Carrier Lifetime and Phase Retardation of the Photoresponse of Photovoltaic Materials

Tsanimir Angelov[1], Vesselin Donchev[1], Stefan Georgiev[1] and Kiril Kirilov[1]

[1] *Faculty of Physics, Sofia University, 5, J.Bourchier blvd., Sofia-1164, Bulgaria*

Abstract. We present a theoretical study of the photo-response of photovoltaic materials to rectangular modulated light excitation with frequency *f*. A simple relation is proposed between its phase retardation $\Delta\varphi$ with respect to the light sequence based on the geometrical centre t_c of the pulse shape. In the case of linear recombination regime, knowing t_c has allowed deriving an analytical expression between $\Delta\varphi$ and the product τf, where τ is the minority carrier lifetime. For quadratic recombination, a numerical analysis shows that $\Delta\varphi$ depends not only on *f* but also on the photon flux Φ, the absorption coefficient α and the recombination coefficient γ. The proposed approach allows from the experimental value of $\Delta\varphi$ to determine τ in the case of linear recombination and the stationary minority carrier lifetime τ_{st} in the case of quadratic recombination (if Φ, α and γ are known).

Keywords: photo-response, phase retardation, carrier lifetime, recombination, photovoltaic materials

1. INTRODUCTION

In the studies of photovoltaic materials, usually one investigates the material response to light excitation. The response, called photo-response, can be measured e.g. as current (Ryvkin, 1964), voltage (Donchev *et al.*, 2010), light emission (Brüggemann and Reynolds, 2006; Chouffot *et al.*, 2009), etc. Studying the dependence of the photo-response on the frequency of the light modulation provides information on the kinetics of the charge carrier generation and recombination processes. Such information is important to determine key material parameters, such as minority carrier lifetime τ and diffusion length.

The photo-response is characterized by the shape of its pulses and by its phase retardation $\Delta\varphi$ with respect to the light excitation sequence with frequency *f*. In the case of sinusoidal modulated light a simple relation exists between τ and $\Delta\varphi$, namely $\mathrm{tg}\Delta\varphi = 2\pi f\tau$, as reported for photoconductivity (Ryvkin, 1964) and photoluminescence (Brüggemann and Reynolds, 2006; Chouffot *et al.*, 2009) processes. A detailed theoretical analysis of ac photoconductivity in amorphous semi-conductors (Longeaud and Kleider, 1992) relates $\Delta\varphi$ with a combination of electron and hole mobilities and concentrations. The situation is more complicated for rectangular light modulation where we could not find a quantitative relation between $\Delta\varphi$ and τ reported in the literature. A qualitative discussion about the relation between $\Delta\varphi$ and the absorption coefficient α is presented in (Donchev *et al.*, 2010) showing that it is realized via the momentary carrier lifetime $\tau(t)$.

In this work, we consider the case of rectangular light modulation and derive a simple analytical relation between $\Delta\varphi$ and τ in the case of linear recombination regime. For quadratic recombination regime, a numerical analysis is performed to study the dependence of $\Delta\varphi$ on *f*, α and the photon flux Φ.

2. GEOMETRICAL CENTRE OF THE PULSE SHAPE

The theoretical way to relate $\Delta\varphi$ and τ is based on determining the geometrical centre of the pulse shape. This is justified, because the common instruments used to study such photo-responses are lock-in amplifiers. These devices amplify a certain frequency of the signal, using two multiplications with two sinusoidal signals with equal frequencies - one main signal and a second one with phase shift of 90 degrees. This way, based on the two products the measured signal is presented as a sinusoidal signal with peak at the geometrical centre of the actual signal and the phase retardation is taken relative to the main signal. The geometrical centre t_c of the pulse shape is calculated as the "centre of masses" of the pulse as follows.

$$t_c = \frac{\int_0^T t[\Delta n(t) - \Delta n(0)]dt}{\int_0^T [\Delta n(t) - \Delta n(0)]dt} \quad , \tag{1}$$

where the integration is over one period of the modulation $T = 1/f$. The phase retardation cannot exceed 90° and correspondingly $T/4 \leq t_c \leq T/2$. It is easy to realize that

$$\Delta\varphi = \frac{360^o}{T}\left(t_c - \frac{T}{4}\right) \tag{2}$$

3. LINEAR RECOMBINATION

In this regime after the beginning of the illumination, the excess carrier density rises exponentially and asymptotically to its stationary value for constant illumination Δn_{st}. If the light excitation is not constant but with rectangular shape, Δn oscillates around half of its stationary value with an amplitude of Δn_{st} - 2a, where a is given by (Ryvkin, 1964):

$$a = \Delta n_{st} \frac{\exp\left(-\frac{T}{2\tau}\right)}{1 + \exp\left(-\frac{T}{2\tau}\right)} \tag{3}$$

To calculate t_c from Eq.1 we need $\Delta n(t)$. It is easy to show that it is given by:

$$\Delta n(t) = a + (\Delta n_{st} - a)\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{4a}$$

for light on, i.e. $t \in \left(0, \frac{T}{2}\right)$ and

$$\Delta n(t) = (\Delta n_{st} - a)\exp\left(-\frac{t - T/2}{\tau}\right) \tag{4b}$$

for light off, i.e. $t \in \left(\frac{T}{2}, T\right)$.

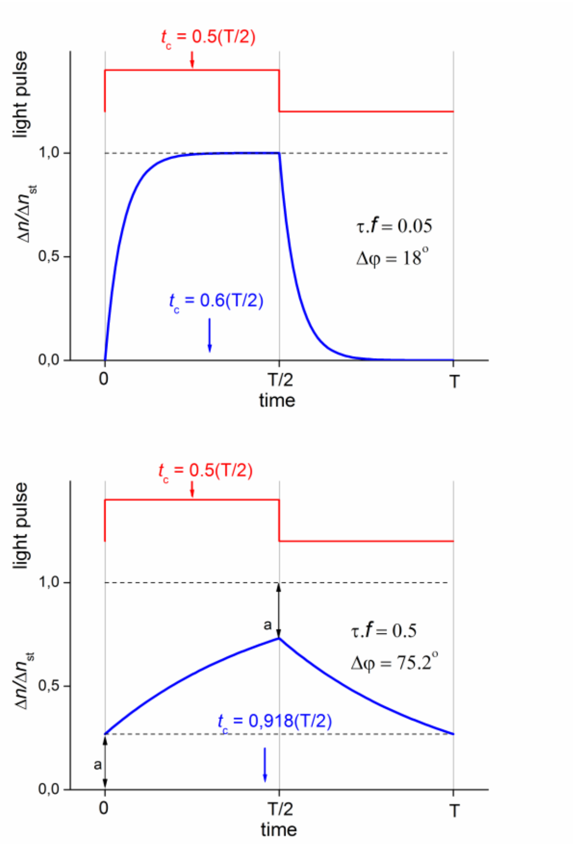

Fig.1 Transients $\Delta n(t)$ for a fast (up) and a slow (down) process with respect to the light modulation in the case of linear recombination. The geometrical centres of the pulses are indicated.

Fig.1 presents the transients $\Delta n(t)$ for a faster and a slower process with respect to the light modulation. Substituting Eq.4 in Eq.1 we solve the integrals analytically and end up with the following formula, relating the phase retardation to the product of the excess carrier lifetime and the excitation frequency.

$$\Delta\varphi(f\,\tau) = 360^o f\,\tau - \frac{180^o}{exp\left(\frac{1}{2f\tau}\right) - 1} \tag{5}$$

The relation presented by Eq.5 is plotted on Fig.2. It is seen that increasing f or τ leads to an increase of $\Delta\varphi$. In addition, $\Delta\varphi$ asymptotically tends to zero for low τf values and to 90° for high τf values. The dependence $\Delta\varphi(\tau f)$ is steepest for intermediate τf values $0.04 < \tau f < 1$. Eq.5 and Fig.2 allows quick and easy determining the minority carrier lifetime of the material under study from the experimental values of the phase retardation and the light modulation frequency.

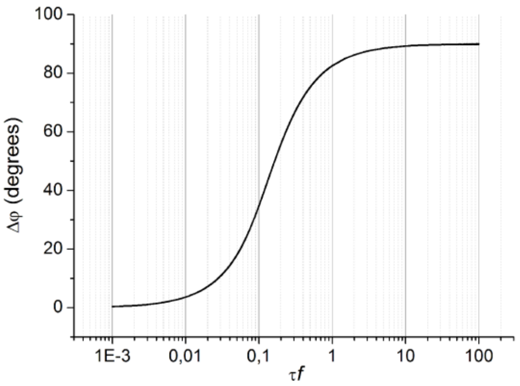

Fig.2 Dependence of the phase retardation on the product of the carrier lifetime and the excitation frequency calculated by means of Eq.5.

4. QUADRATIC RECOMBINATION

The transient $\Delta n(t)$ follows a hyperbolic tangent law in the light semi-period and 1/t law in the dark one (Ryvkin, 1964).

$$\Delta n(t) = \Delta n_{st} th(t\sqrt{\gamma\beta\alpha\Phi}) \tag{6a}$$

$$\Delta n(t) = \Delta n_{st}\frac{1}{t\sqrt{\gamma\beta\alpha\Phi}+1} \tag{6b}$$

with $$\Delta n_{st} = \sqrt{\frac{\beta\alpha\Phi}{\gamma}}\ . \tag{6c}$$

Under rectangular light modulation, Δn oscillates with amplitude equal to Δn_{st} - b - c, where b is its minimum value, while its maximum value is $\Delta n_{st} - c$. It is easy to show that in the light and dark semi-periods the transients are:

$$\Delta n(t) = b + (\Delta n_{st} - b) th(t\sqrt{\gamma\beta\alpha\Phi}) \tag{7a}$$

$$\Delta n(t) = (\Delta n_{st} - c)\frac{1}{(t-\frac{T}{2})\sqrt{\gamma\beta\alpha\Phi}+1}\ , \tag{7b}$$

respectively, where

$$b = \frac{\Delta n_{st} th\left(\frac{T}{2}\sqrt{\gamma\beta\alpha\Phi}\right)}{\frac{T}{2}\sqrt{\gamma\beta\alpha\Phi} + th\left(\frac{T}{2}\sqrt{\gamma\beta\alpha\Phi}\right)}\ , \tag{8}$$

$$c = \frac{\Delta n_{st}\frac{T}{2}\sqrt{\gamma\beta\alpha\Phi}\left(1 - th\left(\frac{T}{2}\sqrt{\gamma\beta\alpha\Phi}\right)\right)}{\frac{T}{2}\sqrt{\gamma\beta\alpha\Phi} + th\left(\frac{T}{2}\sqrt{\gamma\beta\alpha\Phi}\right)}\ . \tag{9}$$

The transients given by Eq. 7 are plotted on Fig.3 for two frequencies – 20 Hz and 200 Hz and α = 428 cm^{-1}, Φ = 3.5x10^{13} cm^{-2}s^{-1}, γ = 1.48x10^{-11}cm^{3}s^{-1}, and assuming a quantum efficiency β = 1. It is worth noting that the value around which Δn oscillates is not 0.5 Δn_{st} (as it was for the linear recombination), but is higher. Indeed, b > c on Fig.3. This is due to the lack of "symmetry" of Δn increase and decrease – as seen from Fig. 3, the decrease is slower than the increase.

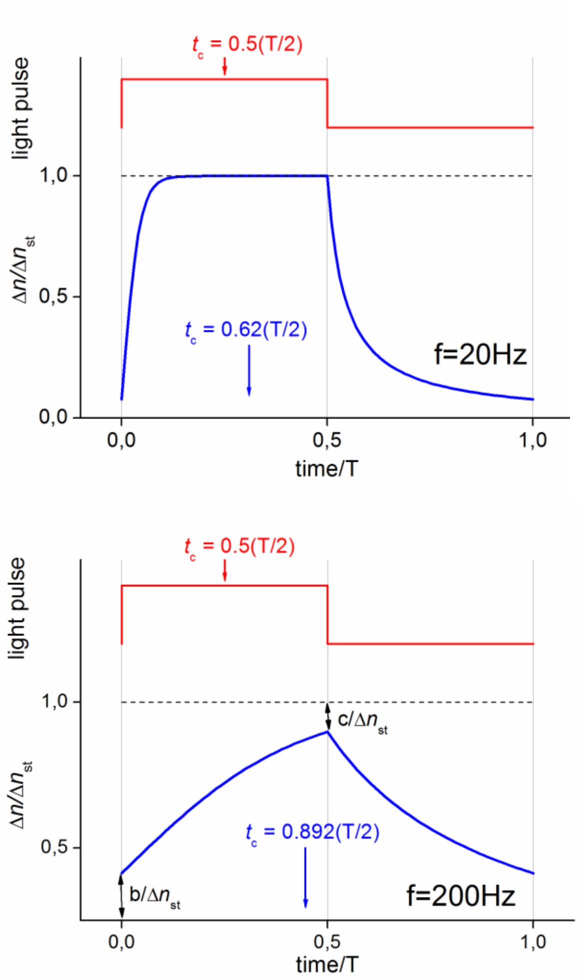

Fig.3 Transients Δn(t) for a fast (up) and a slow (down) process with respect to the light modulation with frequency f in the case of quadratic recombination.

The effective carrier lifetime τ changes with time and the momentary lifetime is calculated as $\tau(t) = 1/\gamma\Delta n(t)$ (Ryvkin, 1964). It is plotted on Fig.4 using the same values of the parameters as in Fig.3. One can see that depending on the modulation frequency, $\tau(t)$ can reach a stationary value τ_{st} during the light semi-period. This value is in fact the relevant one for PV applications. The value of τ_{st} can be determined by choosing appropriate values of α, β, Φ and γ so that t_c, calculated by putting Eq.7 in Eq.1 provides via Eq.2 the experimentally obtained $\Delta\varphi$ value.

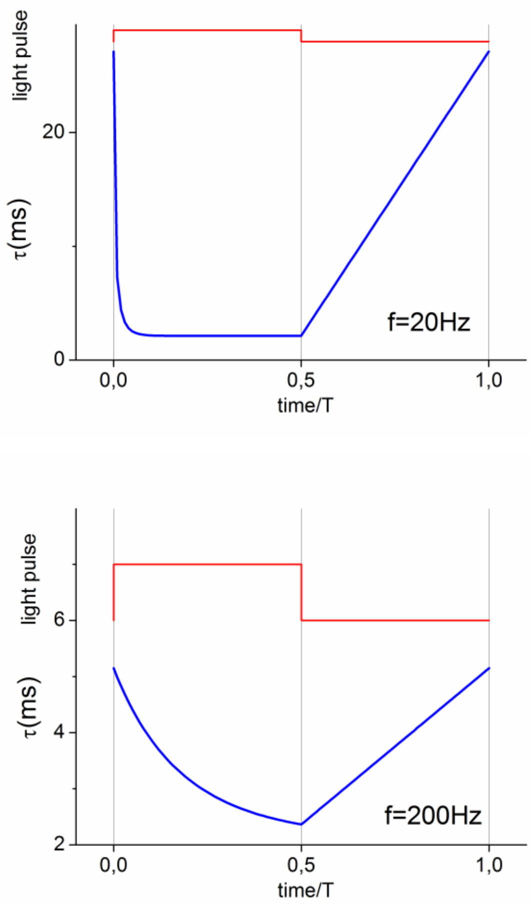

Fig.4 Momentary carrier lifetime for light modulated with 20 and 200 Hz corresponding to the transients from Fig.3.

To study the factors influencing $\Delta\varphi$ a numerical integration of Eq.1 is performed to calculate t_c, and $\Delta\varphi$ is found by means of Eq.2. This is done for $\gamma = 1.48\text{x}10^{-11}\text{cm}^3\text{s}^{-1}$, $\beta = 1$ and a number of values of Φ, α and f. The results are presented on Fig.5. It is seen that at a fixed value of the generation rate $\beta\alpha\Phi$ and low (high) frequency, the phase retardation asymptotically reaches its minimum (maximum) value of 0^o (90^o). On the other hand for a fixed frequency, $\Delta\varphi$ tends to 0^o (90^o) for high (low) values of $\beta\alpha\Phi$. Therefore small phase retardation is achieved at low frequencies and high excitation. It is worth noting also that $\Delta\varphi$ changes quicker for intermediate values of f and $\beta\alpha\Phi$, respectively.

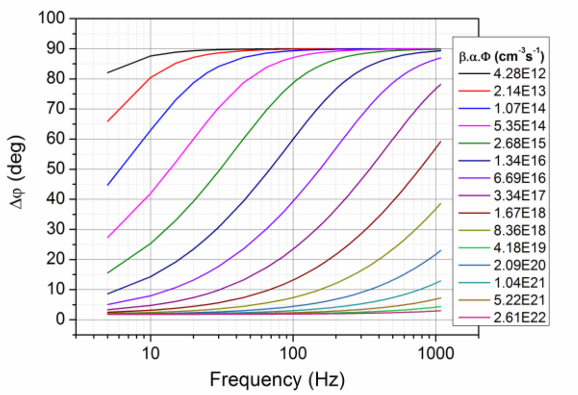

Fig.5 Phase retardation in the case of quadratic recombination regime as a function of the light modulation frequency for a number of values of the generation rate $\beta\alpha\Phi$.

5. CONCLUSIONS

An original relation is proposed between the shape of the photo-response pulse in photovoltaic materials and its phase retardation $\Delta\varphi$ with respect to the light excitation sequence. In the case of linear recombination regime, $\Delta\varphi$ gives directly the minority carrier lifetime via an analytical relation (5) derived in this work. In addition, it is shown that $\Delta\varphi$ asymptotically tends toward 0^o for low values of the product $f\tau$, i.e. for low frequencies and/or fast recombination processes. For high frequencies and/or slow recombination processes $\Delta\varphi$ tends towards 90^o. In the case of quadratic recombination, $\Delta\varphi$ can provide an estimation of the stationary minority carrier lifetime. It asymptotically tends toward 0^o (90^o) for low (high) frequencies and for high (low) values of the generation rate $\beta\alpha\Phi$. The performed analysis have also shown that the value of $\Delta\varphi$ is more sensitive to changes of the light modulation frequency and generation rate when their values are away from the extreme cases of very high, or very low values. Intermediate values of f and $\beta\alpha\Phi$ are therefore more favourable to exploit $\Delta\varphi$ for estimation of the minority carrier lifetime.

AKNOWLEDGEMENTS

The Cost Action MP1406 „Multiscale in modelling and validation for solar photovoltaics (MultiscaleSolar) and the Bulgarian National Science Fund (contract ДКОСТ 01/16) supported this work.

REFERENCES

Brüggemann, R., & Reynolds, S., 2006. Modulated photoluminescence studies for lifetime determination in amorphous-silicon passivated crystalline-silicon wafers. *Journal of Non-Crystalline Solids*, *352* (9), 1888–1891.

Chouffot, R., Brezard-Oudot, A., Kleider, J.-P., Brüggemann, R., Labrune, M., i Cabarrocas, P. R., & Ribeyron, P.-J., 2009. Modulated photoluminescence as an effective lifetime measurement method: Application to a-Si:H/c-Si heterojunction solar cells. *Materials Science and Engineering: B*, *159–160* (Supplement C), 186–189.

Donchev, V., Ivanov, T., Germanova, K., & Kirilov, K., 2010. Surface photovoltage spectroscopy – an advanced method for characterization of semiconductor nanostructures. *Trends in Applied Spectroscopy*, *8*, 27–66.

Longeaud, C., & Kleider, J. P., 1992. General analysis of the modulated-photocurrent experiment including the contributions of holes and electrons. *Phys. Rev. B*, *45* (20), 11672–11684.

Ryvkin, S. M., 1964, *Photoelectric effects in semiconductors*. New York, Consultants Bureau.