Fast Metastable-Defect Creation in Amorphous Silicon by Femtosecond Light Pulses

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The creation of metastable dangling-bond defects in hydrogenated amorphous silicon subjected to short, intense laser pulses is investigated. It is found that pulse excitation leads to an order-of-magnitude increase in the defect creation rate compared to continuous illumination with the same average photon flux and photon energy. This implies that metastable-defect formation depends superlinearly on the density of photoexcited carriers. The much larger defect creation rate in the case of pulse excitation allows us to clarify the origin of saturation effects in the metastable-defect density, that are important for an assessment of the long-term conversion efficiency of amorphous-silicon solar cells.

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Light-induced reversible structural changes are a fundamental phenomenon in many amorphous semiconductors. The best known examples are the reversible photodarkening of chalcogenide semiconducting glasses [1,2] and the light-induced creation of metastable dangling-bond defects in hydrogenated amorphous silicon (*a*-Si:H, "Staebler-Wronski effect") [3-5]. In this article, we present new experimental results for metastable dangling-bond creation using femtosecond laser pulses instead of continuous illumination. These results can serve as a test of the various models proposed so far for light-induced metastability in undoped *a*-Si:H.

The samples used in this study were deposited by glow discharge of silane and had a thickness of 1.5 μm. Illumination was performed at room temperature with an intensity of 300 mW/cm^2 for periods up to 8 h. The photoconductivity and the dangling-bond density (from spin resonance and defect absorption) were measured repeatedly during the illumination runs to monitor the increase in the number of metastable defects. The reversibility of all light-induced effects was verified by annealing at 180 °C for 1 h. Three types of illumination were employed: continuous illumination with a Kr^+-ion laser at 1.92 eV ("cw"), light pulses with a duration of 300 μs and a repetition rate of 330 Hz using the same laser, and ultrashort (defocused) pulses at 2 eV with a duration of 100 fs and a repetition rate of 7 kHz. In the latter case, the laser source consisted of a colliding-pulse mode-locked laser (CPM) operating at 620 nm and amplified by a Cu-vapor-laser-pumped six-pass dye cell. Details of this laser system have been described previously [6]. The low repetition rate of 7 kHz is necessary in order to achieve a complete relaxation of photoexcited carriers between consecutive pulses. The photon energies of the different laser sources correspond to an absorption coefficient in the *a*-Si:H samples of $\approx 10^4$ cm^{-1}.

As a reference for the case of pulse illumination, we first summarize in Fig. 1 the light-induced changes of the ESR spin density N_S and of the photoconductivity σ_{ph} caused by cw irradiation. The spin density increases from $\approx 5\times10^{15}$ cm^{-3} to 10^{17} cm^{-3} after 4 h and eventually reaches a steady state at a level of $\approx 2\times10^{17}$ cm^{-3} after 1 d of illumination. The inverse of N_S is shown in Fig. 1(a) to provide a better comparison with the photoconductivity σ_{ph} in (b). Also shown in Fig. 1 is the exponent γ of the generation-rate dependence of σ_{ph}, $\sigma_{ph} \propto G^\gamma$, where the generation rate G is proportional to the light intensity I.

One of the key features of the metastable-defect creation in Fig. 1 is the strongly sublinear dependence of N_S or σ_{ph} on illumination time. For $t_{ill} \gtrsim 100$ s the time dependence can be described by $\sigma_{ph} \propto 1/N_S \propto t_{ill}^{-1/3}$. Originally, this sublinearity was explained by a kinetic model in which metastable dangling bonds are created by rare nonradiative, bimolecular recombination events between electrons and holes trapped in conduction and valence band tail states [4]. Then, one obtains for the de-

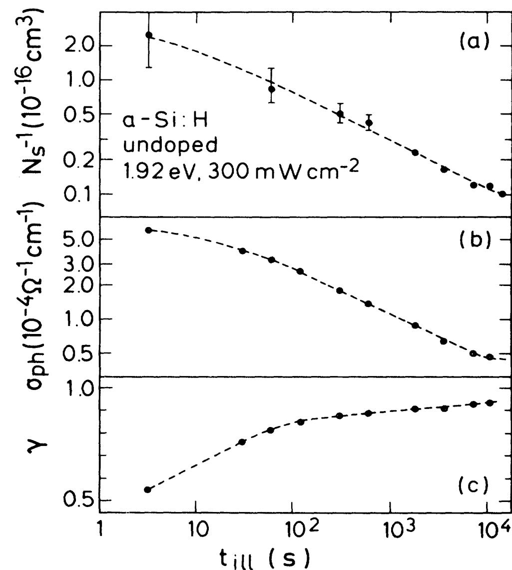

FIG. 1. Dependence of various sample parameters on illumination time t_{ill} during prolonged irradiation of *a*-Si:H with cw light ($\hbar\omega = 1.92$ eV, $I = 300$ mW/cm^2): (a) inverse dangling-bond spin density N_S^{-1}; (b) room-temperature photoconductivity σ_{ph}; and (c) exponent γ of the intensity dependence $\sigma_{ph} \propto G^\gamma$. Note the logarithmic scale for N_S^{-1} and σ_{ph} in (a) and (b). For long times, both quantities follow a $t_{ill}^{-1/3}$ time dependence within experimental accuracy.

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fect creation rate

$$\frac{dN_S}{dt_{\text{ill}}} \propto np \approx n^2 \propto \frac{G^2}{N_S^2}, \tag{1}$$

where we have used the experimental observation that during most of the degradation procedure the electron and hole densities n and p are governed by monomolecular recombination via (stable or metastable) dangling-bond defects: $n,p \propto G/N_S$. Integration of Eq. (1) directly yields the $t_{\text{ill}}^{-1/3}$ time dependence in Fig. 1.

More recently, alternative kinetic models based on stretched-exponential time dependences for structural relaxation processes in a-Si:H [7] have also been applied successfully to cw-light-induced defect formation in this material [8,9]. In the stretched-exponential approach, the defect creation rate is written as

$$\frac{dN_S}{dt_{\text{ill}}} \propto G t_{\text{ill}}^{-\alpha} \{N_S(\infty) - N_S\}, \tag{2}$$

where $N_S(\infty)$ is the "saturated" metastable defect density reached for $t_{\text{ill}} \to \infty$ and $0 \leq \alpha < 1$ is a characteristic parameter related to the time dispersion of relaxation processes in a disordered solid. For a-Si:H it has been suggested that α is determined by dispersive diffusion of hydrogen atoms [9]. The saturated spin density $N_S(\infty)$ is thought to arise either from preexisting charged defects (D^+,D^-), which are converted into paramagnetic, metastable defects (D^0) by carrier trapping [10], or from impurity atoms such as carbon and oxygen being responsible for the creation of metastable defects by an extrinsic mechanism [11]. On the other hand, in the model based on tail-to-tail recombination of photoexcited carriers, saturation occurs because of a balance between light-induced creation of metastable defects and their thermal annealing [4].

For the specific process of metastable-defect creation in a-Si:H we exploited in this study the fact that the same average photon flux, when concentrated into short, intense pulses, can maintain bimolecular recombination even for relatively high densities of recombination centers. Then, processes like defect creation by tail-to-tail recombination should also proceed much faster than for the same photon flux in a cw experiment, and also a kinetic behavior different from the $t_{\text{ill}}^{1/3}$ dependence in Fig. 1 should be observed. The general solution of the carrier rate equations in a semiconductor in which recombination can occur either by bimolecular band-to-band transitions or monomolecular recombination via defects is given by

$$\tilde{n},\tilde{p} = \tilde{G}\{\tilde{N} + [\tilde{N}^2 + \tilde{G}]^{1/2}\}^{-1}, \tag{3}$$

where $\tilde{n}$, $\tilde{p}$, $\tilde{G}$, and $\tilde{N}$ are generalized expressions for the electron and hole densities, the generation rate, and the recombination-center density, for which all rate constants have been set to unity. In Fig. 2, we show a plot of Eq. (3) for different values of $\tilde{N}$ and $\tilde{G}$. The two limiting cases, $\tilde{n} = \tilde{G}^{1/2}$ for $\tilde{N} = 0$ and $\tilde{n} = \tilde{G}/2\tilde{N}$ for large $\tilde{N}$ are

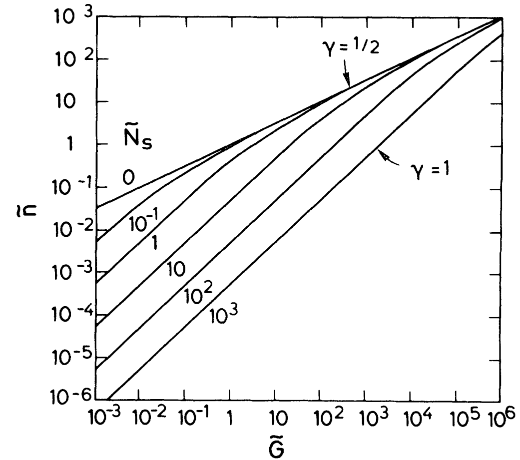

FIG. 2. Generalized excess carrier density $\tilde{n}$ as a function of generation rate $\tilde{G}$ for different densities $\tilde{N}$ of recombination centers. $\gamma = \frac{1}{2}$ and $\gamma = 1$ denote the bimolecular and monomolecular limits, respectively.

clearly seen. $\tilde{N} = 1$ and $\tilde{G} = 1$ approximately correspond to the case of a-Si:H in the annealed, stable state with $N_S \lesssim 10^{16}$ cm^{-3} under illumination with an intensity of ≈ 100 mW/cm^2, for which the recombination is essentially bimolecular ($\gamma \approx \frac{1}{2}$; cf. Fig. 1). The important point in connection with Fig. 2 is that an increase of $\tilde{N}$ quickly changes the recombination to monomolecular. Thus, if we were to maintain a bimolecular recombination for $\tilde{N}$ between 10 and 100 ($N_S \approx 10^{17}$–10^{18} cm^{-3} in a-Si:H), we would need a generation rate of $\tilde{G}$ between 10^2 and 10^4, i.e., 10 W/cm^2 to 1 kW/cm^2. Obviously, such high illumination intensities are prohibitive in a cw experiment because of sample heating. In a pulsed experiment, however, high generation rates are easily achieved for sufficiently short pulses.

In Fig. 3, we show the dependence of $\sigma_{\text{ph}} \approx e\mu_n n$ on illumination time t_{ill} for two examples of pulse excitation: 300-μs pulses at a power of 1 W with a repetition rate ν_{rep} of 330 Hz, and 100-fs pulses with a peak power of 1.5×10^8 W and a repetition rate of 7 kHz. In both cases, the average intensity on the sample, $\bar{I} = \nu_{\text{rep}} \tau_{\text{pulse}} I_{\text{pulse}}$, is equal to 100 mW within 10%, and we show for comparison a cw illumination run with the same intensity and photon energy. The experimental results in Fig. 3 essentially agree with what is to be expected from the bimolecular model for metastable defect creation: With increasing concentration of photons in short pulses, the defect creation and the resulting decrease of σ_{ph} proceed much more rapidly, and the overall time dependence changes from $\approx t_{\text{ill}}^{-1/3}$ (cw) to $\approx t_{\text{ill}}^{-1/2}$ (fs pulses). Whereas for cw illumination a decrease of σ_{ph} by 1 order of magnitude requires an irradiation time of 3 h, the same decrease for fs pulses is obtained after only 5 min. For longer, less-intense pulses a lower defect creation rate is obtained; however, still faster than for the cw case. We have found

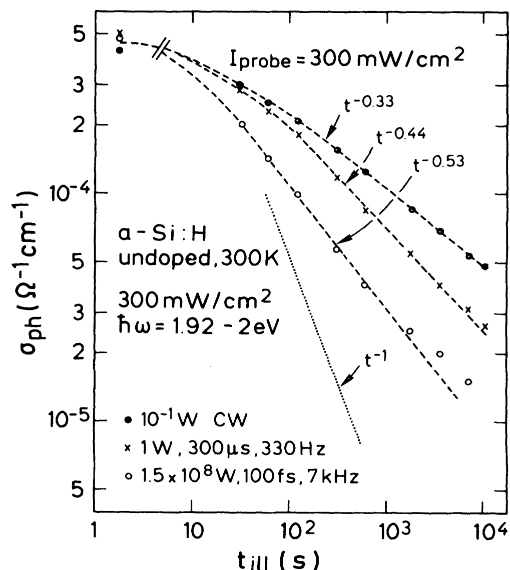

FIG. 3. Decrease of the dc photoconductivity $\sigma_{\rm ph}$ in undoped a-Si:H during illumination with three different methods: continuous illumination (cw, solid circles), 300-μs pulses (crosses), and 100-fs pulses (open circles). In the case of pulse excitation the pulse power and repetition rate were adjusted so as to obtain the same average intensity (100 mW) also used for cw irradiation. The dotted curve shows the t^{-1} dependence expected for a defect creation rate which is independent of the density of already existing defects.

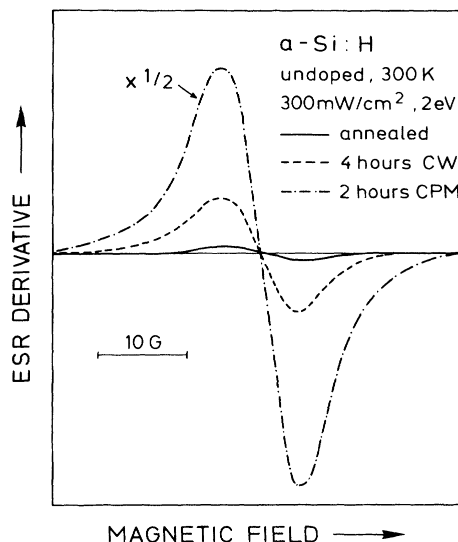

FIG. 4. Electron-spin-resonance spectra showing the dangling-bond spin signal at $g=2.0055$ in the annealed state (solid curve), after 4 h light soaking with continuous laser light (1.92 eV, 300 mW/cm^2, dashed curve), and after 2 h illumination with fs laser pulses (2 eV, 300 mW/cm^2, dash-dotted curve). Note that the trace in the case of fs pulse light soaking has been scaled down by a factor of 2. The respective spin densities are approximately 1×10^{16}, 1×10^{17}, and 6×10^{17} cm^{-3}.

that the length of the laser pulses (and thus the peak power) is quite unimportant for the accelerated defect creation, as long as the pulse length remains short compared to the typical excess carrier lifetime of about 10^{-6} s. In particular, we can exclude multiphoton processes as a possible origin of the accelerated defect creation, since such processes should strongly depend on peak power. No significant changes were observed for peak powers varying between 10^8 W for fs pulses to 10^2 W for μs pulses. Also, a similar acceleration was obtained for illumination with pulsed light sources of different wavelengths.

Obviously, the large increase in the metastable defect creation rate caused by the same average photon flux for pulsed versus cw creation implies a superlinear dependence of $dN_S/dt_{\rm ill}$ on the photoexcited carrier densities, n or p. For a microscopic mechanism with a probability depending linearly or sublinearly on excess carrier density, the time average of $dN_S/dt_{\rm ill}$ over the duration of a pulse would be equal to or even lower than in the case of cw illumination, so that such processes are incompatible with the present experimental results. On the other hand, the G^2 or n^2 dependence for the tail-to-tail recombination model in Eq. (1) immediately provides the superlinearity leading to the increased degradation rate in the case of pulsed excitation, since the time average $\langle n^2(t)\rangle_t$ is much larger for pulsed than for cw excitation. For a simple analysis, we have assumed that after fs pulse excitation and thermalization of the excess carriers into band-tail states the density of trapped charge carriers follows the relation

$$n(t)=n(0)\exp\left(-\frac{t}{\tau}\right),\quad \tau_{\rm pulse}\ll t<\frac{1}{\nu_{\rm rep}}\ll t_{\rm ill}\,, \tag{4}$$

where the initial excess carrier density $n(0)$ for short pulses ($\tau_{\rm pulse}\ll\tau\approx10^{-6}$ s) is directly proportional to the pulse energy $G\tau_{\rm pulse}$, and the lifetime τ of thermalized excess carriers in a-Si:H at room temperature is limited by recombination via dangling-bond defects, $\tau\propto N_S^{-1}$. By discretizing Eq. (1) in terms of individual pulses and substituting Eq. (4) for the (time-dependent) excess carrier density $n(t)$ during each pulse, one obtains for the increase of the metastable defect density with illumination time in the case of pulsed illumination

$$N_S(t_{\rm ill})=\{N_S^2(0)+\tilde{c}\nu_{\rm rep}G^2\tau_{\rm pulse}^2t_{\rm ill}\}^{1/2}. \tag{5}$$

Thus, the $N_S\propto G^{2/3}t_{\rm ill}^{1/3}$ dependence following from Eq. (1) for cw illumination should be replaced by an $N_S\propto G^1t_{\rm ill}^{1/2}$ dependence for pulsed illumination. This is in agreement with the time dependence shown in Fig. 3 for $\sigma_{\rm ph}$, and also the linear dependence on the average pulse energy $G\tau_{\rm pulse}$ in Eq. (5) has been verified experimentally by varying the generation rate G over 1 order of magnitude.

As a final point, we address the saturated metastable-

defect density $N_S(\infty)$ obtained after long illumination times. Three different models for this saturation effect have been discussed: a balance between light-induced creation and thermal annealing, a balance between light-induced creation and light-induced annealing, or a depletion of available defect creation sites [4,8,12]. Among these models, the last one can be discarded on the basis of our present results: As shown in Fig. 4, already after 2 h of fs pulse illumination, the metastable-defect density largely exceeds the saturated density in the cw case. For the same sample, metastable-dangling-bond densities in excess of 10^{18} cm^{-3} have been obtained by long illumination with an unconverted Cu vapor laser ($\lambda = 510$ nm, $\tau_{pulse} = 15$ ns), showing that the saturated defect densities of $\approx 2\times10^{17}$ cm^{-3} observed for cw illumination cannot be due to depletion of a limited density of specific defect creation sites, e.g., impurity-related complexes. In contrast, a balance between creation and thermal annealing is compatible with the experimental results in Fig. 4: Because of the larger defect creation rate in the case of pulsed excitation, the steady-state defect density should occur at higher values than in the case of cw excitation. Note that for both cases the same average light intensity has been employed, so that identical thermal conditions in the sample during irradiation prevail. The third possibility, namely, a balance between light-induced creation and light-induced annealing, would also be consistent with our present results, provided that the probability of light-induced annealing does not increase in the same manner as defect creation when going from cw to pulse excitation.

In conclusion, we have shown that illumination of *a*-Si:H by short, intense light pulses causes a much faster formation of metastable dangling-bond defects than cw irradiation with the same average intensity and photon energy. For fs laser pulses, an increase of the defect creation rate by more than a factor of 30 has been obtained. This result implies a strongly superlinear dependence of the defect creation rate on photocarrier density and is quantitatively consistent with the bimolecular recombination model for metastable defects in *a*-Si:H. The results are incompatible with models involving a linear or sublinear carrier-density dependence of the defect creation rate [e.g., Eq. (2)]. From the fact that the metastable-defect density after prolonged pulse excitation significantly exceeds the constant, "saturated" density obtained after long cw irradiation we can also conclude that this steady-state density is not due to depletion of a limited number of available defect creation sites. Finally, we would like to mention that pulse irradiation can be used for accelerated lifetime testing of *a*-Si:H–based solar cells and photosensors under realistic conditions.

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[1] S. R. Elliott, J. Non-Cryst. Solids **81**, 71 (1986).
[2] D. K. Biegelsen and R. A. Street, Phys. Rev. Lett. **44**, 893 (1980).
[3] D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[4] M. Stutzmann, W. B. Jackson, and C. C. Tsai, Phys. Rev. B **32**, 23 (1985).
[5] S. B. Zhang, W. B. Jackson, and D. J. Chadi, Phys. Rev. Lett. **65**, 2575 (1990).
[6] J. Feldmann, J. Nunnenkamp, G. Peter, E. Göbel, J. Kuhl, K. Ploog, P. Dawson, and C. T. Foxon, Phys. Rev. B **42**, 5809 (1990).
[7] J. Kakalios, R. A. Street, and W. B. Jackson, Phys. Rev. Lett. **59**, 1037 (1987).
[8] D. Redfield and R. H. Bube, Appl. Phys. Lett. **54**, 1037 (1989).
[9] W. B. Jackson, Philos. Mag. Lett. **59**, 103 (1989).
[10] R. S. Crandall, Phys. Rev. B **43**, 4057 (1991).
[11] D. Redfield and R. H. Bube, Phys. Rev. Lett. **65**, 464 (1990).
[12] H. R. Park, J. Z. Liu, and S. Wagner, Appl. Phys. Lett. **55**, 2658 (1989).