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# The nature of the defect states above midgap and their role in the light-induced metastability of a-Si:H

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#### Abstract

Defect states of a-Si:H above midgap, with which the electrons interact through trapping and thermal release and make an important contribution to the imaginary (Y) term of the modulated photocurrent, are determined. Analysis of the 'transition' region between the low- and high-frequency regimes enables the densities and capture coefficients of defect states to be probed. A reasonable fit to the data is obtained by assuming three defect states, and it is suggested that the defects with the higher capture probability are hydrogen-related centers that are removed during the initial stage of light degradation. © 2006 Elsevier B.V. All rights reserved.

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## 1. Introduction

The defect states in the energy gap of a-Si:H and the respective light-induced changes during light degradation have been extensively studied. However, the defect states above midgap have been explored much less than the others. By applying our recently presented analysis of the imaginary (Y) term of the modulated photocurrent (MPC) [1] in the respective spectra of a-Si:H, two different defect states above midgap were determined [2]. During the initial stage of light soaking (LS), the density of these defects was found to decay before metastable dangling bond creation [2]. Since this phenomenon may be crucial for the degradation mechanism, it is important to clarify the origin of the defect states above midgap. In this work, by examining the transition region from the high- to lowfrequency regime of the Y term, all the different kinds of trapping centers of electrons above midgap are extracted. The nature of these centers and their role in the light degradation of a-Si:H are examined.

## 2. Methods and samples

In the MPC experiment, a relatively weak band gap sinusoidal modulated light with a modulation frequency  $\omega$  imposed on a stronger bias light from light emitted diodes are used to illuminate the sample and to induce a MPC. The imaginary (Y) term of the MPC is extracted by means of the phase shift ( $\Phi$ ) and the amplitude ( $i_{ac}$ ) of the MPC [1]. If the majority carriers, i.e. the electrons in a-Si:H, dominate Y term, then this term is directly related to the total effective trapping rates of electrons into all the gap state distributions  $D^i(E^i_{\omega})$  above midgap at each energy  $E_{\omega}^{i}$  below the conduction band edge  $E_{\rm C}$ . Each  $E_{\omega}^{i}$  is given by  $E_{\omega}^{i} = kT \ln[c_{n}^{i}N_{\rm C}/\{\omega^{2} + (\omega_{t}^{i})^{2}\}^{1/2}]$ , where  $N_{\rm C}$  is the density of states at the conduction band edge, kT the thermal energy,  $\omega_t^i$  the characteristic frequency defined by  $\omega_t^i =$  $nc_n^i + pc_p^i$ , where n(p) is the density of free electrons (holes) and  $c_n^i(\hat{c_p^i})$  the capture coefficient for electrons (holes). Since electrons are the majority carriers, we assume  $\omega_t^i \approx nc_n^i$ . The Y term is given by

$$Y = (\pi/2) \sum_{i} H(\omega, \omega_t^i) c_n^i D^i(E_\omega^i) kT, \qquad (1)$$

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where  $H(\omega, \omega_t^i)$  is the so-called *H* function [1], which determines the effective trapping rate into each  $E_{\omega}^i$  level and is given by  $H(\omega, \omega_t^i) = 1 - (2/\pi) \arctan(\omega_t^i/\omega)$ . *H* function is a step function with a step at  $\omega_t^i$ .

In the HF regime taking place for  $\omega \gg \omega_t^i$ , we have  $H(\omega, \omega_t^i) = 1$ . The Y term is independent of the bias light level and reflects the trapping rate into all of the  $E_{\omega}^i$  levels. By decreasing  $\omega$  from higher to lower values, around the highest characteristic frequency  $\omega_t^H$ , which corresponds to the gap states with the highest capture coefficients  $c_n^H, H(\omega, \omega_t^H)$  starts to decay. This suppresses the effective trapping rate into the respective gap state distribution  $D^H(E)$  with the highest capture coefficient. The  $E_{\omega}^H$  is fixed at about the trap quasi Fermi level for electrons  $E_{tn}$  and a characteristic decay or a step is expected in the Y spectrum very similar to that of H function [1]. In general, a similar step is expected in the Y spectrum for  $\omega \approx \omega_t^i$  and can be used to define each  $\omega_t^i$ .

In the LF regime taking place for  $\omega \ll \omega_t^i$  or practically for  $\omega \ll \omega_t^L$ , all of the  $E_{\omega}^i$  levels are practically fixed at  $E_{\text{tn}}$ . In this case, H function is approximated by  $H(\omega, \omega_t^i) =$  $(2/\pi)(\omega/\omega_t^i)$ , which in Eq. (1) gives  $Y = (\omega/n)\sum_i D^i$  $(E_{\rm tn})kT$ . This relation indicates that the Y term decays linearly with decreasing  $\omega$  and is independent of the capture coefficients. In addition, in the LF regime, the ratio  $Y/\omega$ is independent of  $\omega$ , as this ratio is constant giving the total defect density at  $E_{\rm tn}$  level, namely  $Y/\omega = \sum_i D^i (E_{\rm tn}) kT/n$ . Thus for  $\omega \ll \omega_t^L$  the Y/ $\omega$  spectrum represents a plateau and the onset of this plateau indicates roughly the lowest characteristic frequency  $\omega_t^L$ , which corresponds to the gap states with the lowest capture coefficient  $c_n^L$ . It is obvious that if only a single kind of gap states makes an effective contribution to Y, then  $\omega_t^H$  and  $\omega_t^L$  coincide. If there are contributions from gap states with different capture coefficients, then  $\omega_t^H$  and  $\omega_t^L$  differ. An analysis of the MPC in the LF regime has been presented recently by other authors, but only for a single kind of defects [5,6].

In this work, the Y spectra of a-Si:H of a sample prepared by the conventional rf glow discharge technique, denoted as Sample 1, are presented. Moreover, the Y spectra of two other a-Si:H samples prepared at different laboratories, denoted as Samples 2 and 3, are also analyzed, in order to provide a more general validity of our conclusions. Specifically, the Y spectra of Sample 2 are calculated from the MPC data published by Reynolds et al. [3]. Sample 3 was prepared at the energy conversion devices (ECD) and measurements were conducted in the annealed and light exposed states and these results have been recently published [2].

## 3. Results

Fig. 1 presents typical experimental spectra of Y term and  $Y/\omega$  ratio (symbols) of Samples 1 and 2 in the annealed state for two bias light levels. All the spectra at higher frequencies merge revealing the HF regime. As  $\omega$  decreases from high to low values, the Y and  $Y/\omega$  spectra start to

Fig. 1. Experimental spectra of Y ((a) and (b)) and  $Y/\omega$  ((c) and (d)), measured by a bias light intensity of  $7 \times 10^{12}$  (solid circles) and  $2 \times 10^{10}$  cm<sup>-2</sup> s<sup>-1</sup> (open circles) for Sample 1 and a generation rate of  $4 \times 10^{17}$  (solid triangles) and  $2 \times 10^{15}$  cm<sup>-3</sup> s<sup>-1</sup> (open triangles) for Sample 2. Dashed and solid lines indicate the best fits, assuming two and three defect contributions, respectively.

depend on the bias light level, denoting the highest characteristic frequency  $\omega_t^H$ . On the other hand, in the  $Y/\omega$  spectra of lower frequencies an indication of leveling off is observed, denoting the onset of the LF regime and the lowest characteristic frequency  $\omega_t^L$ .

The characteristic frequencies  $\omega_t^H$  and  $\omega_t^L$  differ by about 2-3 orders of magnitude, indicating at least two different defect states with which the electrons interact. This is supported from the fact that these two defects generate two apparent steps in the Y spectra, around  $\omega_t^H$  and  $\omega_t^L$ , respectively. Moreover, these steps represent the expected shift to higher frequencies upon rising the  $E_{\rm tn}$  level to shallower energies by increasing the bias light level [1] (Fig. 1(a) and (b)) and/or decreasing temperature (not shown). Since at each step near  $\omega_t^i$  and lower  $\omega$  the respective  $E_{\omega}^i$  level is fixed at the  $E_{\rm tn}$  level, Y term does not reflect the  $D^i(E)$ distribution. In this region, according to Eq. (1) Y is dominated by the respective  $(\pi/2)H(\omega, \omega_t^i)c_s^i D^i(E_{\rm tn})kT$  product, which reflects the frequency dependence of  $H(\omega, \omega_t^i)$ . The  $\omega_t^H$ ,  $\omega_t^L$  and the  $D^H(\vec{E}_{tn})$ ,  $\vec{D}^L(\vec{E}_{tn})$  are extracted such that the above product provides a good fit to the experimental Y spectra at each step. The  $c_n^H$  and  $c_n^L$  are extracted by means of  $\omega_t^H, \omega_t^L$  and the dc photoconductivity  $\sigma_p$  [1,2]. By shifting the  $E_{tn}$  level with the bias light level at different energies the  $D^{H}(E)$  and  $D^{L}(E)$  are determined, which are plotted in Fig. 2(a).

Although the calculated Y values (dashed lines) using Eq. (1) and the extracted  $c_n^i$ ,  $D^i(E)$  of the two defect contributions reproduce the spectra around the two steps in Fig. 1(a) and (b), the so calculated Y values underestimate



 $10^{0}$ 

(a)

 $10^{0}$ 

 $10^{2}$ 

 $10^{4}$ 

 $10^{1}$ 

(b)

 $10^{3}$ 

 $10^{5}$ 



Fig. 2. Calculated  $D^{H}(E)$ ,  $D^{I}(E)$  and  $D^{L}(E)$  distributions of (a) Samples 1 (solid line) and 2 (dashed line) and (b) Sample 3 in annealed (dashed lines) and LS (solid lines) states.

Table 1 Calculated  $c_n^i$  (cm<sup>-3</sup> s<sup>-1</sup>)

	Sample 1	Sample 2	Sample 3
$c_n^H$ $c_n^I$	$3 \times 10^{-6}$ $1.4 \times 10^{-7}$	$ \begin{array}{c} 1 \times 10^{-6} \\ 8 \times 10^{-8} \end{array} $	$5 \times 10^{-7}$ $2 \times 10^{-8}$
$C_n^L$	$6.8 \times 10^{-9}$	$3.5 \times 10^{-9}$	-

systematically the experimental ones between  $\omega_t^L$  and  $\omega_t^H$ . This issue could be resolved by an increasing  $D^{L}(E)$ towards shallower energies for  $\omega_t^L < \omega$ , which, however, is not observed in Fig. 2(a). On the other hand, since  $E_{\omega}^{H}$  is fixed at  $E_{\text{tn}}$  for  $\omega_{t}^{L} < \omega < \omega_{t}^{H}$ , the energy dependence of  $D^{H}(E)$  has no effect in this region. Hence, it is concluded that there is an additional contribution from a third defect, having a capture coefficient  $c_n^I$  between those of the other two defects. Indeed, a reasonable fit (solid lines) of the experimental Y spectra of Fig. 1(a) and (b) are obtained using three defect contributions in Eq. (1). The capture coefficients  $c_n^i$ , that make the best fit to Y term of all the analyzed samples at about 0.6 eV below  $E_{\text{C}}$  are summarized in Table 1, while the  $D^{I}(E)$  of the third defect is also plotted in Fig. 2(a). As can be seen, despite that the samples come from different laboratories, their defect characteristics are very similar. Thus, in a-Si:H the electrons interact thermally with three distinct defect states above midgap having values of the order of  $10^{-6}$ ,  $10^{-7}$  and  $10^{-9}$  cm<sup>-3</sup> s<sup>-1</sup> for the highest  $(c_n^H)$ , intermediate  $(c_n^I)$  and lowest  $(c_n^L)$  capture coefficients, respectively.

From Sample 3, which was also measured after LS, only the  $D^{H}(E)$  and  $D^{I}(E)$  distributions were extracted, which are plotted in Fig. 2(b) [2]. The contribution from the third defect with the lowest capture coefficient  $(c_n^L)$  and the predicted plateau of  $Y/\omega$  spectrum at low frequencies (not shown here) were not observed, because this sample has been measured in a relatively shorter range of frequencies. Upon LS, we have observed an unusual decay (arrows in Fig. 2(b)) of both defect states before the dangling bond creation near midgap and a simultaneous increase in the capture coefficients of the shallower states [2]. A similar decay of the DOS was also reported recently by deep level transient spectroscopy experiments [4].

## 4. Discussion

The present analysis revealed a complicated pattern of defect structure above midgap of a-Si:H, consisting of three different defect states. These three defect states having large differences in the capture coefficients for electrons cannot be explained by the two possible (neutral and charged) states in which the Si dangling bond can be found above midgap.

The defect states with the lowest capture coefficient  $c_n^L$ and the highest density  $D^L(E)$  could be attributed to neutral normal dangling bonds or antibonding states of strained bonds. On the other hand, the defects with the highest capture coefficients can be attributed, in general, to dangling bonds with a Si–H bond next to them in order to explain their high capture probability [1]. The hydrogen three-bond center, SiHSi [2], and an over-coordinated defect complex [4],  $\equiv$ SiH<sub>2</sub><sup>+</sup>, are good candidates for the two defects with the higher capture coefficients  $c_n^H$  and  $c_n^I$ . This assignment is supported from the fact that both centers could be removed upon LS as recently suggested in Refs. [2] and [4], which can explain the unusual decay of the DOS above midgap (Fig. 2(b)).

#### 5. Conclusion

From the characteristic frequencies defining the onset of the HF and LF regimes of the Y term, the defect states with the highest and lowest capture coefficients were revealed, respectively. Additional defect states with a capture coefficient value between those of the other two defects were found as well. The two defects with the higher capture coefficients can be attributed to hydrogen-related centers. The presence of Si–H bonds in these centers may explain their high capture probability. Moreover, changes in the hydrogen bonding that can take place in these centers may result in their elimination during the initial stage of light degradation.

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