 K to 383 K and electric field strength of 2.86×10^5 V/cm, 3.57×10^5 V/cm and 4.29×10^5 V/cm, for the same illumination intensities. The depth of modulation was approximately equal to 20 %. Making use of expression (18) it has been established that the Maxwell carrier relaxation time in the samples was not shorter then 200 s. According to formula (17), in the experimental frequency range the influence of relaxation effects on the MPCs could then be omitted. As results from (19), the applied sample voltage should meet the condition $V_0 >> 6$ V, whereas from (20) one results $V_0 >> 12$ V. Thus, both the influence of space-charge effects as well as carrier diffusion in the sample on experimental results could also be neglected.

Figure 2 shows the exemplary MPC phase shift $\varphi_1(\omega)$ and amplitude $\Delta I_m(\omega)$ functions obtained for constant sample thickness and constant sample temperature, for three different values of electric field strength. The measured courses are similar to that predicted theoretically. In particular, for lower modulation frequencies the MPC phase shift increases monotonically and exhibits a distinct maximum for

intermediate modulation frequencies whereas the MPC amplitude decreases in entire frequency range. The measurements of the MPCs for higher modulation frequencies were not possible, since the photocurrent became too weak to be detected. For technical reasons the measurements could only be performed for relatively low dc-excitation and no changes in MPCs behaviour due to various position of quasi-Fermi level were observed. As can be seen, with

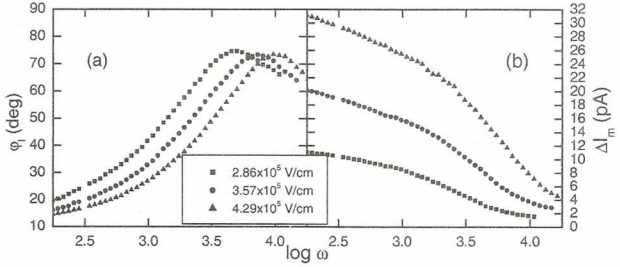

Figure 2. MPC phase shift (a) and amplitude (b) as measured in PVK 7μm thick film at temperature of 343 K and different values of electric field strength

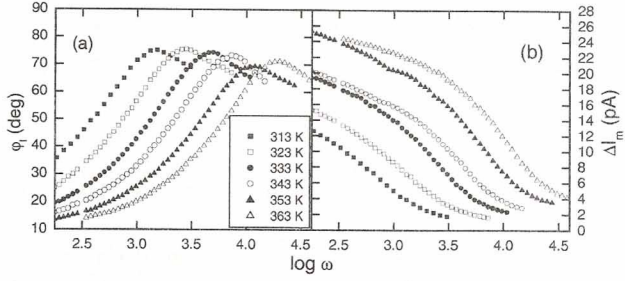

Figure 3. MPC phase shift (a) and amplitude (b) in PVK 7μm thick film at field strength of 3.57×10^5 V/cm for different values of sample temperature

increasing electric field strength the $\varphi(\omega)$ and $\Delta I_m(\omega)$ curves shift towards higher frequencies. The shift of mentioned curves towards higher modulation frequencies have also been observed for for increasing sample temperature at constant sample thickness and

constant electric field strength, as indicated in figure 3. Analogous behaviour of the MPCs was also noticed for remaining sample thicknesses.

In figure 4 we present the plots of MPC phase shift and amplitude curves, obtained for different sample thicknesses, at constant values of temperature and electric field strength. The figure shows that the increase in sample thickness results in shift of both functions towards lower modulation frequencies.

The observed behaviour of the $\varphi(\omega)$ and $\Delta I_m(\omega)$ functions stays in accordance with results of theoretical investigations. From the equation (1) it is seen that shorter free carrier time-of flight t_T should essentially result in shift of the MPC phase and amplitude curves towards higher frequencies and vice versa. As reported in numerous papers on the subject, the effective hole mobility as well as parameters of localized states in PVK could depend on electric field strength. However, according to results from figure 4 the carrier transport was not affected both by changes in

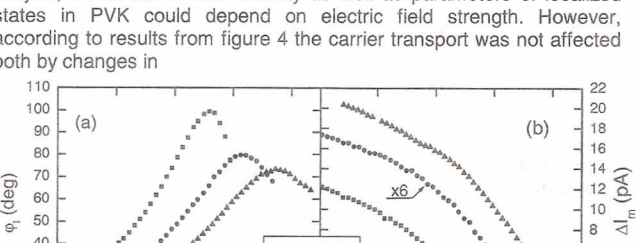

Figure 4. MPC phase shift (a) and amplitude (b) for different values of PVK sample thicknesses, measured at temperature of 343 K and electric field strength of 3.57×10^5 V/cm

temperature as well as by changes in electric field. This means that under experimental conditions, the frequency shift of the MPC phase and amplitude functions was only due to changes in free holes time-of-flight.

Profiles of hole traps in poly(N-vinylcarbazole)

The results of the MPC experiment obtained under various experimental conditions (sample thickness, sample temperature and field strength) have been used to the study of DOS in PVK. Only relative differential and integrated DOS could be obtained, for the

measurements have been performed for relatively low dc-excitation (cf. section 2.2):

$$N_{diff}(\varepsilon) = \frac{C_t}{\mu_0} N_t(\varepsilon), \quad N_{int}(\varepsilon) = \frac{C_t}{\mu_0} \int_{\varepsilon}^{\varepsilon_{f0}} N_t(\varepsilon') d\varepsilon'.$$

In figure 5 we compare the exemplary DOS obtained by means of numerical calculations from the overall courses of the measured MPCs. From the figure it is seen that expression (13) reconstructs the DOS with good accuracy. The visible discrepancies gradually diminish with increasing trap depth, i.e with decreasing modulation frequency. We were not able to calculate the DOS using expressions (14) and (15) because of the lack of high-frequency experimental data.

Figure 6 exhibits the differential and integral DOS profiles in PVK. The solid lines represent the mean values of the trap densities calculated numerically using the set of 50 MPC phase shift and amplitude curves. Dashed lines represent maximal mean-value-errors for individual profiles. It is seen that in the energy interval 0.525 eV–0.625 eV the distributions of hole traps in PVK are not exponential. The mean value of the differential distribution characteristic energy is about 0.05 eV.

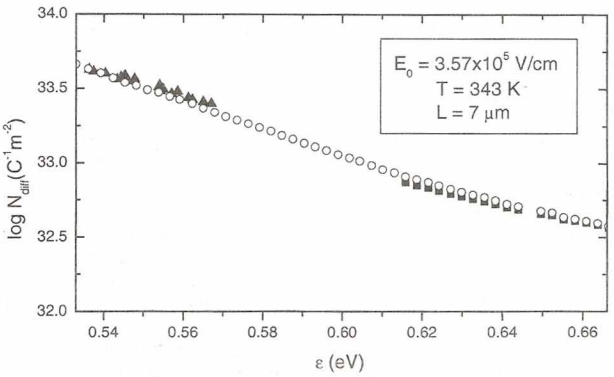

Figure 5. Exemplary differential DOS in PVK, obtained with the use of: (o) – equations (1)-(3) in entire modulation frequency range; (v) – expression (13) for low modulation frequencies; (▲) – expression (16) in intermediate frequency range. The energy scale corresponds to frequency factor $\nu_0 = 10^{12}$ Hz

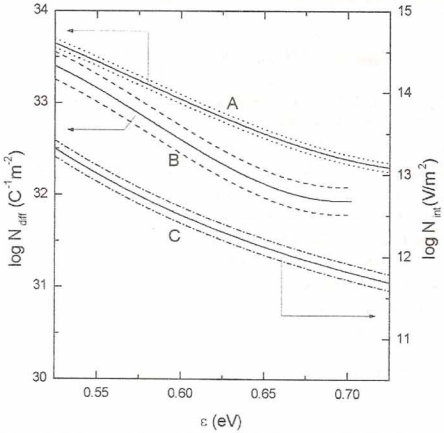

Figure 6. Plots of differential and integral hole trap distributions in PVK. The individual curves are obtained: (A) with the use of equations (4) and (8), (B) – by numerical differentiation of formulae (5) and (9), (C) – using expressions (5) and (9)

CONCLUSIONS

The theory of the MPC experiment in sandwich sample configuration is verified by measurements on poly(N-vinylcarbazole) (PVK). We have investigated the influence of various experimental conditions on the MPCs. The shape of the MPC phase shift and amplitude curves stay in agreement with the theory. The increase/decrease in free hole time-of-flight due to various sample thickness, sample temperature and electric field strength result in a shift of the phase and amplitude curves towards lower/higher frequencies. This also stays in agreement with theoretical predictions.

On the basis of the experimental results, the energetic DOS in PVK has been determined. The approximate expressions for determining the DOS in the low- and intermediate frequency domain are found to be of good accuracy. In the energy interval 0.525 eV–0.625 eV the distributions of hole traps in PVK are not exponential. The mean value of the differential distribution characteristic energy is approximately equal to 0.05 eV.

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