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Determination of the density of states of semiconductors from steady-state photoconductivity measurements

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Abstract

We discuss a method to obtain the density of states of photoconductive semiconductors from the light-intensity-dependence of the steady-state photoconductivity. Considering a material having different species of gap states – i.e., with different capture coefficients – we deduce a simple expression relating the defect density to measurable quantities. We show that the relevant capture coefficient appearing into the formula is that of the states that control the recombination. We check the validity of the approximations and the applicability of the final expression from numerical calculations. We demonstrate the usefulness of the method by performing measurements on a standard hydrogenated amorphous silicon sample.

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Keywords: Silicon; Conductivity; Photoconductivity; Defects

1. Introduction

The measurement of the steady-state photoconductivity σ_{ph} is a useful tool to study the recombination processes taking place within the mobility gap of semiconductors. In particular, the dependence of σ_{ph} on the light intensity has been studied for different semiconductors in numerous publications [1–4]. A power-law-dependence of σ_{ph} on the light flux, $\sigma_{ph} \propto \Phi^{\gamma}$, is typically observed. The Rose model [5] allowed to correlate the γ coefficient to some part of the density of states (DOS), and some authors, like Balberg [6], used measurements of the γ exponent as a function of temperature to estimate the DOS. Mendoza and Pickin [7] could even obtain an explicit formula for the DOS, although neglecting in their treatment the holes contribution and restricting their analysis to a single species of monovalent states. On the other hand, Shen and Wagner [8] concluded that γ is more sensitive to the total number of defects than to their distribution, thus disregarding the possibility to develop a DOS spectroscopy from the dependence of the γ coefficient.

In a recent paper we have proposed a very simple method to estimate the energy-resolved DOS of photoconductive semiconductors from γ measurements as a function of temperature and light intensity [9]. In that work, however, we have described the DOS function by using a single capture coefficient for all the states. In this work we will extend our previous treatment to the case of multiple species of traps in the gap of the semiconductor. Even for this case we will show that it is possible to obtain an analytical expression for γ as a function of the DOS parameters, and that this expression can be inverted to get the DOS at the quasi-Fermi level from measurements of the γ coefficient.

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We will show that the DOS is linked to the capture coefficient of those states that control the recombination, which are not necessarily the states located at the quasi-Fermi level. We will discuss the implications of these results, not only from numerical simulations of the proposed method but also by performing measurements on a standard hydrogenated amorphous silicon (a-Si:H) sample.

2. Analytical expression for γ

Simmons and Taylor [10] described the non-equilibrium steady-state statistics for an arbitrary distribution of trapping states within the gap of a semiconductor. For m species of states, each of them characterized by their respective capture coefficients for electrons and holes, c_n^i and c_p^i (assumed to be energy-independent), the rate equations are

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 0 = G - \sum_{i=1}^{m} \int_{E_V}^{E_C} c_n^i n [1 - f^i(E)] N^i(E)\,\mathrm{d}E + \sum_{i=1}^{m} \int_{E_V}^{E_C} e_n^i(E) f^i(E) N^i(E)\,\mathrm{d}E, \quad (1)$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = 0 = G - \sum_{i=1}^{m} \int_{E_V}^{E_C} c_p^i p f^i(E) N^i(E)\,\mathrm{d}E + \sum_{i=1}^{m} \int_{E_V}^{E_C} e_p^i(E) [1 - f^i(E)] N^i(E)\,\mathrm{d}E, \quad (2)$$

where n (p) is the electrons (holes) concentration in the extended states; t, the time; G, the optical generation rate; E_V, the energy at the top of the valence band; E_C, the energy at the bottom of the conduction band; $N^i(E)$, the DOS for the ith species of state at the energy E; $f^i(E)$, the corresponding occupation function; and $e_n^i(E)$ [$e_p^i(E)$], the emission rate for electrons (holes). The occupation function for each species of state is given by

$$f^i(E) = \frac{c_n^i n + e_p^i(E)}{c_n^i n + c_p^i p + e_n^i(E) + e_p^i(E)}. \quad (3)$$

Replacing Eq. (3) into (1), and using the definition of the quasi-Fermi levels for electrons and holes trapped at each species of state, E_{tn}^i and E_{tp}^i [10], we can approximate the generation rate by

$$G = \sum_{i=1}^{m} \int_{E_{tp}^i}^{E_{tn}^i} \left[\frac{c_n^i n c_p^i p}{c_n^i n + c_p^i p} \right] N^i(E)\,\mathrm{d}E. \quad (4)$$

In addition, the condition of charge conservation between dark equilibrium and steady-state illumination gives the following equality

$$n_0 - p_0 + \sum_{i=1}^{m} \int_{E_V}^{E_C} f_0(E) N^i(E)\,\mathrm{d}E = n - p + \sum_{i=1}^{m} \int_{E_V}^{E_C} f^i(E) N^i(E)\,\mathrm{d}E, \quad (5)$$

where the subscript 'zero' stands for dark equilibrium values. In defective semiconductors under the usual illumination conditions the concentration of excess free carriers is negligible compared to the concentration of trapped carriers, so the terms $(n_0 - p_0)$ and $(n - p)$ can be neglected compared to the integrals in Eq. (5). Moreover, in a low-temperature approximation we have $f^i(E) \approx 0$ for $E > E_{tn}^i$, $f^i(E) \approx c_n^i n/(c_n^i n + c_p^i p)$ for $E_{tp}^i < E < E_{tn}^i$, and $f^i(E) \approx 1$ for $E < E_{tp}^i$. Thus, Eq. (5) turns into

$$\sum \frac{c_p^i p}{c_n^i n + c_p^i p} \int_{E_{tp}^i}^{E_{F0}} N^i(E)\,\mathrm{d}E = \sum \frac{c_n^i n}{c_n^i n + c_p^i p} \int_{E_{F0}}^{E_{tn}^i} N^i(E)\,\mathrm{d}E, \quad (6)$$

where E_{F0} is the dark equilibrium Fermi level. We now define the 'lifetimes'

$$\frac{1}{\tau_n'^i} = \frac{c_n^i c_p^i p}{c_n^i n + c_p^i p} \int_{E_{tp}^i}^{E_{F0}} N^i(E)\,\mathrm{d}E,$$
$$\frac{1}{\tau_p'^i} = \frac{c_p^i c_n^i n}{c_n^i n + c_p^i p} \int_{E_{F0}}^{E_{tn}^i} N^i(E)\,\mathrm{d}E. \quad (7)$$

Thus, from Eq. (4) we get

$$G = n \sum \frac{1}{\tau_n'^i} + p \sum \frac{1}{\tau_p'^i}, \quad (8)$$

and from Eq. (6)

$$\sum \frac{1}{c_n^i \tau_n'^i} = \sum \frac{1}{c_p^i \tau_p'^i}. \quad (9)$$

Defining average capture coefficients as $c_n^M = \sum(1/\tau_n'^i)/\sum[1/(c_n^i \tau_n'^i)]$ and $c_p^M = \sum(1/\tau_p'^i)/\sum[1/(c_p^i \tau_p'^i)]$ from Eqs. (8) and (9) we obtain

$$G = \left(c_n^M n + c_p^M p\right) \sum \frac{c_n^i n}{c_n^i n + c_p^i p} \int_{E_{F0}}^{E_{tn}^i} N^i(E)\,\mathrm{d}E. \quad (10)$$

In the following we will consider the case where electrons are the majority carriers (if holes were the majority carriers, a similar final expression valid for holes would be obtained), with capture coefficients for electrons and holes not too different, so that $c_n^i n \gg c_p^i p$ for all i. For this case, from Eq. (10) we obtain

$$G = c_n^M n \sum \int_{E_{F0}}^{E_{tn}^i} N^i(E)\,\mathrm{d}E. \quad (11)$$

Moreover, if $n \gg p$ all the quasi-Fermi levels for trapped electrons are almost equal to the quasi-Fermi level for free electrons, E_{Fn},

$$E_{tn}^i \approx E_{Fn} = E_{F0} + k_B T \ln\left(\frac{n}{n_0}\right), \quad (12)$$

where k_B is Boltzmann's constant and T, the absolute temperature. Defining the γ coefficient as $\frac{1}{\gamma} = \frac{n}{G}\frac{\mathrm{d}G}{\mathrm{d}n}$ and performing the derivative of Eq. (11), using Eq. (12) we simply get

$$\frac{1}{\gamma} = 1 + \frac{k_B T c_n^M n}{G} \sum N^i(E_{Fn}). \quad (13)$$

This expression provides the explicit analytical dependence of the γ coefficient on the DOS. Thus,

$$N^{\mathrm{TOT}}(E_{\mathrm{Fn}}) \cong \frac{G}{k_{\mathrm{B}} T c_n^M n}\left[\frac{1}{\gamma} - 1\right], \tag{14}$$

where $N^{\mathrm{TOT}}(E_{\mathrm{F}n})$ is the total density of states at the free electron quasi-Fermi level. As $E_{\mathrm{F}n}$ can be shifted by a variation of temperature and/or generation rate, Eq. (14) provides the basis for a DOS spectroscopy. The average capture coefficient is

$$c_n^M = \frac{\sum_{i=1}^{m} \frac{c_n^i c_p^i p}{c_n^i n + c_p^i p} \int_{E_{tp}^i}^{E_{\mathrm{F0}}} N^i(E)\,\mathrm{d}E}{\sum_{i=1}^{m} \frac{c_p^i p}{c_n^i n + c_p^i p} \int_{E_{tp}^i}^{E_{\mathrm{F0}}} N^i(E)\,\mathrm{d}E}, \tag{15}$$

which is approximately equal to the maximum c_n^i between $E_{\mathrm{F}p}$ and E_{F0}. As can be seen from Eqs. (14) and (15), the DOS at $E_{\mathrm{F}n}$ (in the upper part of the band gap) depends on the average capture coefficient over the lower part of the band gap. This will be shown in the next section from experimental and simulated results.

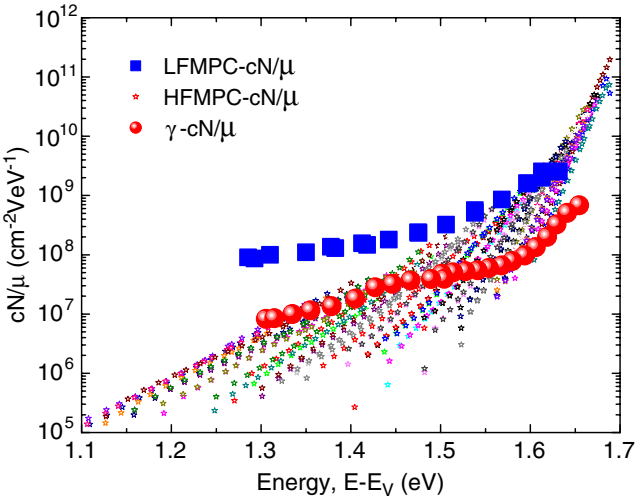

Fig. 1. Experimental results on a standard a-Si:H sample. The cN/μ values are estimated from the modulated photoconductivity in the high frequency (HFMPC-cN/μ) and low frequency (LFMPC-cN/μ) regimes, and from γ-coefficient measurements (γ-cN/μ).

3. Results and discussion

To test the technique we performed measurements on a standard a-Si:H sample, deposited from pure silane by plasma-enhanced chemical vapor deposition at a temperature of 423 K, an rf power of ≈5 mW/cm^2 and a gas pressure of 40 mTorr. We measured the photoconductivity and the γ coefficient as a function of temperature, from 100 to 405 K in 10–15 K steps, at a generation rate $G = 1 \times 10^{20}\,\mathrm{cm^{-3}\,s^{-1}}$ provided by a He–Ne laser ($\lambda =$ 633 nm). The γ coefficient was measured by recording the photoconductivity with the full flux of the light beam and with a lower flux obtained by means of a neutral density filter. The γ-DOS distribution was calculated from Eqs. (12) and (14), approximating the electron concentration by $n = \sigma_{\mathrm{ph}}/(q\mu_n)$, where q is the absolute value of the electron charge. In the same experiment we also measured the modulated photocurrent (MPC) in both high frequency and low frequency regimes (HFMPC and LFMPC, respectively). In each regime we calculated the DOS from the simple analytical expressions published in Refs. [11,12], respectively.

The results are shown in Fig. 1, where to avoid uncertainties with the values of the capture coefficients or the mobilities we present the cN/μ products. There are some points to be noted. First, the HFMPC-cN/μ and LFMPC-cN/μ distributions agree well in the conduction band-tail (CBT) region, but disagree by about one order of magnitude at energies around 1.3 eV. Second, the HFMPC-cN/μ and γ-cN/μ distributions agree for energies up to ~1.45 eV, but disagree by about one order of magnitude in the CBT region. To understand these disagreements, we will analyze more deeply what is really measured by each of the applied methods.

In the γ method we obtain the γ-$c^M N/\mu$ values directly from experimental quantities like the generation rate, the photoconductivity and γ [see Eq. (14)]. However, c^M is an average capture coefficient over the recombining states [see Eq. (15)]. The LFMPC technique provides directly the value of $N(E_{\mathrm{F}n})$ from an analytical expression involving the generation rate, the temperature, and the phase shift of the ac photocurrent measured at low frequencies, without involving any c value [12]. The HFMPC technique gives the quantity cN/μ from experimentally known parameters (like the ac generation rate and the modulus of the resulting ac photocurrent), and the c involved is that of the probed states [11]. In summary, in the γ-cN/μ the c value is that of the states controlling the recombination, in the HFMPC-cN/μ the c value is that of the probed states, and in the LFMPC-cN/μ a c value has to be introduced, since the method only provides the N value.

It is thus clear that the disagreement between the different methods implies a non-constancy of the capture coefficients. At low temperatures, only the CBT is probed. This fact allows us to obtain the c value, c^{CBT}, that provides a good matching between the LFMPC- and HFMPC-cN/μ values in the CBT region. In the same region the γ-cN/μ is about one order of magnitude below the LFMPC- and HFMPC-cN/μ because the states that control the recombination at these low temperatures [probably the dangling bond (DB) states or even the valence band-tail (VBT) states] have a capture coefficient about one order of magnitude lower than that of the CBT states. On the other hand, the fact that in the DB region the LFMPC-cN/μ values are about 10 times higher than the HFMPC-cN/μ values means again that these defect states have a capture coefficient around 10 times lower than that of the CBT states. Remember that the LFMPC method gives directly the N value, so it is clear that the c^{CBT} that provides a good agreement between the LFMPC- and HFMPC-cN/μ in the CBT region is higher than the c^{DB} that would provide

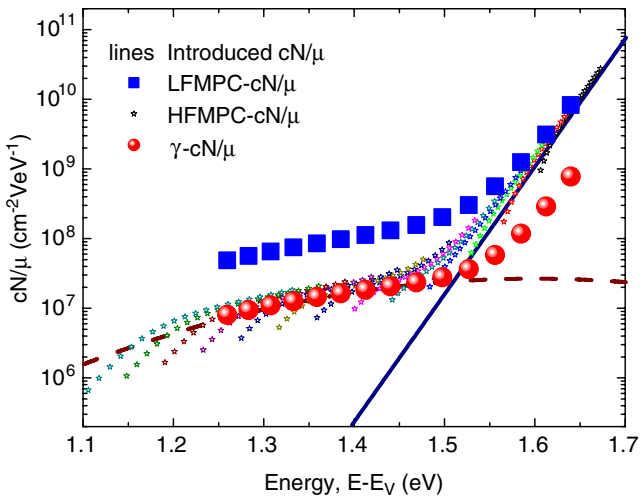

Fig. 2. Numerical calculation showing the application of the three methods (HFMPC, LFMPC, and γ) to an introduced DOS consisting of two different defect distributions. The solid line represents the CBT states and the dashed line the DB states. This DOS reproduces the main experimental trends shown in Fig. 1.

a good agreement in the DB region. The agreement between the HFMPC- and γ-cN/μ values in the DB region implies that in the high temperature range the DB states are controlling the recombination.

From the preceding arguments we deduce that we can reasonably reproduce our experimental results by assuming two species of states: the CBT states, with a relatively high capture coefficient, and the DB plus VBT states, with a capture coefficient around 10 times lower. To confirm this hypothesis we performed numerical calculations by using two computer codes developed independently in Argentina and in France [13]. We introduced in our codes the DOS distribution shown in Fig. 2 (lines), where the solid line represents the CBT states with capture coefficients $c_n^{\mathrm{CBT}} = c_p^{\mathrm{CBT}} = 10^{-8}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, and the dashed line represents the DB states with capture coefficients $c_n^{\mathrm{DB}} = 10^{-9}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ and $c_p^{\mathrm{DB}} = 10^{-8}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$. The VBT states (not shown) are also considered to have the same capture coefficients as the DB states, $c_n^{\mathrm{VBT}} = 10^{-9}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ and $c_p^{\mathrm{VBT}} = 10^{-8}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$. The simulated results for the application of the three methods are also shown in Fig. 2, where it can be seen that the main experimental behaviors are well reproduced. In the CBT region the LFMPC- and HFMPC-cN/μ distributions agree whereas the γ-cN/μ is one order of magnitude below, while in the DB region the HFMPC- and γ-cN/μ distributions agree and the LFMPC-cN/μ is ten times higher.

We are thus quite confident on the interpretation that we have made of the experimental results. We consider that, for this sample, the DOS shape is given by the LFMPC distribution shown in Fig. 1, since this method provides directly the $N(E_{\mathrm{Fn}})$ values. We have measured $N(1.3\,\mathrm{eV}) \approx 10^{17}\,\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$, and we have estimated for these DB states a capture coefficient around $10^{-9}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$. The CBT has a characteristic energy of ~18 meV and a capture coefficient around $10^{-8}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, and the DOS at the conduction band edge is around $5 \times 10^{21}\,\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$.

4. Conclusion

We have shown that the DOS above the dark Fermi level can be estimated from measurements of the temperature and light-intensity-dependence of the steady-state photoconductivity. The proposed technique is experimentally very simple, since only dc measurements are needed. The method has been checked by numerical simulations and applied to a standard hydrogenated amorphous silicon sample. Results have been compared with those deduced from the modulated photocurrent experiment in both HF and LF regimes. The observed differences in the reconstructed DOS spectroscopies have been explained by the different capture coefficients of conduction band-tail, valence band-tail and dangling bond states. It should be stressed that the combination of the proposed method with the HF and LF MPC methods can provide trustable DOS estimations, can clearly reveal the presence of different species of traps in the semiconductor, and can offer good insight into the different capture coefficients.

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[13] One of the codes (DeOSt) is available on the web at <www.lgep.supelec.fr/scm>.