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Critical comparison of light-induced changes in sub-band-gap absorption and photoconductivity in hydrogenated amorphous silicon

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This work compares changes in the density of states due to light-induced degradation estimated by photoconductivity with those measured by photothermal deflection spectroscopy (PDS) on a series of hydrogenated amorphous silicon (*a*-Si:H) films having different valence bandtail widths (E_0). We find that the photoconductivity measurements indicate orders of magnitude larger defect density changes than do the PDS measurements as the valence bandtail becomes broader. This conflict is resolved by showing that this difference is due to changes in the recombination rate coefficient K with valence bandtail width. The absolute change in K increases exponentially with E_0 . However, the change in K relative to the K of the annealed state decreases with E_0 , explaining why poor material shows a smaller light-induced effect.

There has been considerable work on the light-induced degradation phenomenon in hydrogenated amorphous silicon (*a*-Si:H).¹ In general, prolonged illumination causes the photoconductivity σ of the material to decrease and the sub-gap density of states (DOS) to increase. Several authors have tried to relate these two parameters. In particular, Stutzmann *et al.*² found that the photoconductivity is inversely proportional to the electron spin resonance (ESR) signal; therefore, they write $\sigma \sim 1/N_s$, and show that this relation holds during degradation for device quality material. Wronski *et al.*³ repeated these measurements using both ESR and the integrated subgap DOS obtained using photothermal deflection spectroscopy (PDS), and obtained similar results. Therefore, in the above relationship, N_s can represent either the total number of spins (ESR) or the integrated subgap density of states (PDS), which agrees with the work of Jackson and Amer.⁴ If this relationship were universal, then the photoconductivity change could be used as a direct measure of the increase in subgap DOS arising from the degradation.

In this letter we report measurements of the change in photoconductivity as well as changes in the subgap DOS resulting from light-induced degradation of a series of *a*-Si:H and amorphous silicon carbon (*a*-SiC:H) samples having different valence bandtail widths E_0 . We find that the photoconductivity measurements, in contrast to the previous results,^{2,3} indicate significantly larger defect density changes upon light soaking than do the PDS measurements as the valence bandtail becomes broader. We demonstrate that these large photoconductivity changes are governed not so much by the increase in the subgap DOS but rather by changes in the electron-hole pair recombination rate coefficient K as the bandtail width changes. Furthermore, we find that the amount of light degradation becomes larger in absolute magnitude as the Urbach edge (E_0) widens, but that the relative change upon light soaking, compared to the initially prepared material, is smaller, which is consistent with other results.¹

The samples were deposited on Corning 7059 glass by rf glow discharge of silane and/or silane-methane gas mixtures

in a deposition system described elsewhere.⁵ For the *a*-Si:H films, the rf power and/or the substrate temperature were varied from their optimum values (70 mW/cm², 250 °C) used to deposit device quality material, while the carbon content was varied to change the properties of the *a*-SiC:H films. Such variations had been shown previously to produce films with differing valence bandtail widths.^{6,7} The samples, having thicknesses typically between 1–2 μ m, were first annealed at 170 °C for 1 h to reach the initial state *A*. To reach state *B*, they were then light soaked for 22 h under a General Electric model ELH lamp calibrated to 100 mW/cm². Room-temperature and atmosphere photoconductivity measurements in both states *A* and *B* were made using the same light. The Urbach edge width was measured using PDS, and the subgap DOS for states *A* and *B* were obtained following the procedure of Jackson and Amer.³ For the DOS values, the range of integration was from half the optical band gap to the energy value where the sub-band-gap absorption meets the valence bandtail. Table I lists the relevant measured parameters.

Assuming that $\sigma \propto 1/N_s$, then the difference

$$\Delta N_s = 1/\sigma_B - 1/\sigma_A \quad (1)$$

between the reciprocal photoconductivities in states *B* and *A* should give a measure of the number of light-induced defects.² The number of defects produced by light soaking was also determined from the difference in subgap absorption in states *A* and *B* as measured by PDS. These data are shown in Fig. 1, where the light-induced defect densities determined both from the photoconductivity measurements [$\Delta N(\text{PC})$] and from the PDS measurements [$\Delta N(\text{PDS}) = N_B - N_A$] are plotted versus E_0 . As can be seen, the $\Delta N(\text{PC})$ measurements show a dramatic increase with increasing E_0 , whereas the $\Delta N(\text{PDS})$ measurements show little change. Note that the present changes in photoconductivity are similar in magnitude, on our device quality material, to those observed by Kuwano *et al.*⁸ for films deposited in their superchamber system after ~ 20 h of light soaking, while the present $\Delta N(\text{PDS})$ results are consistent with those of Skumanich and Amer.⁹ The present results differ from those reported

TABLE I. Properties of *a*-Si:H and *a*-SiC:H samples as a function of increasing valence bandtail width E_0 .

Sample no.	Deposition ^a cond.	L (μm)	E_0 (meV)	H^b (at. %)	N_A^c (10^{16})	N_B^c (10^{16})	σ_A^d (10^{-6})	σ_B^d (10^{-6})	K_A^e	K_B^e	ΔK	$\Delta K/K_A$
1		1.0	49	8.0	2.6	3.4	217	14.8	0.0018	0.02	0.018	10.11
2	133 mW	1.3	50	6.8	1.1	2.1	111	8.4	0.008	0.058	0.05	6.21
3		1.8	51	5.8	0.6	1.1	92	13.7	0.022	0.066	0.044	2.01
4		0.7	54	11.6	2.2	4.1	17.2	6.8	0.026	0.036	0.01	0.38
5	167 mW	2.5	57	6.8	1.3	1.9	18	1.9	0.043	0.28	0.237	5.51
6	200 °C	1.2	58	12.8	2.2	3.6	12.8	3.1	0.036	0.089	0.053	1.47
7	220 °C	1.5	60	10.0	1.8	2.8	6.1	3.0	0.092	0.12	0.028	0.30
8	170 °C	1.3	64	13.5	2.1	3.7	11.1	1.5	0.043	0.19	0.147	3.42
9	150 °C	2.5	67	16.8	2.1	3.7	0.5	0.3	0.88	1.00	0.12	0.14
10	$X_C = 0.035$	1.7	76	12.0	1.5	2.4	1	0.3	0.68	1.6	0.89	1.31
11	$X_C = 0.143$	1.4	80	16.6	11.4	14.3	0.01	0.01	7.3	12.7	5.39	0.74

^aThe relevant deposition parameters (rf power, substrate temperature), when different from the optimum values, are noted. The last two samples are *a*-SiC:H alloys.

^bThe H content was determined from the area under the 630 cm^{-1} infrared Si-H absorption peak.

^cThe units are cm^{-3} .

^dThe units are $(\Omega\text{ cm})^{-1}$.

^eArbitrary units.

earlier.^{2,3} In particular, for none of the present samples do we see a one-to-one relationship between changes in the photoconductivity and changes in PDS upon light soaking, either for device quality material ($N_A \sim 5 \times 10^{15}\text{ cm}^{-3}$) or for material with a wider valence bandtail. That is, for a given change in photoconductivity upon light soaking, we see a much smaller PDS change than do either Stutzmann *et al.*² or Wronski *et al.*³

Clearly, then, we need to examine the assumptions under which the defect densities are obtained by these two techniques. First of all, PDS measures transitions from filled to empty states. The photoconductivity, however, as defined by

Eq. (1), is influenced only by those states between the hole and electron quasi-Fermi levels. If all the light-induced defects were created near midgap, then the PDS and photoconductivity results should show a one-to-one correspondence. If, on the other hand, the states were created throughout the gap, the PDS would then measure a larger light-induced change than would the photoconductivity. For most of our samples, however, the reverse is true; that is, the PDS measurements indicate a significantly smaller number of defect states than do the photoconductivity measurements. Therefore, the simple picture that $\sigma \propto 1/N_s$ must not always be true.¹⁰

We suggest that the difference between the number of light-induced states as measured by PDS and photoconductivity has to do with the nature of the recombination process itself. If recombination involved only direct capture of free electrons and holes at the dangling bond states, which are characterized by a single capture cross section, then there should be a one-to-one correspondence between the PDS and photoconductivity results. This assumes, as outlined previously, that all the light-induced states are generated between the quasi-Fermi levels. In reality the recombination process is more complicated.¹¹ It involves first trapping by tail states, followed by subsequent tunneling to and recombination in the deep trap states (dangling bonds). Therefore, both the tail state density and the recombination pathway involving the tail states play an important role. In all likelihood, it is the hole being trapped in a valence bandtail state that determines the recombination rate.¹¹

To explore this, we note in Fig. 1 that $\Delta N(\text{PC})$ increases exponentially as the width of the valence bandtail increases, suggesting that the wider bandtails play a role in the increased light-induced effect as measured by the change in photoconductivity. Note that the range of $\Delta N(\text{PC})$ values for the present samples is much larger than the range of $\Delta N(\text{PDS})$ values; we believe the larger $\Delta N(\text{PC})$ values reflect changes in the recombination rate constant as a result of light soaking.

We can check this idea by modifying the photoconduc-

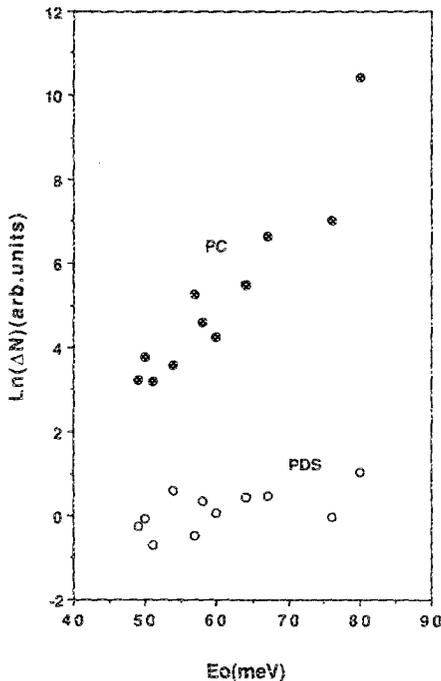


FIG. 1. Natural logarithm of the density of light-induced defects (arbitrary units) as determined from photoconductivity measurements $\Delta N(\text{PC})$ and from PDS measurements $\Delta N(\text{PDS})$, plotted vs the width of the Urbach edge E_0 .

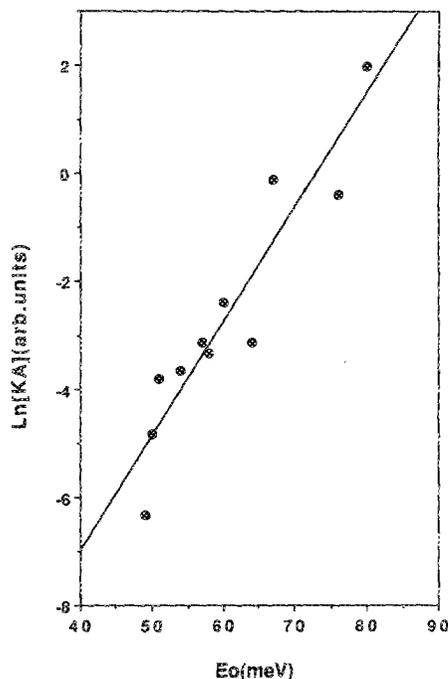


FIG. 2. Natural logarithm of the recombination rate coefficient (arbitrary units) for the initial state $\ln(K_A)$ vs the Urbach edge E_0 .

tivity density of states relationship to include a variable recombination rate coefficient; i.e., we now write $\sigma \sim 1/N_s K$, where K is the rate coefficient for recombination at a dangling bond. Note that K is equivalent to A_N in Eq. (1) of Wronski *et al.*,³ except that in our case we assume it to be variable, i.e., a function of valence bandtail width. Since we have already measured both the photoconductivities and the densities of midgap states (dangling bonds) in states A and B , we can directly determine K_A , K_B , and $\Delta K = K_B - K_A$. These results are also tabulated in Table I, while the K_A vs E_0 data are plotted in Fig. 2. The data in Fig. 2 are representative of the changes observed in all K parameters with valence bandtail broadening. It is clear that both K_A and K_B increase dramatically with E_0 , thus giving credence to the above recombination model involving the tail states. We also see, however, that ΔK increases with E_0 . Note that using Eq. (1) to determine ΔN_s from the photoconductivity data would incorrectly suggest that a large number of midgap states had apparently been generated to produce such a large change in $\Delta N(\text{PC})$. This is clearly at variance with the PDS results. The changes in photoconductivity are seen to be due more to changes in K than in N_s . This is consistent with the results of McMahon *et al.*,¹¹ who found that light soaking increases the transition rate between holes in the deeper valence band-

tail states and the dangling bonds. The present data suggest that, as the valence bandtail broadens, the valence bandtail to dangling bond transition rate for the hole increases. In addition, this increase in E_0 leads to a larger change in K on light soaking. These results show clearly that an *increased* light-induced effect occurs in nondevice quality material. However, the relative change upon light soaking compared to the initially prepared material (state A) is smaller, which is consistent with other results.¹

Finally, we comment that the changes we have observed are virtually independent of the initial state density N_A . In particular, except for samples 3 and 11 in Table I, the initial DOS (N_A) is almost constant, whereas the initial photoconductivity (σ_A) changes by nearly a factor of 500 as E_0 increases. The present results are clearly different from what we would expect, based upon the experiments of Stutzmann *et al.*² and Wronski *et al.*³

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¹See, for example, in *AIP Conference Proceedings No. 157 on Stability of Amorphous Silicon Alloys and Devices, Palo Alto, CA 1987*, edited by B. L. Stafford and E. Sabisky (American Institute of Physics, New York, 1987).

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¹⁰Z. E. Smith and S. Wagner [*Mater. Res. Soc. Proc.* **95**, 551 (1987)] have suggested that $\sigma \sim (1/N_s) \gamma \exp(E_A - E_p) (1 - \gamma) / KT$, where $\gamma = T_0 / (T_0 + T)$. Taking $\gamma = 0.8$, the smallest value that we measure for our samples, and the measured movement of the Fermi level with light soaking of at most 0.1 eV, we find that we are unable, using this approach, to reconcile the differences between the present $\Delta N(\text{PC})$ and $\Delta N(\text{PDS})$ results.

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