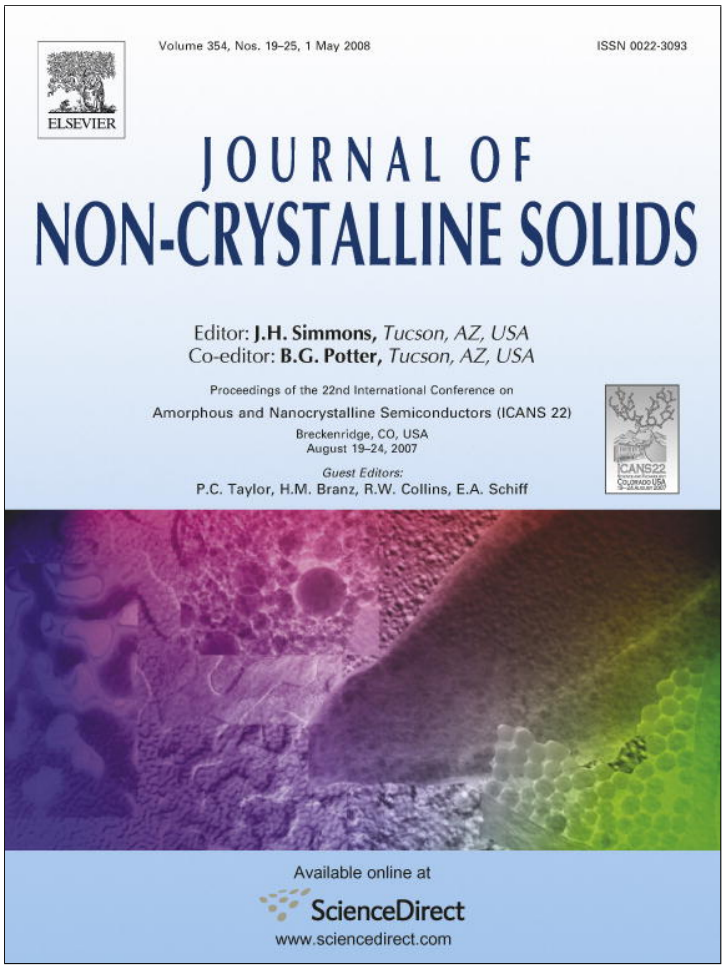

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Modulated photoconductivity in the high and low frequency regimes

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Abstract

Different methods have been proposed to use modulated photoconductivity (MPC) measurements in order to extract information about the density of states (DOS) within the gap of defective semiconductors. Depending on the frequency of the modulation, two regimes have to be considered: the high frequency (HF) and the low frequency (LF) regimes. In this paper, we use computer-generated data, obtained from the complete solution of the MPC equations, to test the different procedures proposed to treat the MPC data in both regimes. We show that Brüggemann's method provides an accurate reconstruction of the introduced DOS provided the capture coefficients are known, while in the LF limit of Kounavis' method a factor of two is missing. We also test the accuracy of different procedures proposed to extract the capture coefficients of the defects, which are necessary to get absolute DOS values in the methods that utilize the HF regime. The LF–MPC method, on the other hand, has the advantage that the capture coefficients are not needed.

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Keyword: Photoconductivity

1. Introduction

Amorphous and nanocrystalline semiconductors usually exhibit a considerable density of localized energy levels within the forbidden gap, associated with defect states. These levels are generally the most efficient recombination centers, thus controlling the electrical transport properties. Among the methods developed to obtain the density of states (DOS) within the gap of photoconductive semiconductors, the modulated photoconductivity (MPC) technique attracted considerable attention due to its accuracy and experimental simplicity [1–9]. In this method, a biased sample is illuminated with a light flux partially modulated with a pulsation ω, while the modulus $|\sigma_{ac}|$ and phase shift Φ of the resulting ac photoconductivity are recorded. Depending on the frequency of the modulation, two regimes have to be considered: the high frequency (HF) regime, where trapping and release processes dominate the photoconductivity, and the low frequency (LF) regime, where recombination dominates [3,10,11].

In this paper we will discuss different methods proposed to extract the DOS from MPC measurements, both in the HF and LF regimes. We will also test the accuracy of different procedures proposed to extract the capture coefficients of the defects, which are necessary to get absolute DOS values.

2. The modulated photoconductivity in the different regimes

Let us consider a semiconductor having m species of trapping states within its gap, each species with a density $N^i(E)$ and with capture coefficients c_n^i (c_p^i) for electrons (holes). Writing n_{dc} (p_{dc}) the electron (hole) concentration in the extended states generated by the dc contribution of the light, it has been shown in previous works [1–5] that in the HF regime, established when $\omega \gg \omega_t^i = c_n^i n_{dc} +$

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$c_p^i p_{dc}$ for all the species of states, and for the case that electrons dominate the photoconductivity, the following expressions provide the basis for a DOS spectroscopy

$$\sum_{i=1}^{m} \frac{c_n^i N^i(E_{\omega n}^i)}{\mu_n} = -\frac{2qG_{ac}}{\pi k_B T} \frac{\sin(\Phi)}{|\sigma_{ac}|}, \quad (1)$$

$$E_c - E_{\omega n}^i = k_B T \ln\left(\frac{c_n^i N_c}{\omega}\right), \quad (2)$$

where μ_n is the electron mobility, q is the absolute value of the electron charge, G_{ac} is the ac generation rate, k_B is Boltzmann's constant, T is the absolute temperature, and N_c is the effective DOS at the conduction band edge. Note that each species of states will be responding at a different energy $E_{\omega n}^i$ for the same frequency of the light excitation, so a proper energy scaling could be difficult. However, usually there is only one dominant level, and Eq. (2) simply transforms into $E_c - E_{\omega n} = k_B T \ln(\frac{c_n N_c}{\omega})$.

On the other hand, when the MPC experiment is performed at low frequencies such that $\omega \ll \omega_t^i$ for all i, the equations providing the basis for a DOS spectroscopy would be [12–14]

$$\sum_{i=1}^{m} N^i(E_{Fn}) = -\frac{2G_{dc}}{k_B T} \frac{\tan(\Phi)}{\omega}, \quad (3)$$

$$E_c - E_{Fn} = k_B T \ln\left(\frac{q\mu_n N_c}{\sigma_{dc}}\right), \quad (4)$$

where E_{Fn} is the electron quasi-Fermi level, G_{dc} is the dc generation rate, and σ_{dc} is the dc photoconductivity. If we compare Eqs. (3) and (4) with Eqs. (1) and (2), the main differences are that, (i) the total DOS at E_{Fn} can be directly deduced from Eq. (3) whereas only the sum of the products $c_n^i N^i/\mu_n$ is extracted from Eq. (1), and (ii) the energy scaling needs the knowledge of μ_n in Eq. (4) and the knowledge of c_n in Eq. (2) provided that there is a dominant species of states.

In a previous publication Kounavis [7] proposed a single formulation to describe both the HF and LF regimes of the MPC, the expressions being

$$\sum_{i=1}^{m} \frac{H^i c_n^i N^i(E_{\omega n}^i)}{\mu_n} = -\frac{2qG_{ac}}{\pi k_B T} \frac{\sin(\Phi)}{|\sigma_{ac}|}, \quad (5)$$

$$E_c - E_{\omega n}^i = k_B T \ln\left(\frac{c_n^i N_c}{\left[\omega^2 + (\omega_t^i)^2\right]^{1/2}}\right), \quad (6)$$

where $H^i = 1 - \frac{2}{\pi}\arctan\left(\frac{\omega_t^i}{\omega}\right)$. It can be easily shown that, for $\omega \gg \omega_t^i$ (HF–MPC), H^i tends to 1 and Eq. (5) reduces to Eq. (1), while Eq. (6) reduces to Eq. (2). Thus, Kounavis' formulas reduce to Brüggemann's formulas in the high frequency limit. On the other hand, for the case $\omega \ll \omega_t^i$ (LF–MPC), a series expansion of H^i gives to the first order $H^i \cong \frac{2}{\pi}\frac{\omega}{\omega_t^i}$. Furthermore, if electrons dominate the conductivity we have $\omega_t^i \cong c_n^i n_{dc}$ and $|\sigma_{ac}| \cong q\mu_n|n_{ac}|$. Thus, Eq. (5) reduces to

$$\sum_{i=1}^{m} N^i(E_{\omega n}^i) = -\frac{n_{dc}G_{ac}}{k_B T|n_{ac}|} \frac{\sin(\Phi)}{\omega}. \quad (7)$$

In the LF regime the phase shift tends to zero, so $\sin(\Phi) \cong \tan(\Phi)$. Moreover, we can write $n_{dc} = G_{dc}\tau_{dc}^n$ and $|n_{ac}| = G_{ac}\tau_{ac}^n$. Since the occupation of the gap states is defined by the dc illumination, we can expect $\tau_{dc}^n \cong \tau_{ac}^n$. Thus, Eq. (7) reduces to Eq. (3) except for a factor of 2. We will show in the following that this factor is necessary for the correct reconstruction of the DOS.

3. Results and discussion

A numerical simulation called DEOST has been developed at LGEP, and it can be found on the website www.lgep.supelec.fr/scm/. Independently, a similar code has been developed at INTEC. In these simulation codes, all the transport and defect parameters of a semiconductor can be chosen, and the MPC can be calculated at any T, ω and G_{dc}. In order to illustrate the theory of the MPC and the DOS reconstructions, we will use the DOS distribution presented in Fig. 1, which is similar to hydrogenated amorphous silicon but with a flat distribution of deep defect states. All the states belong to the same species and have $c_n = c_p = 2 \times 10^{-8}$ cm^3 s^{-1}. This distribution leads to a dark Fermi level located at 1.1 eV above E_v, while a mobility gap $E_G = 1.8$ eV is assumed. The slightly n-type character is further reinforced by assuming mobilities $\mu_n = 10$ cm^2 V^{-1} s^{-1} and $\mu_p = 1$ cm^2 V^{-1} s^{-1}. Choosing a dc generation rate $G_{dc} = 10^{17}$ cm^{-3} s^{-1}, the solution of the continuity and charge neutrality equations provides the concentrations of electrons and holes as a function of temperature shown in the inset of Fig. 1, implying that electrons are the majority carriers in the whole explored temperature range.

Assuming $G_{ac} = G_{dc}/20$, pulsations in the range $0.1 \leqslant \omega \leqslant 5 \times 10^5$ s^{-1}, and temperatures in the range

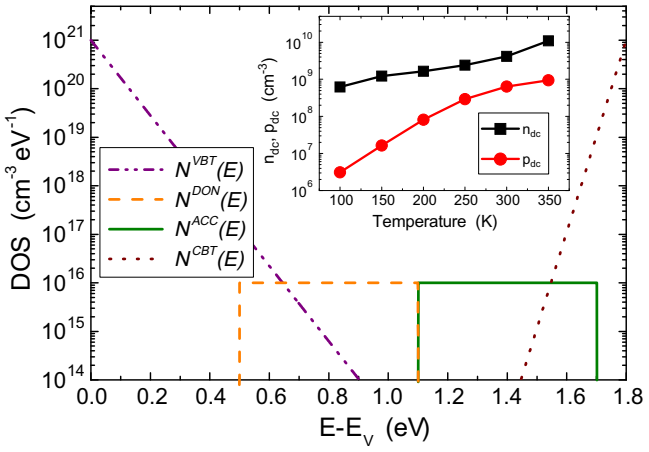

Fig. 1. DOS distribution introduced in our calculations, typical for hydrogenated amorphous silicon except for the flat deep defect distributions. The temperature dependence of the electrons and holes concentrations are shown in the inset.

$100\ \mathrm{K} \leqslant T \leqslant 350\ \mathrm{K}$ in 50 K steps, we have numerically solved the system of equations that provides the modulus and phase shift of the ac photocurrent. Then, we applied the different methods to reconstruct the introduced DOS. Fig. 2 presents the results, where the lines are the introduced DOS, the crosses result from the application of Brüggemann's method [2], the squares from the low frequency limit of Kounavis' method [7] and the stars from the LF–MPC method [12,13].

To set the energy scale in Brüggemann's method [Eq. (2)] and to get absolute DOS values [Eq. (1)], the correct values of c_n and μ_n have been used (not known *a priori* in an experiment). To set the energy scale in Kounavis' method [Eq. (6)] the correct values of c_n and c_p have been used (c_p is needed to calculate ω_t, although the approximation $\omega_t \cong c_n \times n_{\mathrm{dc}}$ could also have been used). The value of ω_t is also needed to calculate H, while μ_n is used to get absolute DOS values [Eq. (5)]. In the LF–MPC method, the correct value of μ_n was used to get $E_{\mathrm{F}n}$ [Eq. (4)], while c_n is not needed. When the pairs of data $(\omega;\Phi)$ are introduced into Eq. (3) to get the total DOS, all the values of $\tan(\Phi)$ that depend linearly on ω give the same value for $N(E_{\mathrm{F}n})$. This can be used as a criterion to evaluate the LF region: all the frequencies providing the same DOS value belong to the low frequency region of the MPC spectrum. Note that in Fig. 2, each 'star' is in fact a group of up to 20 data points, all of them giving the same DOS value. From Fig. 2 it is also clear that Kounavis' method underestimates the introduced DOS in the defect region by a factor of 2, what proves that the factor 2 appearing in Eq. (3) is indeed correct. The LF–MPC formula provides the right values for $N(E)$, except for the highest temperature when the electron quasi-Fermi level gets too close to the dark Fermi level. Moreover, the LF–MPC method does not require knowledge *a priori* of the values of the capture coefficients, which is a drawback of Kounavis' and Brüggemann's methods. The determination of the capture coefficients (or, equivalently, of the transition pulsation ω_t, i.e., the pulsation determining the transition from the LF to the HF regime) is a fundamental point in the formulations of Brüggemann and Kounavis. One method, proposed in Ref. [3], is based on plotting $\cos(\Phi)/|I_{\mathrm{ac}}|$ vs. ω and detecting the end of the plateau region at low pulsations. The application of this method is exemplified in Fig. 3(a) for the same computer-generated data as before ($100\ \mathrm{K} \leqslant T \leqslant 350\ \mathrm{K}$, $G_{\mathrm{dc}} = 10^{17}\ \mathrm{cm^{-3}\ s^{-1}}$). The results are shown in Fig. 4 as circles, and can be compared to the actual values (squares). Note that some of the values are higher and others are lower than the actual ones, due to uncertainties in the estimation of the end of the plateau region. Nevertheless, all the values are within a factor of 1.75 from the actual ones.

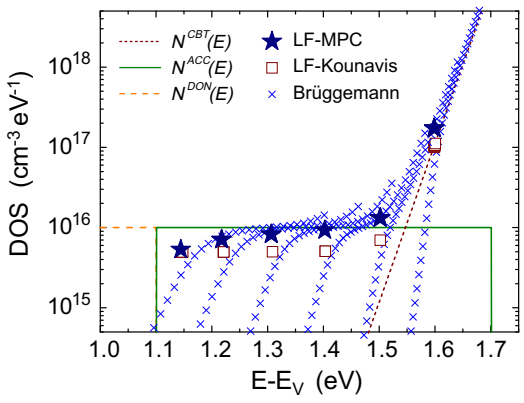

Fig. 2. Results of the application of the different methods (symbols) to reconstruct the introduced DOS (lines).

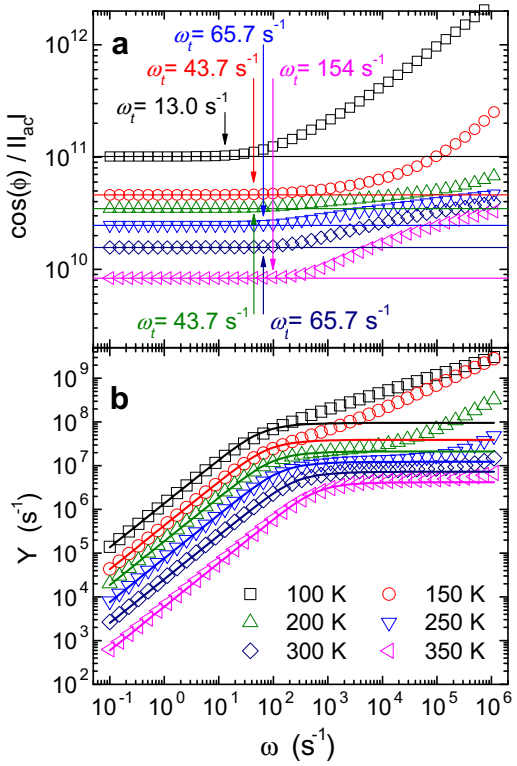

Fig. 3. Illustration of different methods to obtain the transition frequency ω_t: plots of $\cos(\Phi)/|I_{\mathrm{ac}}|$ as a function of ω in (a) and fits of Y vs. ω (Kounavis' method) in (b).

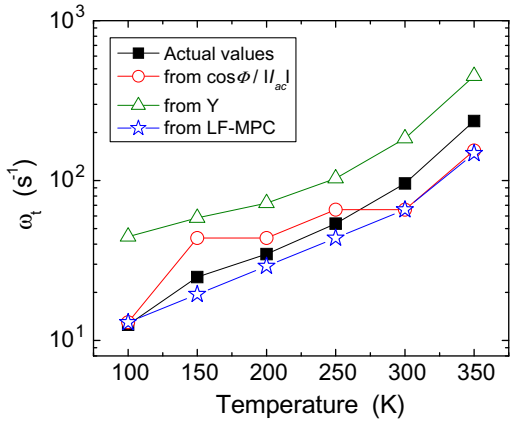

Fig. 4. Transition pulsations ω_t as a function of temperature, where the actual values and the results of the different methods presented in Fig. 3 are shown.

Another procedure to determine the transition pulsation has been described by Kounavis in Refs. [7,15], and will be briefly recalled here. Starting from Eq. (5), Kounavis defines Y, the imaginary term of the MPC, by $Y = -\mu_n q G_{ac} \frac{\sin(\Phi)}{|\sigma_{ac}|} \cong \frac{\pi}{2} k_B T H c_n N(E_{\omega n})$. This term can be obtained experimentally (provided μ_n is known), and contains the information on the DOS. The weighting function H determines the individual contribution to the imaginary term of every species of states. In the emission-limited regime that takes place at $\omega \gg \omega_t$ one has $H = 1$ and the Y spectrum presents a leveling off at a value that depends on the defect density. Upon decreasing ω, at $\omega = \omega_t$ the function H decreases by a factor of 2 from unity. If ω is further decreased so that $\omega \ll \omega_t$, H tends to zero linearly with ω, and the same happens to the Y term. Based on these facts, Kounavis proposes in Refs. [7,15] to determine ω_t by making a plot of Y vs. ω and fitting this term with a 'normalized' H function. This procedure is shown in Fig. 3(b), where the symbols correspond to the Y terms obtained from our computer-generated data, while the solid lines are fits with the functions $H^{fit} = C\left[1 - \frac{2}{\pi} \arctan\left(\frac{\omega_t^{app}}{\omega}\right)\right]$. Here, C and ω_t^{app} are the fit parameters, and a weighting factor proportional to ω^{-1} has been used. The results are also shown in Fig. 4 as triangles. Although these values exhibit the same trend as the actual ones, they deviate from them in as much as a factor of 3.5, especially for the lowest temperatures. Such an overestimation in ω_t would lead to an underestimation of the DOS by approximately the same factor.

As mentioned before, the LF–MPC method itself provides a criterion to evaluate the transition between the HF and LF regimes: all the pairs of data $(\omega; \Phi)$ that provide the same value for $N(E_{Fn})$ when introduced into Eq. (3) belong to the LF region. If we estimate ω_t as the value of ω that leads to a 10% departure from the constant DOS value, we get the result shown as stars in Fig. 4. As can be seen, the values present the same trend and are all within a factor of 1.6 from the actual ones, what can be taken as an acceptable precision for the estimation of the capture coefficients.

4. Conclusion

We have analyzed three different methods to determine the DOS within the gap of defective semiconductors from MPC measurements. We have used computer-generated data and a particular DOS distribution to show that in the LF limit of Kounavis' method a factor of two is missing. We have also shown that Brüggemann's method (or equivalently, Kounavis' method in the HF limit) correctly reproduce the introduced DOS provided the values of the capture coefficients are known; while the LF–MPC method does not require these values. We have tested three procedures proposed to determine the capture coefficients from MPC data, showing that, although not completely accurate, the method presented in this work – based on the LF–MPC data – may provide a good estimation for these values. However, a perfectly accurate method to derive experimentally the capture coefficients is still missing.

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