

Light-induced creation of metastable defects in hydrogenated amorphous silicon studied by computer simulations of constant photocurrent measurements

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The light-induced degradation of an intrinsic hydrogenated amorphous silicon sample has been studied from the evolution of the sub-band-gap absorption coefficient. The experimental results have been modeled using detailed numerical analysis, obtaining the defect distribution within the gap for each illumination time. These results have been compared with those previously obtained from a direct deconvolution of the absorption coefficient spectra [J. A. Schmidt, R. Arce, R. H. Buitrago, and R. R. Koropecski, *Phys. Rev. B* **55**, 9621 (1997)]. We have found, in agreement with our previous work, that (i) the defect density shows the presence of more charged than neutral defects, as predicted by the defect pool model, and (ii) the concentration of charged and neutral defects evolve with the same time dependence, thus contradicting Schumm's generalized model of defect equilibration. [S0163-1829(99)08907-9]

The understanding of the defect structure in hydrogenated amorphous silicon (*a*-Si:H) is of paramount importance for the improvement of solar cells and other devices based on this material. Comprehensive models have been developed for the defect formation and its evolution as a function of illumination time.¹⁻⁵ However, more experimental data are still necessary in order to test the predictions of these models. As the density of states (DOS) determines the optical properties of the material, the sub-band-gap absorption coefficient spectrum [$\alpha(h\nu)$] can be used to gain information about the defect structure. The integrated defect density (N_D) and the Urbach energy (E_U) can be easily obtained from a measurement of $\alpha(h\nu)$. Moreover, it is also possible to obtain the energetic distribution of the defect density $N_D(E)$. To this purpose, two approaches can be made. One is to apply an appropriate deconvolution technique to the $\alpha(h\nu)$ data, as discussed in previous works.⁶⁻⁸ The other approach (convolution approach) is to model the defect distribution with a function having some free parameters, which are determined from a fitting of the measured spectra.⁹⁻¹¹

In a previous article¹² we have used the first approach, studying the light-induced degradation of an *a*-Si:H sample by means of the deconvolution procedure proposed by Jensen.⁸ The $\alpha(h\nu)$ spectra used for the deconvolution were obtained by the constant photocurrent method (CPM) using the standard hypothesis of this technique.¹³ The occupied DOS showed the presence of two peaks between the valence band and the Fermi energy, which were assigned to the neutral (D^0) and negatively charged (D^-) dangling bonds. We have found more charged than neutral defects, in accordance with the prediction of the defect pool model.^{2,3} We have also found that both defect densities evolve as $t_{\text{ill}}^{1/3}$, where t_{ill} is the illumination time. This is in agreement with ESR measurements, which show a spin density growing with the same time dependence^{14,15} and verifies that the spin density is proportional to the total density of defects.

On the other hand, in a recently published paper,¹⁶ we have presented a steady-state photoconductivity model for *a*-Si:H. The model includes the full set of transitions be-

tween localized and extended states, considering the midgap states as amphoteric. We have developed a computer simulation code that, starting from a given functional form for the DOS, allows us to obtain the true absorption coefficient of the material. Based on this convolution approach, we have shown that the standard procedure used in the CPM technique leads to errors in the determination of the absorption coefficient. Moreover, new experimental evidence,¹⁷ based on the photon energy dependence of the Rose factor γ , gives support to this ascertainment. Since in Ref. 12 we have used the standard CPM procedure to obtain the $\alpha(h\nu)$ spectrum, it would be important to analyze those results by using the complete photoconductivity model of Ref. 16.

The functional form of the midgap DOS is a subject presently under debate. The standard defect model implies that most of the dangling bond states are occupied by one electron, meaning that almost all defects are neutral. On the other hand, the defect pool model suggests a defect equilibration process that leads to the existence of more charged than neutral defects even in undoped samples. Our computer simulation code allows to fit the $\alpha(h\nu)$ spectra with either defect model, thus giving the possibility to test the accuracy of each model in reproducing the absorption spectra. As a result of the fitting we obtain the defect distribution within the material gap, thus implementing the second approach mentioned above.

In the present work we use computer simulations of CPM spectra, based on the model of Ref. 16, in order to study the defect structure of *a*-Si:H. We compare the results obtained when the defect distribution is described with the standard DOS (Ref. 18) and the defect pool models. We study the charge state of the defects in the annealed state and as a function of the light-induced degradation. In this way we are able to test the predictions of those models that extend the defect chemical equilibrium concept to the photodegradation process. Finally, we compare the defect density obtained from the direct deconvolution of the $\alpha(h\nu)$ spectrum with the one obtained from our computer simulation.

Sample preparation and characterization has already been described in Ref. 12. The dc constant photocurrent measure-

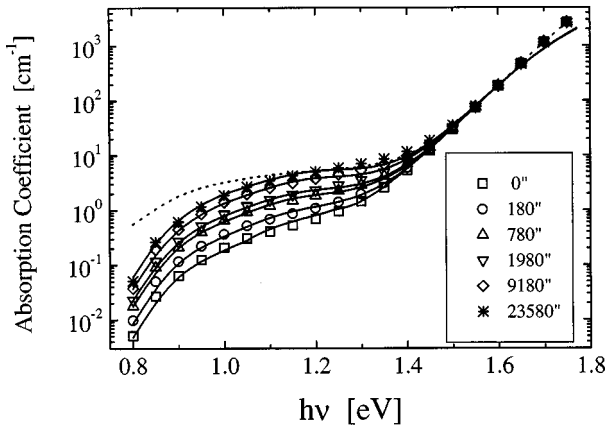


FIG. 1. Evolution of the absorption coefficient as a function of the illumination time. We show the absorption coefficient measured by the CPM (α_{MEAS} , solid line) and the fitting based on the steady-state photoconductivity model of Ref. 16 (α_{CPM} , symbols). The fitting has been performed with a defect distribution dictated by the defect pool model. We also show (dotted line) the $\alpha(h\nu)$ spectrum that is obtained when the defect distribution is given by the standard DOS model (for the final state, $t_{\text{ill}} = 23\,580$ s).

ments were performed using a double monochromator system. The photocurrent was kept constant by controlling the intensity of the incident light with a computer program. Following the standard procedure, the “absolute” values of α (named hereafter α_{MEAS}) were obtained by matching the CPM data to the results of conventional optical measurements at 1.7 eV. We took CPM spectra after the following illumination times: 0, 180, 780, 1980, 9180, and 23 580 sec. Measurements of the CPM spectra were performed at room temperature, under vacuum (better than 10^{-6} Torr), and without changing the position of the sample within the cryostat. The suppression of the interference pattern from the CPM spectra was done by using the transmittance spectra,¹⁹ followed by a final smoothing using FFT filtering. All spectra were treated in the same way, taking into account the comparative nature of this study.

The steady state photoconductivity model has been described in detail in Ref. 16. For each photon energy our computer code determines the photon flux $\phi(h\nu)$ required to keep the photocurrent constant. Following the standard CPM procedure, we get the simulated absorption coefficient from $\alpha_{\text{CPM}}(h\nu) = \text{const}/\phi(h\nu)$. We will call this simulated absorption coefficient α_{CPM} , to distinguish it from the one obtained from the experimental CPM data, α_{MEAS} . A fitting of α_{CPM} to α_{MEAS} allows us to obtain the defect distribution within the gap.

Figure 1 shows the evolution of the measured and simulated absorption coefficients as a function of the illumination time. As can be seen, they are in good agreement for the whole range of illumination times. If we assume a defect distribution dominated by the neutral defects, as suggested by the standard DOS model, we find an increased absorption coefficient in the low photon energy region, followed by a flat zone (see Fig. 1). This result is in agreement with those published by Stiebig and Siebke.²⁰ Since this behavior is not observed in our measurements, we have performed the fitting with a defect distribution the functional form of which is dictated by the defect pool model. The DOS consists of de-

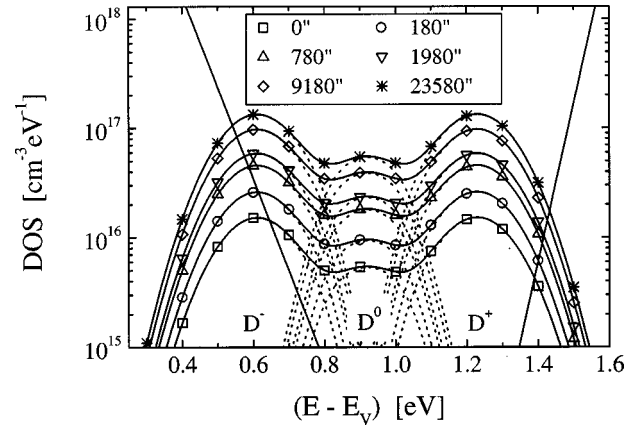


FIG. 2. Evolution of the defect density as a function of the illumination time. The defect states are shown divided according to their occupancy in equilibrium: unoccupied (D^+), occupied by one electron (D^0), and occupied by two electrons (D^-). The band tails keep constant, while the densities of charged and neutral defects grow uniformly.

fect states (D^-, D^0, D^+), exponential band tails, and parabolic bands. Since α_{MEAS} increases only in the midgap region, the bands and the band tails have not been changed as a function of t_{ill} . Moreover, it is not expected that the light soaking may lead to any changes in the position or width of the defect peaks. Thus, in accordance with Sakata *et al.*,¹⁰ we have kept these parameters constant when fitting the evolution of the defect density. The resulting DOS is shown in Fig. 2. The parameters used for the fitting are typical for good-quality *a*-Si:H. The mobility gap was taken as $E_\mu = 1.8$ eV. According to Street,²¹ the density of states at the band edges was chosen to be $3.7 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$. The best fit was obtained with an inverse logarithmic slope equal to 52 meV for the valence-band tail and 30 meV for the conduction-band tail. The correlation energy was taken as 0.2 eV, as usually assumed in the literature.² The (+/0) transition of the defect peaks lay at 0.61 eV (D^-), 0.92 eV (D^0), and 1.23 eV (D^+). The capture cross sections for electrons and holes were taken the same, with values 3×10^{-15} and $3 \times 10^{-16} \text{ cm}^2$ for the charged and neutral defects, respectively. The Fermi level position was taken from dark conductivity activation energy measurements. In the CPM experiment, as well as in the simulation, the photocurrent was chosen to be eight times larger than the dark current.

Figure 3 shows the evolution of the density of charged and neutral defects as a function of the illumination time. The defect densities have been obtained from the simulation of the CPM experiment (this work) and from the direct deconvolution of the $\alpha(h\nu)$ spectra following Jensen’s method (Ref. 8). From this figure, two important results can be obtained. First, the density of charged defects surpasses the density of neutral ones, in accordance with the predictions of the defect pool model. Second, 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.

The density of charged defects in intrinsic *a*-Si:H is still a controversial topic. While some authors agree with the traditional point of view that the density of neutral defects largely exceeds the density of charged defects,^{22,23} other authors

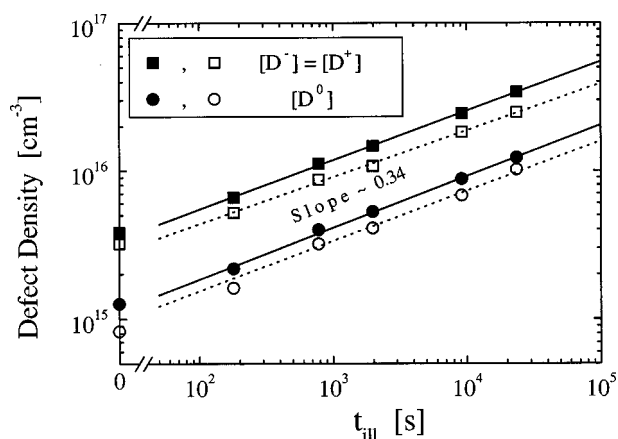


FIG. 3. Integrated defect density as a function of the illumination time, as given by Jensen's deconvolution procedure (Ref. 8, open symbols) and by our convolution procedure (solid symbols).

support the opposite opinion.¹⁻³ However, an increasing amount of recent observations^{1,24-26} tends to confirm that the density of charged defects is not negligible in intrinsic *a*-Si:H. Our results agree with these later measurements, since the ratio of the areas of the D^-/D^0 peaks (as obtained from Fig. 2) is 2.8. From the direct deconvolution of the $\alpha(h\nu)$ spectrum (Ref. 12) we had already obtained a similar result, $[D^-]/[D^0]=2.6$.

The light-induced degradation of *a*-Si:H samples is usually assumed to proceed through the creation of mainly neutral defects. However, in accordance with Stiebig and Siebke,²⁰ we have not found a decrease in the charged to neutral defect ratio upon light soaking. This behavior is in agreement with results of ESR-PDS comparisons, where a linear correlation between the spin density and the integrated subgap absorption was found.²³ On the other hand, this behavior contradicts the predictions of Schumm's generalized model of chemical equilibrium,³ where a strong increase in the D^0 density is anticipated. This means that more work is needed in order to apply thermal equilibrium concepts to the light-induced creation of defects.

As can be seen from Fig. 3, both the simulation of the CPM experiment and the direct deconvolution of the $\alpha(h\nu)$ spectra agree in the main results, i.e., the existence of more

charged than neutral defects and the evolution of both defect densities with the same time dependence. However, it can also be noticed that the defect density obtained from the deconvolution procedure is systematically lower than that obtained from the model approach. This disagreement can be understood by taking into account that the deconvolution procedure is based on the absorption coefficient measured by CPM, which according to the results of Ref. 16 underestimates the true absorption coefficient of the material. This important result, namely that dc CPM does not give an accurate estimation of the true absorption coefficient in the low-energy region ($h\nu < 1.3$ eV), has also been confirmed from CPM measurements performed under different photocurrent levels.¹⁷ Consequently, the deconvolution procedure also underestimates the defect density. On the other hand, the simulation of the CPM experiment allows to correct the problems of the method, since the fitting of α_{MEAS} gives as a result the true absorption coefficient and the defect density (see Ref. 16). Thus, we believe that the model approach offers a closer estimate to the actual DOS of *a*-Si:H.

In summary, we have studied the light-induced degradation of an intrinsic *a*-Si:H sample from the evolution of the subgap absorption coefficient. We followed the approach of fitting the $\alpha(h\nu)$ spectra, obtaining as a result the defect distribution within the gap for each illumination time. We have reached two important conclusions: (1) the defect density responds to the predictions of the defect pool model, with more charged than neutral defects, and (2) the concentration of charged and neutral defects evolve with the same time dependence, meaning that light soaking does not preferably create D^0 states. The first point gives support to the defect pool model, while the second casts doubt over Schumm's generalized model of defect equilibration. These two conclusions agree with our previous findings, obtained from the direct deconvolution of the $\alpha(h\nu)$ spectra.¹² There is, however, a disagreement in the magnitude of the defect density, which we believe is caused by a failure of the CPM in reproducing the actual absorption coefficient of the material.

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