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Dispersive model for the kinetics of light-induced defects in *a*-Si:H

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The kinetics of light-induced defect generation (Stabler-Wronski effect) in hydrogenated amorphous silicon (*a*-Si:H) was investigated for a wide range of illumination intensities and temperatures. A model is proposed to account for the kinetics of defect generation, based on the interconversion of silicon weak bonds with an exponential distribution of binding energies into dangling bonds. Illumination increases the defect density by reducing the energy barrier for defect formation and the defect formation energy. The model reproduces the observed time evolution of the defect density and establishes a connection between the Stabler-Wronski effect and the weak-bond model.

The degradation of the opto-electronic properties of hydrogenated amorphous silicon (*a*-Si:H) under illumination (Stabler-Wronski effect[1]) and under carrier accumulation is a major limitation for the application of this material in electronic devices, particularly for solar cells. Degradation is associated with the breaking of weak silicon-silicon (or silicon-hydrogen) bonds and the creation of silicon dangling bonds.[2] These defects are recombination centers with electronic states close to the center of the band gap. Defect generation is closely related to the presence of both photogenerated electrons (n) and holes (p), which increase the rate of defect formation. In fact, the time dependence of light-induced defect generation around room temperature is well accounted for by a model proposed by Stutzmann *et al.*, where the defect formation rate is proportional to the recombination rate np.[3] Recently, metastability in *a*-Si:H has also been explained in terms of stretched exponentials, which also describes the kinetics of light-induced defect generation and annealing.[4,5] None of these models fully accounts for both the temperature and light intensity dependence of defect kinetics.[5]

Recently, we demonstrated that the steady-state density of light-induced defects in *a*-Si:H can be understood in terms of a chemical equilibration model involving the interconversion of silicon weak bonds into defects.[6] The model is similar to the one introduced to describe defect formation by doping,[7] carrier-induced defects in metal-insulator-semiconductor structures,[8] and thermal quenching[9] in *a*-Si:H. The effect of illumination is to reduce the effective defect formation energy, shifting the chemical equilibrium and enabling more weak bonds to be converted into defects.

A natural question at this point is whether a similar model can be extended to account for the kinetics or time dependence of light-induced defect generation. In this paper, we investigate the kinetics of light-induced defect generation over a wide range of temperatures (250 to 400 K) and illumination intensities. The experimental results are well explained by a model with an energy distribution of barriers for the kinetics of defect generation similar to the one used to account for the steady-state defect density under illumination.[6] The dispersive character of the model arises from the existence of an exponential energy distribution of barrier heights for defect formation (weak-bond model).

The samples used in this study are 1 μm thick undoped-*a*-Si:H films grown by glow discharge decomposition of pure silane. Prior to each soaking experiment, the samples were annealed in the dark at 500 K for at least 2 h, and then slowly cooled down (<2 K/min) to the soaking temperature. In the light-soaking experiments the light source was either a tungsten-halogen lamp with filters to cut wavelengths below 630 nm, or the 647.1 nm line of a Kr^+ laser to insure uniform defect generation. The time dependence of the defect density during soaking was measured using a variation of the constant photocurrent method (CPM) described in Ref. 6, which consists of measuring the ratio r of the CPM signal at the photon energies of 1.15 and 2.0 eV. The defect density is proportional to r. This procedure allows the determination of the defect density in a relatively short time (30 to 40 s). We verified that annealing effects are negligible within this 30 s interval for the whole temperature range investigated here.

Figures 1(a) and 1(b) show a double logarithmic plot of the time dependence of the defect density at different temperatures, at a fixed illumination intensity of $F=2.8$ W/cm^2, corresponding to a generation rate at 350 K of 4×10^{22} cm^{-3}s^{-1}. Figure 1(b) is the corresponding curve for $F=580$ mW/cm^2 ($\sim1.0\times10^{22}$ cm^{-3}s^{-1}). The defect density increases with illumination from an initial value of $\sim10^{16}$ cm^{-3} to a maximum value around 10^{17} cm^{-3} for long illumination times. A clear saturation in the defect density is only achieved at temperatures above 350 K, and the saturation values depend weakly on illumination intensity and on temperature.[6,10] In the mid-range of defect densities (around 5×10^{16} cm^{-3}) the curves are approximately linear, indicating a power-law dependence on time of the form $N_s\sim t^{\epsilon}$ with ϵ between 0.2 and 0.3. A similar dependence has been measured by Lee, Ohlsen, and Taylor,[11] and is somewhat weaker than the time dependence reported by Stutzmann *et al.* where $\epsilon=\frac{1}{3}$.[3] The power-law range shrinks for high temperatures (>350 K) due to the increase in the initial defect density by thermal generation of defects and a decrease in the steady-state values,[9] and at low illumination intensities due to a reduction in the saturation defect density.

In the following, a model for the kinetics of defect generation is introduced, based on the density of states

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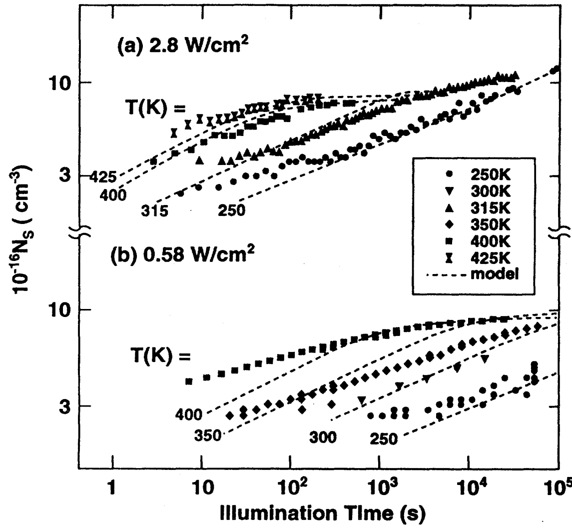


FIG. 1. Time evolution of the light-induced defect density in a-Si:H measured at different temperatures, measured by a variation of the CPM method described in the text, for illumination intensities of (a) 2.8 W/cm^2 and (b) 0.58 W/cm^2. The dashed lines are calculated using the model for light-induced defect creation presented in the text [see Eq. (6)].

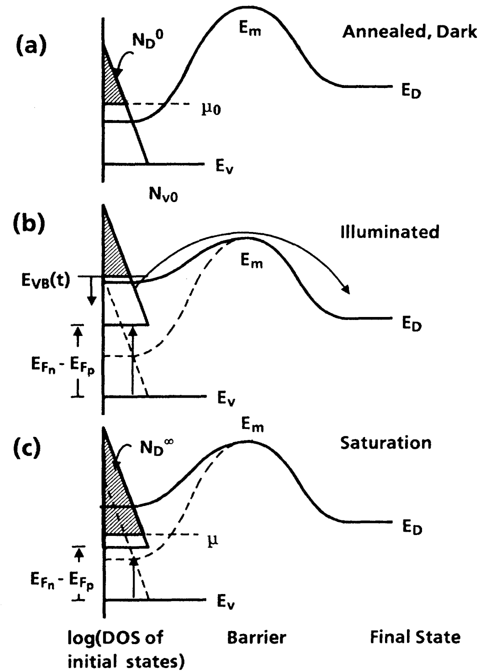


FIG. 2. (a) Schematic representation of the density of states of a-Si:H in the annealed state in the dark. E_v is the valence-band mobility edge, E_m is the maximum barrier for defect creation, and E_D is the defect level in the gap. The weak Si–Si bonds are assumed to have an exponential energy distribution and in equilibrium all weak bonds with energy larger than defect chemical potential, μ_0, are converted into defects, as indicated by the shaded area. (b) Defect generation process under illumination. The quasi-Fermi levels for electrons and holes are denoted by E_{F_n} and E_{F_p}, respectively. Under illumination the energy of the weak-bond configuration increases relative to that of the defect configuration. The arrows in the diagram indicate how the different energy levels change with time, as more defects are formed. (c) Steady-state equilibrium under illumination with a steady-state defect chemical potential μ.

(DOS) diagram of Fig. 2(a). In the diagram, E_v is the valence-bond mobility edge and E_D is the position of the defect level in the gap. A single energy level for the neutral defects is assumed. The valence-band tail is assumed to have an exponential distribution of states given by $N_v(E_{VB}) = N_{v0}\exp(-E_{VB}/kT_v)$, where T_v is the characteristic temperature of the order of 500 K. Recently, we showed that the steady-state defect density under illumination can be described by a chemical equilibration process involving photogenerated electrons (e) and holes (h), weak bonds (Si-Si), silicon-hydrogen bonds (Si-H), and defects, described by the reaction:[6,7]

$$\mathrm{SiH} + (\mathrm{SiSi}) + e + h \rightleftharpoons (\mathrm{Si}-) + (\mathrm{SiHSi}-)\,. \qquad (1)$$

In this reaction a weak-bond reacts with the hydrogen from a SiH bond generating two dangling bonds (Si–) and (Si–H–Si–). A similar reaction accounts for the equilibrium defect density of a-Si:H in the annealed state.[9] The model assumes that ionic and multielectronic contributions for the energy difference between reactants and products can be neglected in comparison to the one-electron contribution. In this case, the formation energy $2U_f$ of a pair of dangling bonds from a weak bond with electronic state E_{VB} in the gap is the energy $2(E_D - E_{VB})$ necessary to promote the electrons in the original weak bond to the defect state, minus the energy separation $(E_{F_n} - E_{F_p})$ between the electron and hole quasi-Fermi levels, i.e., $2U_f(E_{VB}) = 2(E_D - E_{VB}) - (E_{F_n} - E_{F_p})$.

The chemical equilibrium between defects and weak bonds in the steady-state condition under illumination can be described by a temperature and light intensity dependent defect chemical potential $\mu = [2E_D - (E_{F_n} - E_{F_p}) + kT\ln(N_D^\infty/N_H]/2$.[6,9] Here, N_D^∞ is the total density of converted weak bonds and N_H is the hydrogen concentration. The position of the defect chemical potential in the dark (μ_0) and under illumination (μ) are shown in Figs. 2(a) and 2(c), respectively. At 0 K, all weak bonds with energy $E_{VB} > \mu$ (or μ_0) are converted into defects, as indicated by the shaded areas in Fig. 2. At finite temperatures, the steady-state distribution of converted weak bonds $N_v^c(E_{VB})$ is expressed by

$$N_v^c(E_{VB}) = \frac{N_v(E_{VB})}{1 + \exp[2(\mu - E_{VB})/kT]}\,. \qquad (2)$$

With increasing illumination, μ shifts towards the valence band and more weak bonds are converted into defects.

Equations (1) and (2) give the steady-state defect density under illumination, which depends only on the reaction reactants and products. The generation kinetics, on the other hand, depends on the barriers between the intermediate states of the reaction process. We will assume that the reaction rate limiting step involves the excitation over a barrier whose height E_B varies linearly with the energy E_{VB} of the dangling bond being converted, i.e.,

$E_B = E_m - n_l E_{VB}$, where n_l is a constant and E_m is the activation energy associated with the conversion of a strong silicon-silicon bond. We assume further that an electron hole pair is involved in this particle process, so that the rate is proportional to the np product and the effective barrier is reduced by $E_{F_n} - E_{F_p}$. The effective activation energy U to convert a weak bond of energy E_{VB} is then given by

$$U(E_{VB}) = E_m - n_l E_{VB} - (E_{F_n} - E_{F_p}) . \tag{3}$$

The correlation to the defect kinetics is now straightforward for low temperatures, where the characteristic width kT_v of the distribution of activation energies is large compared to kT. In this case, after an illumination time t all weak bonds with effective barrier height $U(E_{VB}) < kT \times \ln(\nu_0 t)$ are converted into defects, where ν_0 is a characteristic attempt frequency for excitation over the barrier. With increasing time, weak bonds with progressively smaller energies $E_{VB}(t) = [E_m - (E_{F_n} - E_{F_p}) - kT \times \ln(\nu_0 t)]/n_l$ and larger barrier U are converted to defects. The situation is illustrated in Fig. 2(b), where the arrows indicate how the different energy levels change as more and more defects are formed with increasing illumination times.

The bond density $N_D(t)$ converted to defects after illumination time t is

$$N_D(t) = \int_{E_{VB}(t)}^{\infty} N_v(E')dE' \sim \int_{E_{VB}(t)}^{\infty} N_v^c(E')dE' . \tag{4}$$

In the last integral, the distribution of weak bonds $N_v(E')$ was replaced by the distribution $N_v^c(E_{VB})$ of weak bonds that are actually converted to defects in the steady-state situation after long illumination times [see dashed lines in Fig. 2(c) and Eq. (4)]. This approximation provides a way of incorporating saturation effects in the kinetics of defect formation, which occurs when $E_{VB}(t)$ lies below the steady-state chemical potential under illumination μ. Only the distribution of weak bonds actually converted to defects in the steady-state situation participate in the kinetics: the other weak bonds with electronic states below μ are assumed to be in equilibrium with defects after the time t, having equal conversion and annealing rates.

The solution of Eq. (4) requires knowledge of the dependence of the quasi-Fermi potentials E_{F_n} and E_{F_p} on the defect density and on the illumination intensity. We will assume the following simple approximations for E_{F_n} in terms of G and N_s:

$$E_{F_n} - E_c = kT \ln \left[\frac{G^{\gamma_n}}{A_n N_c N_s^{\delta_n}} \right] . \tag{5}$$

A similar expression applies to E_{F_p}. Here, $\gamma_{n,p} \sim 1$, $0.6 < \delta_{n,p} < 1.2$,[5,12] E_c is the mobility gap, and $N_c(N_v) = 2.9 \times 10^{19} (T/300\ \mathrm{K})^{3/2}$ (Ref. 13) is the effective density of state at the conduction- (valence-) band mobility edge, and A_n (A_p) is the effective capture probability of the recombination centers for electrons (holes).

Integration of Eq. (4) under the assumption that $T \ll T_v$ yields the following expression for the defect density $N_s(t) = 2N_D(t)$:

$$N_s(t) = 2N_D(t) = \begin{cases} 2(kT_v N_{v0})^{n_l \epsilon/\beta} \left[\dfrac{(\nu_0 t) G^{\gamma_n + \gamma_p}}{A} e^{-(E_m - E_c)/kT} \right]^{\epsilon} & \text{if } E_{VB}(t) < \mu \text{ or } N_D(t) < \dfrac{T_v}{T_v + T'} N_D^{\infty}, \quad (6a) \\ 2N_D^{\infty} \left[1 - \dfrac{T'}{T_v - T'} \left(\dfrac{N_D^{\infty}}{k(T_v + T')N_{v0}} \right)^{T_v/T'} \left(\dfrac{(\nu_0 t) G^{\gamma_n + \gamma_p}}{A N_D^{\delta_n + \delta_p}(t)} e^{-(E_m - E_c)/kT} \right)^{T/n_l T'} \right] & \text{otherwise,} \quad (6b) \end{cases}$$

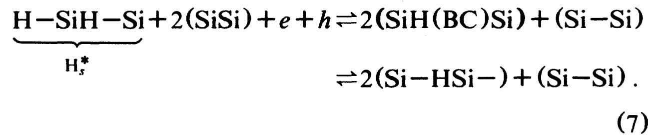
with $\beta = T/T_v$, $1/T' = 2/T - 1/T_v$, $A = 2^{\delta_n + \delta_p} A_n A_p N_c N_v$, and $\epsilon = \beta/[n_l + (\delta_n + \delta_p)\beta]$.

Equations (6a) and (6b) describe the kinetics of light-induced defect generation for low defect densities and near saturation, respectively. Far from saturation, a power-law dependence $N_s(t) \sim G^{(\gamma_n + \gamma_p)\epsilon} t^{\epsilon}$ is predicted. Taking the experimentally measured value of $\epsilon \sim 0.2$–0.3 (see Fig. 1), and assuming $T_v = 550$ K and $\delta_{n,p} = \gamma_{n,p} = 1$, we obtain a value $n_l \sim 1$ for the proportionality constant relating the defect formation energy to the weak-bond energy E_{VB}. At room temperature, this yields $N_s \sim G^{0.52} \times t^{0.26}$, which is close to the dependence determined experimentally.[3,11]

The dashed lines in Fig. 1 were calculated using Eq. (6) for the experimental conditions displayed in the figure. We assumed $E_m - E_c = 0.4$ eV (0.5 eV) and $\nu_0 = 2 \times 10^9\ \mathrm{s}^{-1}$ ($1 \times 10^{11}\ \mathrm{s}^{-1}$) in Fig. 1(a) [Fig. 1(b)]. The following parameters were used: $E_c = 1.6$ eV, $T_v = 550$ K, $N_{v0} = 2 \times 10^{20}\ \mathrm{cm}^{-3}\mathrm{eV}^{-1}$, $A_n = 3 \times 10^{-9}\ \mathrm{cm}^3/\mathrm{s}$, $A_p = 0.8 \times 10^{-9}\ \mathrm{cm}^3/\mathrm{s}$,[3] and $\delta_{n,p} = \gamma_{n,p} = 1$. These parameters are similar to those used to model the equilibrium defect density as a function of the temperature,[9] and the dependence of the saturation values of light-induced defects on illumination intensity and temperature.[6] For each curve, the saturation defect density was set equal to the measured value at each temperature. The initial defect density in the annealed state, and its temperature dependence, was not taken into account. The calculations reproduce reasonably well the experimental data in the low-temperature region and, in particular, the temperature dependence and the behavior of the defect density near saturation. At room temperatures, saturation effects become important for defect densities above 70% of the steady-state density. The dispersive model underestimates the temperature dependence of the defect density for high temperatures. As mentioned previously, Eq. (6) is only valid for temperatures substantially smaller than the characteristic temperature of the weak-bond distribution, so that a good agreement is not expected for temperatures above 400 K.

A value of n_l close to unity in Eq. (3) indicates that the rate limiting barrier for defect generation varies linearly with the dangling-bond energy E_{VB}. In the framework of the weak-bond model, this indicates that the creation of just one defect from a weak bond is involved in overcom-

ing the barrier. A possible microscopic model for light-induced defect formation is the dissociation of a diatomic hydrogen complex (H_2^* model).[14,15] The complex consists of a hydrogen at a bond center site [H(BC)] and a second hydrogen in an interstitial tetrahedral site [$H(T_d)$]. The complex itself has no electronic state in the gap and its dissociation reaction can be written as



$$\underbrace{\mathrm{H{-}SiH{-}Si}}_{H_2^*}+2(\mathrm{SiSi})+e+h \rightleftharpoons 2(\mathrm{SiH(BC)Si})+(\mathrm{Si{-}Si}) \rightleftharpoons 2(\mathrm{Si{-}HSi{-}})+(\mathrm{Si{-}Si})\,. \quad (7)$$

In the reaction, the H_2^* complex dissociates. The unpaired H reacts with a (SiSi) weak bond leading to the formation of two dangling bonds of the form (SiHSi−), as in Eq. (1). The rate-limiting process is the dissociation of the H_2^* complex. The initial energy of the H_2^* before dissociation depends on the strain of the Si−Si broken by the H pair, and is therefore roughly proportional to E_{VB} and distributed exponentially. The barrier to dissociate requires the occupation of the bonding and antibonding states of the H_2^* by an electron and a hole, respectively.[14] The levels are ~2.7 eV apart in crystalline silicon, but with the Coulomb attraction between the localized electron-hole pair the energy is estimated to be reduced by ~0.6 eV. Hence, the barrier is expected to be $\sim 2.1-(E_{F_n}-E_{F_p})-\alpha' E_{VB}$, which is the same as Eq. (2) with $E_m=0.5+E_c=2.1$ eV and $\alpha'=n_l=1$. Once the levels are occupied by an electron and a hole, the H_2^* complex dissociates with small or negligible barrier into two dangling bonds. Although not necessarily unique, the H_2^* dissociation model is thus consistent with the kinetics of light-induced defect formation observed in the experiments.

In conclusion, we reported experimental data on the kinetics of light-induced temperatures. This paper establishes that the kinetics of light-induced defect formation is consistent with chemical equilibration models assuming a distribution of energy barriers for defect formation. The kinetic results are consistent with a microscopic model attributing defect formation to the dissociation of paired H. Combined with our previous results showing that the same model can account for the steady-state defect densities, chemical equilibration with distribution of barriers must be considered a strong candidate for light-induced defect formation.

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[1]D. L. Stabler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).

[2]H. Dersch, J. Stuke, and J. Beichler, Appl. Phys. Lett. **36**, 456 (1981).

[3]M. Stutzmann, W. B. Jackson, and C. C. Tsai, Phys. Rev. B **32**, 23 (1985).

[4]R. H. Bube and D. Redfield, J. Appl. Phys. **66**, 820 (1988).

[5]W. B. Jackson, Philos. Mag. Lett. **59**, 103 (1989).

[6]P. V. Santos, W. B. Jackson, and R. A. Street (unpublished).

[7]K. Winer, Phys. Rev. B **41**, 12 150 (1990).

[8]W. B. Jackson, J. M. Marshall, and M. D. Moyer, Phys. Rev. B **39**, 1164 (1989).

[9]R. A. Street and K. Winer, Phys. Rev. B **40**, 6236 (1989).

[10]H. R. Park, J. Z. Liu, and S. Wagner, Appl. Phys. Lett. **55**, 2658 (1989).

[11]C. Lee, W. D. Ohlsen, and P. C. Taylor, in *Proceedings of the 18th International Conference on the Physics of Semiconductors*, edited by O. Engström (World-Scientific, Singapore, 1986), p. 1085.

[12]C. R. Wronski, Z. E. Smith, S. Aljishi, V. Chu, K. Shephard, D.-S. Shen, R. Schwartz, D. Slobodin, and S. Wagner, in *Stability of Amorphous Silicon Alloy Materials and Devices,* Proceedings of an International Conference, edited by B. L. Stafford and E. Sabisky, AIP Conf. Proc. No. 157 (AIP, New York, 1987), p. 70.

[13]N. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Rinehardt and Winston, New York, 1976).

[14]S. B. Zhang, W. B. Jackson, and D. J. Chadi, Phys. Rev. Lett. **65**, 2575 (1990).

[15]W. B. Jackson, Phys. Rev. B **41**, 10257 (1990).