

Light soaking effect on defect states distribution of Hydrogenated amorphous silicon investigated By means of constant photocurrent technique

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Abstract - In the present paper we have investigated, by using the constant photocurrent method in dc-mode (dc-CPM), the effect of the light soaking (LS) on the deep defect density (N_d) and the slope of the Urbach tail (E_0) of a slightly phosphorus-doped hydrogenated amorphous silicon (a-Si:H) film prepared by Plasma-Enhanced Chemical Vapour Deposition (PECVD). By applying the derivative method, we have converted the measured data into a density of states (DOS) distribution in the lower part of the energy gap. The evolution of the sub-band-gap absorption coefficient $\sigma(h\nu)$ and the CPM-determined density of gap-states distribution within the gap versus the illumination time leads to: (i) an increase in the deep defect absorption without any significant changes in the Urbach tail (exponential part), (ii) a presence of more charged than neutral defects as predicted by the defect pool model, and (iii) a saturation point of the degradation of both optical absorption coefficient and density of deep states of slightly P-doped sample measured by dc-CPM. The constant photocurrent technique in dc-mode as a spectroscopy method for the defect distribution determination is, therefore, most reliable to study the light soaking effect on the stability of hydrogenated amorphous silicon layers used in solar cells manufacturing.

Résumé - Nous avons utilisé dans ce travail la technique du photo courant constant pour étudier l'effet de l'illumination intense et prolongée sur la distribution énergétique des défauts profonds du silicium amorphe hydrogéné légèrement dopé de type n préparé par la technique de décomposition chimique en phase gazeuse assistée par plasma (PECVD). En appliquant la méthode de dérivée de Pierz et al., on a pu convertir les spectres d'absorption mesurés en densités d'états électroniques (DOS) à l'intérieur du gap de mobilité, vis-à-vis la durée d'illumination. L'évolution du coefficient d'absorption optique mesuré par CPM, et par conséquence la densité et la distribution d'états énergétiques à l'intérieur du gap, nous montre que: (i) une augmentation du coefficient d'absorption optique et la densité d'états dans la région d'absorption due aux défauts profonds sans aucune changement significatif dans la région d'absorption due au queue de bande de valence, (ii) la présence de défauts chargés est plus importante que les défauts neutres, et ceci est en accord avec les prédictions du modèle de 'defect pool', et (iii) un niveau de saturation de dégradation du coefficient d'absorption optique et la densité d'états profonds du silicium amorphe hydrogéné faiblement dopé de type n, est observé pour des durées d'illumination longues. La technique du photo courant constant peut être donc utilisée comme étant une méthode spectroscopique pour étudier l'effet de l'illumination prolongée sur la stabilité des matériaux utilisés en fabrication des cellules solaires en particulier le silicium amorphe hydrogéné.

Keywords: Constant photocurrent method - Optical absorption spectrum - Light soaking - Hydrogenated amorphous silicon - Defect states.

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1. INTRODUCTION

Hydrogenated amorphous silicon solar cells quality is closely linked to the deep defect density and the slope of the Urbach tail of a-Si:H layers. Light soaking or so-called the Staebler and Wronski effect (S-W) on these layers results in an increase of the deep defect density within the gap [1].

Despite this latter effect has been extensively studied by many authors [2-4], definitely rules for the mechanism of light-induced degradation of a-Si:H is still not made. In order to study S-W effect many techniques are used. Among them are certainly, the photoconductivity measurement techniques which are extremely used for the study of the optoelectronics properties of light soaked amorphous materials such as hydrogenated amorphous silicon (a-Si:H).

In particular those which measure photoconductivity for photons of energy lower than the gap such as the photo-thermal deflection spectroscopy (PDS) [5], the dual beam photoconductivity (DBP) [6] and the constant photocurrent technique (CPM) [7, 8].

These sub-band gap absorption technique have been used to determine the DOS in the lower energy range of the band gap near the valence band, while other techniques such as the transient photoconductivity (TPC) [9] and modulated photoconductivity (MPC) [10] have been used to determine the DOS in the upper energy range of the gap, close to the conduction band.

The CPM technique has the advantage compared to the other techniques of being insensitive with the surface defects. It can thus be used to better understanding the nature and the energy distribution of the defects in the gap starting from the measurement of the optical absorption coefficient.

The basic idea of CPM technique is to maintain the photocurrent constant during the measurement of the optical absorption spectrum under monochromatic illumination by varying the intensity of the incident light [11].

This condition ensures a constant rate of generation and a constant mobility-lifetime product of the free charges. This technique can be configured according two modes, the continuous mode (dc-CPM) [12, 13] or the periodic mode (ac-CPM) [14], both are largely used.

In the present work, we have used the dc-CPM to measure the dc- $\sigma(h\nu)$ of slightly P-doped hydrogenated amorphous silicon a-Si:H for different illumination times T_{ill} . Then, we have applied the derivative method of Pierz *et al.* [15] to convert the measured data into a DOS distribution in the lower part of the energy-gap.

The article will be organized then as follows: section 2 presents the experimental details used for the preparation of the sample as well as the dc-CPM set up, in section 3 we discuss the different results obtained and we will finish our work by a conclusion.

2. EXPERIMENTAL DETAILS

The sample 'P272' was prepared by Plasma-Enhanced Chemical Vapour Deposition (PECVD). The sample has a coplanar structure and was slightly doped by adding 3 vppm of phosphine ' PH_3 ' gas into the deposition gas ' SiH_4 '. Coplanar Al electrodes of 0.5 mm gap width and 5 mm length were deposited on top of the film of 1 μm thickness, and the voltage applied across the gap was 400V (i.e. an electric field 8×10^3

V.cm⁻¹). To get the Fermi energy level E_F of our sample, we have measured the dark conductivity σ_d over a wide temperature range.

As well known, the linear behaviour of σ_d with the inverse of the temperature T represented on logarithmic scale allow us to fit the σ_d data with:

$$\sigma_d(T) = \sigma_0 \cdot \exp\left(-\frac{E_C - E_F}{k_B \cdot T}\right) \quad (1)$$

Where σ_0 is a conductivity characteristic of transport in extended states and it is equal to 150 $\Omega^{-1} \text{ cm}^{-1}$ for a-Si:H. $E_C - E_F$ is the difference in energy between the lower band conduction edge and the Fermi level. k_B is the Boltzmann's constant.

As Fermi energy is defined to be the slope of $\log(\sigma_d) = f(1/T)$ curve, we can obtain then the value of E_F by a simple calculation. We found E_F of our sample equal to 0.51 eV from conduction band edge.

The schematic of the dc-CPM experiment which have been used in this work is shown in figure 1. A xenon lamp was used as a light source (1). The monochromator (2) had a grating of 600 grooves/mm and the filter wheels (3) were used for scanning wavelength. The dc-current was measured by a picoamperemeter (4) but the light intensity was monitored by a locking amplifier (5). In this technique, absorption coefficients, $\sigma(h\nu)$ were obtained as the inverse of the incident photon number $1/\phi_{ph}$, under a constant photocurrent I_{ph} .

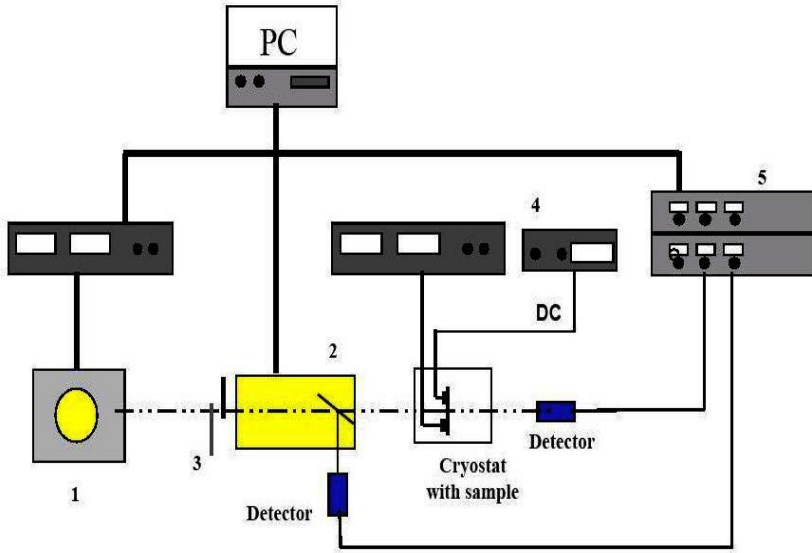


Fig. 1: DC-constant photocurrent technique set up

3. RESULTS AND DISCUSSION

In the present work, all measurements of the CPM spectra were performed at room temperature without changing the position of the sample within the cryostat.

The photocurrent was kept constant by controlling the intensity of the incident light ϕ_{ph} with a computer program. Furthermore and to cause the light induced degradation of our slightly doped a-Si:H sample, another strong and prolonged illumination has been used (approximately 100 mW.cm^{-2}).

The following illumination times were selected: 0, 400, 1000 and 4000 sec in order to cover a wide range and reach the saturation point. We took CPM spectrum after each time separately. The absolute values of each CPM spectra were obtained by matching the CPM data to the results of conventional optical measurements at 1.7 eV. The suppression of the interference pattern from all CPM spectra were done by a final smoothing using a suitable filtering operation for each of them.

Figure 2 illustrate the evolution of the measured absorption coefficients as function of the illumination time. As we can see from these measurements, while the valence-band tail present no significant change as the sample was degraded, we observe a steady increase of the absorption coefficient in the deep defect region till saturation for the last illumination time.

In order to obtain the electronic density of states distribution, we have applied a suitable filtering operation for each of the initial CPM data of figure 2. We obtain, as shown in figure 3, the measured absorption coefficients free of the interference pattern from which we have derivate the density of states of our sample by applying the derivative method of Pierz *et al.* [15].

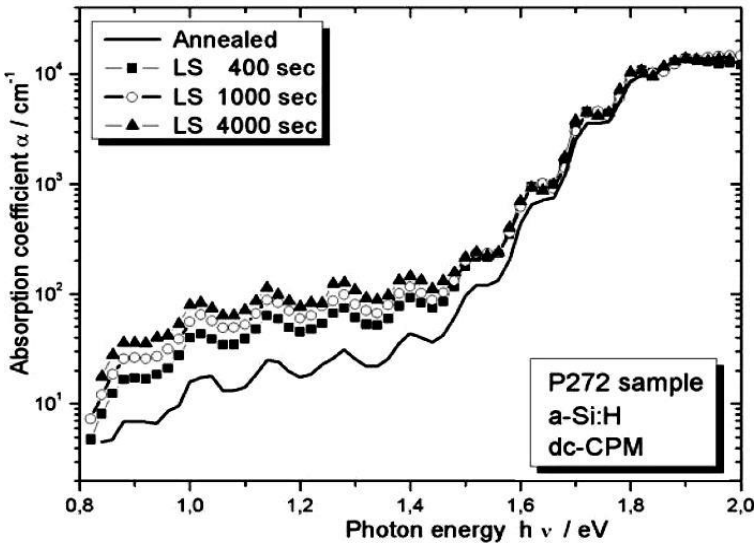


Fig. 2: Evolution of the measured absorption coefficients versus the illumination time

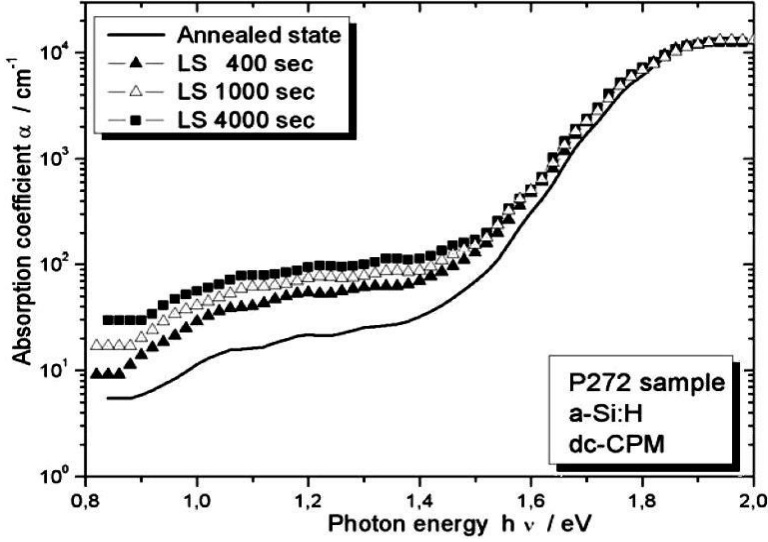


Fig. 3: Smoothed CPM spectrum of slightly doped a-Si:H versus the illumination time after a suitable smoothing operation

The resulting DOS is shown in figure 4. It can be seen that, as the illumination time increases, two peaks grow in the midgap region between the valence band and the Fermi energy in slightly P-doped a-Si:H, while the Urbach tail E_0 remains practically unchanged. In a previous work, Sakata *et al.* [16] and Schmidt *et al.* [17] found two distinct defect states in the lower midgap of undoped a-Si:H.

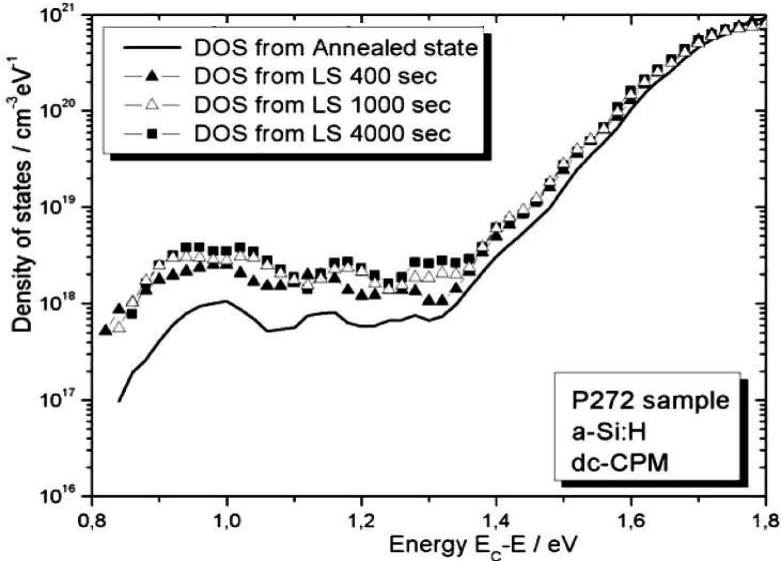


Fig. 4: Density of filled states, obtained by the derivative method applied to the absorption coefficients data, for different illumination times, annealed state is also shown.

In the following figure, the contribution to optical absorption coefficient from the valence band-tail has been substracted. As it can be seen in this figure, the occupied density of defect states consist of two Gaussian peaks that evolve with illumination time until saturation.

The Gaussian shape is commonly assumed to describe the deep defect density and it comes from a statistical energy distribution for the defect sites [17]. In accordance with Schmidt *et al.* [17], the nature of the defect states produced by a strong and prolonged illumination are expected to be unchanged.

So, we fit the evolution of the two peaks with Gaussians of constant position and width. The best fit for our complete set of curves was obtained with peak energy position from the conduction band at 0.98 ± 0.01 eV and 1.16 ± 0.01 eV, being the width 0.11 ± 0.01 eV and 0.06 ± 0.01 eV respectively.

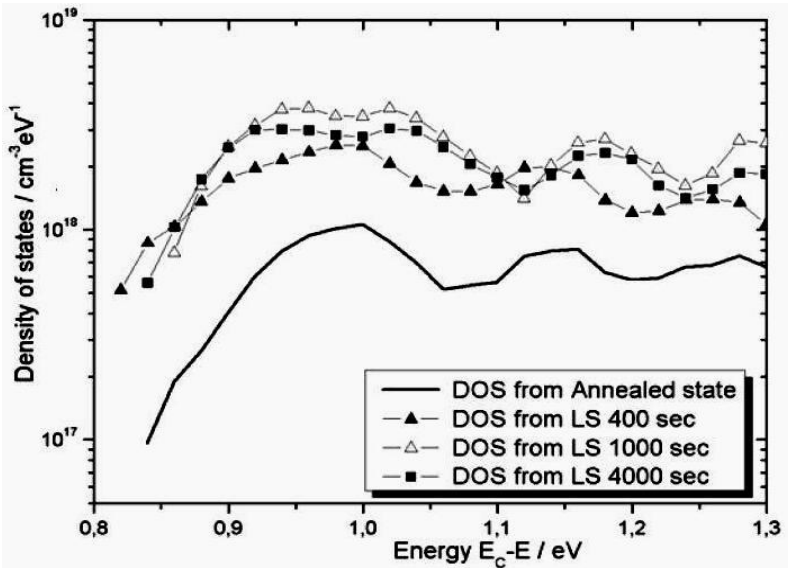


Fig. 5: Evolution of the defect density of midgap states with illumination time

The areas of both peaks tend to increase monotonically as a function of illumination time till saturation, as shown in figure 5.

From this figure, three essential results can be obtained: Firstly, the density of negatively charged defects are greater than the density of neutral ones, in accordance with the prediction of the defect pool model in slightly P-doped materials [18].

Secondly, light induced degradation phenomenon tend to be saturated in the long time limit where the density of defects exceeds the initial defect density by a factor of 2 or more. Thirdly, both defect densities evolve with the same time dependence, which is very close to the $t_{\text{ill}}^{1/3}$ dependence measured for the spin density by ESR [17].

To elucidate the last remark and by assuming that the defects are homogeneously distributed throughout the sample, we have estimated the evolution of the integrated defect density N_d by integrating the excess subgap absorption. In fact, by subtracting

the contribution from the Urbach tail, we can get the evolution of the integrated defect density with the illumination time by using the following formula:

$$N_d = \int (\alpha - \alpha_{\text{urbach}}) \cdot dE \quad (2)$$

4. CONCLUSIONS

In this paper and by means of the constant photocurrent method in dc regime (dc-CPM), we have investigated the defect states in slightly P-doped a-Si:H sample under light soaking condition in term of evolution of the measured sub-gap absorption coefficient and density of states distribution as function of illumination time.

The derivative method applied to the dc- $\sigma(h\nu)$ data allowed us to obtain the occupied density of states. The measurement results in terms of absorption spectrum and deep defect density shows an increase of both with illumination time until saturation. The dominant metastable defects are the dangling bonds.

In fact, their densities pass from $5 \cdot 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ in an initial state to $5 \cdot 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ in a degraded state while the tail states remains basically constant. The DOS showed the presence of two Gaussian distribution between the valence band and the Fermi energy with two peaks.

These two peaks have a constant positions and widths which do not changed considerably with illumination. We have assigned the peak closer to the valence band to the negatively charged defects D and the other peak (midgap peak) to the neutral dangling bonds D_0 .

We have also found that the densities of both defects grow as $t_{\text{ill}}^{1/3}$. This is in agreement with ESR measurements, which show a spin density growing with the same time dependence. In the end, it is useful to extend this study of dc-CPM technique to the ac-CPM technique.

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