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Journal of Non-Crystalline Solids



journal homepage: www.elsevier.com/ locate/ jnoncrysol

a-Si:H transport parameters from experiments based on photoconductivity

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ARTICLE INFO

Article history: Received 9 June 2011 Received in revised form 3 November 2011 Available online 10 December 2011

Keywords: Hydrogenated amorphous silicon; Transport parameters; Photoconductivity; Density of states

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is one of the major thin film materials used for solar energy conversion and lots of researches have been carried on for measuring its transport parameters to optimize the deposition conditions and its properties. Several techniques developed to determine a-Si:H transport parameters are based on its photoconductivity property and only the light excitation spatial and temporal distributions are varied from one experiment to the other. Considering the subset of experiments in which carrier generation is achieved by band to band excitation we can quote the following methods. The simplest one is the steady-state photoconductivity (SSPC) in which one records the evolution of the film photoconductivity with temperature T and/or generation rate G. More sophisticated techniques were designed as the modulated photocurrent (MPC) technique [1]. Other experiments are based on illuminating the film with interferences created by two laser beams. The grating can be fixed as in the steady state photocarrier grating (SSPG) [2], moving at a constant velocity along the film surface [3], or be modulated at a given frequency [4]. Each of these techniques brings some insight on the transport parameters and/or density of states (DOS) of the studied thin film.

In this paper we review some of them and show what information they bring and how complementary they are. Besides, we propose a new method, we show which information can be extracted from it, and demonstrate that an accurate DOS spectroscopy can be done with it. Combined with MPC it should also lead to the determination of important parameters as the electronic extended states mobility μ_{η} .

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ABSTRACT

In this paper we review some of the techniques based on the photoconductivity property of hydrogenated amorphous silicon (a-Si:H) from which it is possible to extract transport parameters as well as density of states (DOS) spectroscopies. We also present a new experiment based on the steady state photocarrier grating technique. We show that combined with simple steady state photoconductivity it gives information on the DOS. The comparison of these results with those of other techniques used for DOS measurements theoretically allows determination of transport parameters in a-Si:H.

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2. Experiments

2.1. Theoretical background

The MPC technique was first proposed by Oheda [1]. Basically, the sample is illuminated by a light flux, modulated at an angular frequency ω , giving an expression of $G = G_{dc} + G_{ac} \cos(\omega t)$, where the indexes *dc* and *ac* stand for steady and alternating components and $G_{ac} << G_{dc}$. Starting from the continuity equations, and after some calculations, one finally finds that [5,6]

$$\frac{N(E_{\omega})c_{\rm n}}{\mu_{\rm n}} = \frac{2}{\pi k_{\rm B}T} q G_{\rm ac} \frac{\sin\phi}{|\sigma_{\rm ac}|} \tag{1}$$

with

$$E_{\rm c} - E_{\rm \omega} = k_{\rm B} T \ln\left(\frac{c_{\rm n} N_{\rm c}}{\omega}\right),\tag{2}$$

where $k_{\rm B}$ is the Boltzmann constant, q the electron charge, $N(E_{\omega})$ the DOS at the energy E_{ω} , $c_{\rm n}$ the electron capture coefficient of the states at E_{ω} , $E_{\rm c}$ the conduction band edge energy, $N_{\rm c}$ the equivalent density of states at $E_{\rm c}$, $\sigma_{\rm ac}$ the modulus of the photoconductivity resulting from $G_{\rm ac}$ and ϕ its phase shift referred to the excitation. All the quantities on the right hand side of Eq. (1) being known, Eqs. (1)–(2) would offer an easy DOS spectroscopy by varying T and ω , provided $c_{\rm n}$ and $\mu_{\rm n}$ were known and assuming for $N_{\rm c}$ the same value as for crystalline silicon. Since this is not the case, we should look for other experiments to estimate these transport parameters.

Eqs. (1)–(2) are derived assuming that the carrier contribution to the alternating current is controlled by trapping/release of carriers from the states at E_{ω} . This regime is obtained with high frequency

^{0022-3093/\$ –} see front matter $\ensuremath{\mathbb{C}}$ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jnoncrysol.2011.11.018

of excitation, hence its name: the high frequency (HF) MPC. If the frequency is lowered the carrier contribution is controlled by recombination and one reaches the low frequency (LF) regime of the MPC technique. In this regime we have shown that a DOS spectroscopy is also possible according to the following equations [7]

$$N(E_{\rm fn}) = \frac{2G_{\rm dc}}{k_{\rm B}T} \frac{\tan(\phi)}{\omega},\tag{3}$$

with

$$E_{\rm c} - E_{\rm fn} = k_{\rm B} T \ln \left[\frac{q \mu_{\rm n} N_{\rm c}}{\sigma_{\rm dc}} \right], \tag{4}$$

 $E_{\rm fn}$ being the position of the electron quasi Fermi level and $\sigma_{\rm dc}$ the steady-state photoconductivity.

The reader can note that if both techniques, HF- and LF-MPC, are applied to the same sample, by adjusting both the energy scales and the DOS it should be possible to estimate c_n and μ_n . However, experimentally we have found that there was often a temperature range in which $tan(\phi)$ was negative and therefore the LF-MPC DOS spectroscopy was impossible.

The reason for this behavior was found after a study of the SSPC technique. This experiment is well known for the relation between σ_{dc} and G_{dc} : $\sigma_{dc} \propto G_{dc}^{\gamma}$. For some semiconductors one may observe $\gamma > 1$ in some temperature range, a situation detailed by Rose and called sensitization [8]. This phenomenon occurs when different types of states with different capture coefficients are present in the gap. A new analysis of the MPC experiment in the LF regime has shown that if the gap states are such that the sensitization phenomenon occurs then, in a given range of temperature close to that in which the sensitization appears, one may observe a negative phase shift instead of a positive one [9].

The SSPG technique was designed by Ritter *et al.*[2] to estimate the minority carrier diffusion length L_d . In this experiment the sample is illuminated by two laser beams, interfering if they are both vertically polarized or just superimposing if the polarizations are crossed. The grating spacing Λ is fixed by the angle between the beams and one records the variations of the ratio β of the current flowing in the sample with and without interferences as function of Λ to deduce the L_d value.

The SSPG configuration can be used to perform measurements adding a temporal variation to the excitation as in the moving grating technique (MGT) [3] or the modulated photocarrier grating (MPG) [4] techniques. Using the same set-up as for SSPG, placing an Electro-Optic Modulator (EOM) on the trajectory of one beam, the phase of the light can be modulated, the resulting intensity of the light impinging the surface of the film being

$$I(\mathbf{x},t) = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos\left(\frac{2\pi x}{\Lambda} \pm \omega t\right),\tag{5}$$

where I_1 and I_2 are the respective intensities of each light beam, x the space coordinate, ω the angular frequency driving the EOM and the plus sign is for the first half of a period and the minus sign for the second half. According to Eq. (5) the grating is periodically moving with a constant velocity in one direction for half a period and in the other direction for the second half of the period. The current density δJ_{OPG} flowing in the film as a result of this oscillating photocarrier grating (OPG) can be measured with a lock-in amplifier synchronized at the frequency of the signal driving the EOM.

2.2. Experimental results

MPC and SSPC experiments were performed on a polymorphous a-Si:H film deposited onto a glass substrate and fitted with two parallel ohmic electrodes 1 mm apart. Details on the deposition conditions can be found in ref. [10] (sample #803242). The LF-MPC was performed illuminating the sample with red light emitting diodes ($\lambda = 650$ nm) at a high G_{dc} of the order of 3×10^{19} cm⁻³ s⁻¹, in a frequency range 1–300 Hz, and varying the temperature in the 100–450 K range in 10 K steps. Two data treatment procedures were applied, a first one in which the DOS was deduced from the slope of tan(ϕ) versus ω at low ω values, and a second treatment in which the DOS was deduced from the first *positive* slope of the variation of tan(ϕ) versus ω . The HF-MPC was achieved with the same red light as for the LF-MPC, with G_{dc} of the order of 10^{17} cm⁻³ s⁻¹ and G_{ac} 3 times lower. The frequency of the modulation was varied in the range 12 Hz–40 kHz, and the temperature was varied from 450 K to 120 K in 30 K steps. For both experiments, each data point for a couple (ω , T) is the average of 10 successive measurements, one each second, and the error was estimated to be of the order of $\pm 8\%$ of the average value.

The SSPC measurements were performed with the same light source and the same generation rate as for LF-MPC to check for the occurrence of a sensitization.

In Fig. 1, we show the Nc/μ values (open diamonds) obtained for different couples (ω, T) in the HF-MPC experiment. We shall recall that the DOS shape is given by the upper envelope of all the spectra obtained at different T, one for each color. The departure of the spectra from the upper envelope originates from the influence of G_{dc} as shown elsewhere [6]. The DOS is made of a conduction band tail (CBT) visible at low energies, probed at low T, and deep states at higher energies, probed at high T. In the LF-MPC technique (circles in Fig. 1) we determine the *N* values (Eq. (3)) and at low *T* we may assume that LF-MPC and HF-MPC are probing only the CBT. We have then adjusted the $c_n N_c$ and $\mu_n N_c$ parameters, following Eqs. (1–4), so as to obtain the same Nc/μ in the CBT region for both experiments. The final values are displayed in Fig. 1 and the energy scales coming from Eqs. (2) and (4) were fixed according to this. It can be seen that the Nc/μ obtained at high T for both experiments do not match. This indicates that the deep states capture coefficient is clearly different from that of the CBT. To obtain a good match, at say 0.6 eV, between the Nc/μ determined from the HF-MPC and the Nc/μ calculated from the N values of the LF-MPC we should choose a c approximately ten times lower. In between the CBT and the deep states we obtained negative values of the phase shift in the LF-MPC experiment. This peculiar region is shown by open circles and N was calculated taking the first positive values of $tan(\phi)$. This behavior indicates that the studied film presented a sensitization phenomenon in a given range of temperature, a result confirmed by the SSPC measurements giving γ values higher than one for temperatures in between say 200-260 K.



Fig. 1. Nc/μ determined from HF-MPC (open diamonds) and LF-MPC (circles) measurements. Error bars are within the size of a symbol.

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