PHYSICAL REVIEW B **69**, 193204 (2004)

Pulsed-illumination study of metastable defect creation time scales in hydrogenated amorphous silicon

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(Received 28 October 2003; revised manuscript received 14 January 2004; published 26 May 2004)

By degrading a-Si:H samples with pulsed illumination, we establish an upper bound to the rise and decay times of possible light-induced slow precursors to photodegradation of photoconductivity in hydrogenated amorphous silicon. Our 200-mW/cm^2-exposure pulses have a far lower peak intensity than previous pulsed studies and degradation results can therefore be compared directly with continuous illumination of the same intensity. We study pulse times from 40 μs to 30 ms separated by dark times from 360 μs to 300 ms. The observed degradation dependence on pulse and dark times can be traced to room-temperature annealing during the dark time between pulses and is not attributable to slow precursors. The experiments show that any degradation precursor rise time that is slower than the electron-hole recombination time must still be shorter than 40 μs and that any precursor fall time must be shorter than 360 μs.

DOI: 10.1103/PhysRevB.69.193204 PACS number(s): 61.80.Ba, 73.50.Pz, 73.61.Jc, 61.43.−j

The metastable light-induced degradation[1] of carrier lifetimes and electronic quality in hydrogenated amorphous silicon (a-Si:H) remains a difficult scientific problem.[2] Understanding and solving the problem of degradation is critical to more widespread application of this inexpensive semiconductor. Metastable photoconductivity degradation exhibits at least three distinct time scales. The shortest of these time scales is the electron-hole recombination time, which determines the rise and fall times of the photocarrier concentration. Photocarriers are the primary precursor to degradation in a-Si:H.[3] The longest time scale is the degradation saturation time, set by a balance of light-induced creation against light-induced and thermal annealing.[4] Saturation of the defect density requires hours or days of degradation, depending on the light intensity. The easiest-to-observe time dependence controls the threefold-coordinated Si dangling-bond (DB) density through many orders of magnitude in time, from seconds to hours of degradation; it is a roughly $t^{1/3}$ increase caused by a gradual fall of the defect-precursor density due to DB creation.[5,6] In the Stutzmann recombination model,[5] the precursor is electrons and holes. In the Branz hydrogen collision model,[6] the controlling precursor is mobile hydrogen.

The Branz model predicted a fourth time scale, slower than the electron-hole recombination time, associated with the rise and fall time of the light-induced mobile H precursor density. Early indications of a fourth time scale in degradation came from laser-pulsed illumination experiments. Laser-pulsed degradation of undoped a-Si:H has a higher efficiency per absorbed photon than during cw illumination.[7,8] Stutzmann *et al.* explained this observation by assuming that the degradation of the a-Si:H sample continues between laser pulses, because the electron population has a slower decay time than the light pulse.[8] However, fast σ_{ph} measurements show that σ_{ph} decays as fast as the light pulse.[9] Branz[6] proposed that a slow-decaying secondary precursor could explain these results and attributed the effect to residual light-induced mobile H persisting after each pulse of illumination (in the dark). Of course, there are other possible slow precursors to degradation. For example, Fritzsche suggested that widespread structural changes might lead to creation of DB's that relieve light-induced strain-fields.[10] Thus, the slow, secondary, precursor to light-induced defects might be the local strain field.

In this paper we describe an experimental search for a fourth degradation time scale by a comparative study of photoconductivity (σ_{ph}) under low-intensity pulsed and continuous degradation. Our preliminary studies had revealed a pulse-time dependence of degradation that seemed to suggest a precursor rise time of about 100 μs.[11] In this paper, we show that the observed degradation dependence on pulse and dark times can be traced to room-temperature annealing during the dark time between pulses and is not attributable to slow precursors. The experiments establish upper bounds to precursor rise and fall times and constrain metastability models.

We report detailed results for a device-quality a-Si:H film grown by plasma-enhanced (PE) chemical vapor deposition (CVD) at the Electrotechnical Laboratory (now renamed AIST) in Japan. The sample has coplanar thermally evaporated chromium top electrodes 3.6 mm long and separated by 0.5 mm. We confirmed our main findings on PECVD samples obtained from the University of Chicago and the National Renewable Energy Laboratory (NREL).

For good reproducibility of the data, we anneal, degrade, and measure samples *in situ*; i.e., once mounted, the sample is not moved between experiments. The samples are illuminated with the focused light of a red laser diode (663 ± 2 nm) that produces 200 mW/cm^2 on the sample. The laser diode is driven by a power supply which can be externally modulated with a function generator to produce light pulses of rectangular shape with a rise and fall time of 1 μs. We measured the corresponding rise and decay times of σ_{ph} to be 1.5 μs. For the experiments reported in this paper, we use pulses (t_p) of from 40 μs to 30 ms separated by dark intervals (t_d) of from 360 μs to 300 ms. Thus, the photocarrier pulses are close to rectangular in time. The light intensity is kept the same for continuous (cw) and pulsed exposures (see Fig. 1, inset).

We define $\eta = t_p/(t_p + t_d)$ as the duty cycle of the pulsed illumination. The illumination time t_{ill} is t_p times the number of pulses. We call the accumulated dark time during the exposure t_d^{tot}. The sum of t_{ill}, t_d^{tot}, and any additional measurement time is the total experimental time t_{expt}.

A cartridge heater mounted in the sample holder is used for *in situ* annealing. The sample temperature T is measured with a thermocouple pressed on a piece of Corning 7059 substrate within 1 cm of the sample. The samples are preannealed at 200 °C for 8–20 h and again at 190 °C for 20 min before each exposure. A N_2 gas flow through the sample compartment provides cooling and slows oxidation. The light of 650-nm red light emitting diodes (LED's) at an intensity of about 3 mW/cm^2 is used for σ_{ph} measurements. Each experiment is operated by a computer in an automated mode for maximum consistency in annealing, exposure, and conductivity measurements. As data were taken at different intervals in different experiments, we have sometimes interpolated to estimate σ_{ph} at common analysis times.

All degradation is made near room temperature. We used three different techniques to measure the temperature rise of test films during cw illumination: First, we replace the sample with a solar cell and monitor the change in open circuit voltage (V_{OC}). Second, a sample with a predeposited nickel meander was mounted in the sample holder, and the change in Ni resistance was calibrated against T. Third, we monitored the temperature-dependent change in transmittance of a probe He-Ne laser beam in the film. We consistently find negligible heating. The rise in T is certainly below 5 °C and probably less than 2 °C during our light soaks. This is consistent with the T rise, $\Delta T \approx 1$ °C, obtained by a thermal conductivity calculation that assumes a perfect heat sink behind the glass substrate. Our determination of ΔT for cw light exposure is sufficient to set this upper bound; ΔT for pulsed exposure must always be smaller. For further details, see Ref. 12.

Figure 1 compares the photoconductivity decay during degradation with 200 mW/cm^2 of continuous red light to the decay under the same intensity of $t_p = 40$ μs pulses separated by $t_d = 10$ ms. Clearly, pulsed illumination degrades photoconductivity less rapidly than cw when plotted against illumination time t_{ill}.[13] Figure 2 shows a variety of degradation experiments with different t_p, t_d, and duty cycles η. In each of these experiments, the light is turned on for t_{ill} of 70–110 min, but results are plotted against a horizontal axis showing total experimental time t_{expt} rather than the more conventional t_{ill} (as in Fig. 1). The duty cycle η of the exposure light is the main factor determining the σ_{ph} decays, so we have labeled the experiments by η. There is little dependence on t_p or t_d. Figure 3 shows explicitly the dependence on pulse time of the photoconductivity measured after $t_{\mathrm{ill}} = 10$ min of illumination for the experiments of Fig. 2. The dashed line shows the value of σ_{ph} after cw illumination for $t_{\mathrm{ill}} = 10$ min. It is again clear that there is little dependence of degradation upon pulse time when the duty cycle (and therefore t_{expt}) is held fixed.

Room-temperature annealing[12,14,15] causes the weak dependence on η seen in Fig. 3. A smaller duty cycle permits more time for thermal annealing of light-induced defects between illumination pulses. This room-temperature annealing is particularly important when photoconductivity, rather than defect density, is measured.[14] To make the annealing effect plainer, Fig. 4 compares the room-temperature "anneal" recovery of σ_{ph} in the dark (A) after 84 min of cw exposure (●) to σ_{ph} at the end of $t_{\mathrm{ill}} = 84$ min of $t_p = 40$ μs degradation experiments with different t_d (solid symbols). Here, the bottom horizontal axis, labeled t_d^{tot}, shows the total time the sample spends at room temperature in the dark, whether during the period of pulsed degradation or after cw exposure.

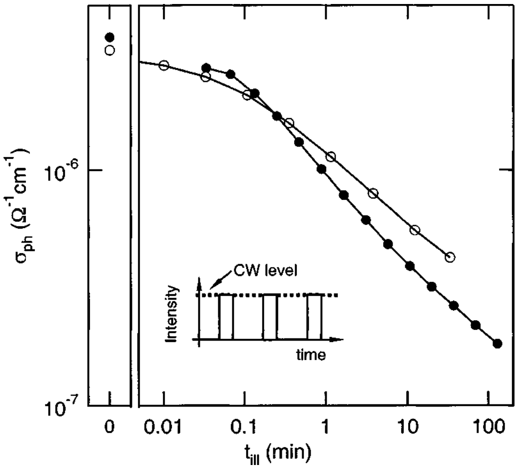

FIG. 1. Photoconductivity decays during degradation with 200 mW/cm^2 of red light used either continuously (●) or in 40-μs pulses separated by $t_d = 10$ ms (○). The $t = 0$ points outside the main figure indicate the annealed photoconductivities before illumination. Inset is a schematic comparison of the pulsed (solid line) and cw illuminations (dashed line), emphasizing the identical intensity levels used.

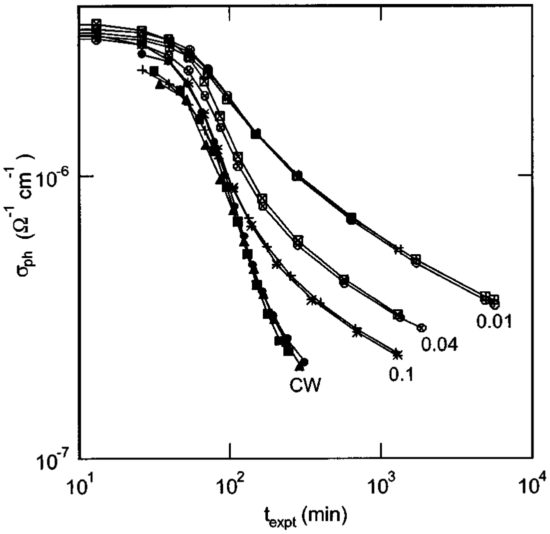

FIG. 2. The results of typical cw and pulse degradation experiments, plotted against total experimental time. The duty cycles are as indicated in the figure, with $t_p = 0.04$, 0.4, and 3 ms for $\eta = 0.01$; $t_p = 0.04$ and 4 ms for $\eta = 0.04$; and $t_p = 0.04$ and 30 ms for $\eta = 0.1$. Duty cycle, not t_p, determines the degradation rate.

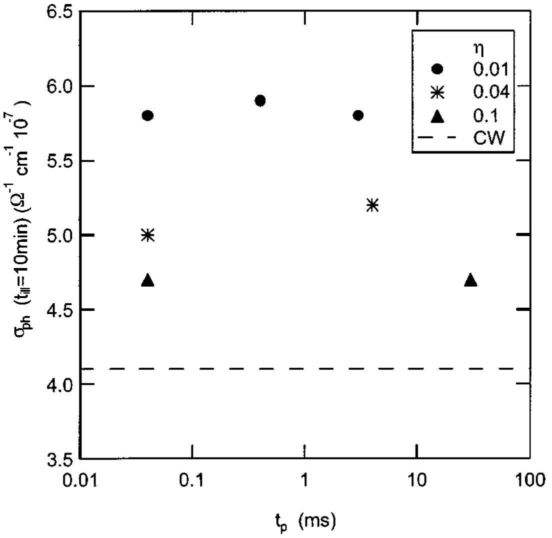

FIG. 3. σ_{ph} after 10 min of illumination vs t_p for the data of Fig. 2. Here cw and three other duty cycles are shown, as indicated in the legend.

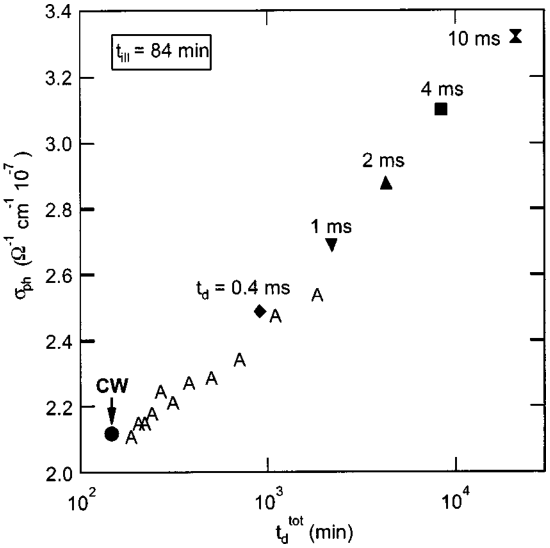

FIG. 4. σ_{ph} for various experiments, after illumination for $t_{\mathrm{ill}} = 84$ min. The cw experiment is indicated by the solid circle (●); subsequent room-temperature dark “anneals” are shown with the symbol A. The other symbols indicate pulsed degradation experiments with fixed $t_p = 40\ \mu$s and various t_d (labeled). The bottom axis is the accumulated dark time in the experiments, evidently the crucial experimental variable.

The time for σ_{ph} measurements is considered dark time and therefore included in t_d^{tot}; thus t_d^{tot} for the cw experiment is not zero. Note that after 84 min light soaking plus an anneal, σ_{ph} is nearly independent of whether the illumination is cw before the anneal or is made up of pulses interspersed with the annealing. We clearly see the continued progression of room-temperature annealing as the duty cycle is decreased (because the total dark time increases).

Thus, nearly all differences between cw and pulsed degradation at these time scales are well understood as room-temperature annealing effects during the dark time between pulses. We find no obvious effect of t_p or t_d that is not accounted for by this effect. We conclude that for our 200-mW/cm^2 light intensities, the degradation must occur mainly while the light pulse is on. This means that any putative slow precursor to degradation must rise with a time constant of less than 40 μs, our shortest t_p. Further, any precursor must decay (after the light is extinguished) with times less than 360 μs, our shortest t_d.

A study by Stradins *et al.*[16] at shorter time scales, using pairs of much more intense laser and flashlamp pulses, revealed that the degradation increases when pulse pairs are close together. An excess degradation, not accounted for by photocarrier distribution overlap or T rise, was observed for separations as long as 645 ns. No effect was seen for flashlamp pulses separated by 10 μs. Stradins *et al.*[16] conclude that if a slow precursor causes the effect, it must have a decay time in the range of from 645 ns to 10 μs after a pulse is extinguished. This precursor time scale would be too fast to be observed in our experiments.

In conclusion, there is no precursor to metastable degradation of photoconductivity in a-Si:H observable in our light-induced degradation with about 200 mW/cm^{-2} illumination. Our experiment comparing degradation with pulsed illumination to continuous (cw) illumination excludes any putative degradation precursors with rise times in the range from 40 μs to about 30 ms and also excludes decay times slower than 360 μs. This intermediate time scale might have been expected to describe the rise time of some secondary precursor to degradation produced by the electron-hole recombination. We note that Stradins *et al.*[16] may have observed an intermediate time scale in the range from 645 ns to 10 μs for degradation with intense pulses.

The authors thank Richard Crandall, Pauls Stradins, Qi Wang, Hellmut Fritzsche, and Martin Stutzmann for helpful discussions. Samples were graciously supplied by A. Matsuda, H. Fritzsche, and B. Nelson. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-98G010337.

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[13] By chance, the annealed-state photoconductivity (shown by the boxed points in Fig. 1) was slightly higher before the cw illumination and a crossing of the curves is observed at $t \sim 15$ s. In other runs, this crossing is not seen. We focus in this article on the more robust long-time illumination differences.

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