Rate equation for metastable defects in hydrogenated amorphous silicon: The form of the light-induced annealing term

R. Meaudre, M. Meaudre, and S. Vignoli

Département de Physique des Matériaux, Université de Lyon I, 43 Boulevard du 11 Novembre 1918,
F-69622 Villeurbanne Cédex, France

Experimental evidence for light-induced annealing of defects in a-Si:H has recently been reported. However the experimental data about the removal of the defects under illumination are so limited that considerable uncertainty remains about the form of the light-induced term in the defect rate equation and its thermal activation energy. We here analyze the kinetics of light-induced creation and annealing of metastable defects in terms of a dispersive model. Our analysis suggests that the light-induced annealing term is proportional to the product of defect density and the carrier density. The activation energy of the light-induced annealing prefactor is about 0.45 eV.

Light-induced degradation of the properties of hydrogenated amorphous silicon (a-Si:H) is one of the major obstacles to the use of this material in electronic devices. Since the discovery of this effect[1] and despite considerable study, the light-induced reversible phenomena are poorly understood on a microscopic level. For this reason various models have been proposed for the kinetics of defect creation and annealing.[2] Very recently,[3,4] it has been experimentally shown that the rate of annealing of defects can be accelerated by illumination. Furthermore it has been shown[3] that illumination can increase or decrease the rate of annealing as compared to the dark annealing rate. These observations have sparked new interest and inspired new works[5-7] in the field since they question the most up-to-date sophisticated phenomenological models.[3] However the experimental data about the removal of the defects under illumination are so limited that the form of the light-induced annealing term is not precisely known. The aim of this paper is to address the problem.

Light-induced recovery of defects has been included in some theories[8] which led to the following rate law for the metastable defects:

$$\frac{dN}{dt} = \left[\frac{t}{\theta}\right]^{-\alpha}\left[C_1 R(N_t - N) - v_2 N - C_2 RN + v_1(N_t - N)\right] . \tag{1}$$

The meaning of the parameters is given in Ref. 8; we just recall here that N is the density of defects at time t and N_t is the maximum density of sites that can be converted to metastable defects. The quantity R represents only those recombination processes that are involved in defect creation and defect annealing processes; it can be written $R = G$ or $R \propto G^2/N^2$, G being the volume photoexcitation rate. $\alpha = 1 - \beta$ and θ characterize the dispersive behavior.

Since the same R occurs in light-induced generation and annealing, Eq. (1) is incompatible with the previously cited[3-7] experimental results. Therefore in a previous paper we suggested that it should be replaced by another equation [Eq. (2) in Ref. 3] in which we now introduce dispersive behavior in the form originally proposed by Bube and Redfield,[8]

$$\frac{dN}{dt} = \left[\frac{t}{\theta}\right]^{-\alpha}\left[C_d\frac{G^2}{a^2 N^2} - \lambda'NG - v_2 N + v_1(N_t - N)\right] , \tag{2}$$

where C_d and λ' are two temperature-dependent parameters. The disadvantage of Eqs. (1) and (2) is that they contain four terms. Furthermore, the physical meaning of the light-induced annealing term $-\lambda'NG$ is not obvious. Thus we prefer to make the carrier concentration explicitly appear:

$$\frac{dN}{dt} = \left[\frac{t}{\theta}\right]^{-\alpha}[C_n np - \lambda Nc] . \tag{3}$$

Here $n(t)$ and $p(t)$ are the concentrations of electrons and holes in the conduction and valence bands, $c(t)$ is a carrier concentration equal to $n(t)$ or $p(t)$, and λ is a temperature-dependent parameter.

The mechanism of defect creation due to the np product has been shown to work under illumination[9] and in the dark.[10] The physical meaning of the light-induced annealing term $-\lambda Nc$ is that the capture of carriers into defects triggers the light-induced annealing of the latter. Under illumination, in the case of monomolecular recombination, we have[9] $n = n_0 + G/A_n N$ and $p = p_0 + G/A_p N$, where A_n and A_p are the effective capture rates of the recombination centers (taken as N) for electrons and holes, and n_0 and p_0 are the carrier concentrations in the dark. Equation (3) becomes

$$\frac{dN}{dt} = \left[\frac{t}{\theta}\right]^{-\alpha}\left[C_d\frac{G^2}{A_n A_p N^2} + C_d\frac{G}{N}\left[\frac{p_0}{A_n} + \frac{n_0}{A_p}\right]\right.$$

$$\left. -\frac{\lambda G}{A} + C_d n_0 p_0 - \lambda N c_0\right] , \qquad (4)$$

where A is equal to A_n or A_p, depending on whether annealing is due to electrons or holes. c_0 is then equal to n_0 or p_0, respectively.

We now compare Eqs. (2) and (4) with experimental data. Let us first consider the annealing of defects in the dark and under cw illumination. The most complete data available to date being those of Gleskova, Morin, and Wagner,[5,7] we have used these data to show in Fig. 1 the dispersive behavior of the defect density, in qualitative agreement with Eqs. (2) and (4).

For any given temperature let us now consider two times such that N has the same value during relaxation in the dark or under illumination. We then obtain

$$Y(N) = \left[t'^\alpha\frac{dN}{dt}\right]_{i,N} - \left[t^\alpha\frac{dN}{dt}\right]_{d,N}$$

$$= \theta^\alpha\left[C_d\frac{G^2}{a^2 N^2} - \lambda' NG\right] \qquad (5)$$

from Eq. (2) and

$$Y(N) = \theta^\alpha\left[C_d\frac{G}{A_n A_p N^2}(G + p_0 A_p N + n_0 A_n N) - \frac{\lambda G}{A}\right] \qquad (6)$$

from Eq. (4). i and d are for illumination and dark, respectively. When $n \gg n_0$ and $p \gg p_0$, we then have

$$N^2 Y(N) = \theta^\alpha\left[C_d\frac{G^2}{a^2} - \lambda' GN^3\right] , \qquad (5')$$

$$N^2 Y(N) = \theta^\alpha\left[C_d\frac{G^2}{A_n A_p} - \frac{\lambda G}{A}N^2\right] , \qquad (6')$$

when the annealing term is $-\lambda' NG$ or $-\lambda Nc$, respectively.

$Y(N)$ has been calculated from the data in Refs. 5 and 7, with the values of $\alpha = 1 - \beta$ taken from Fig. 1.

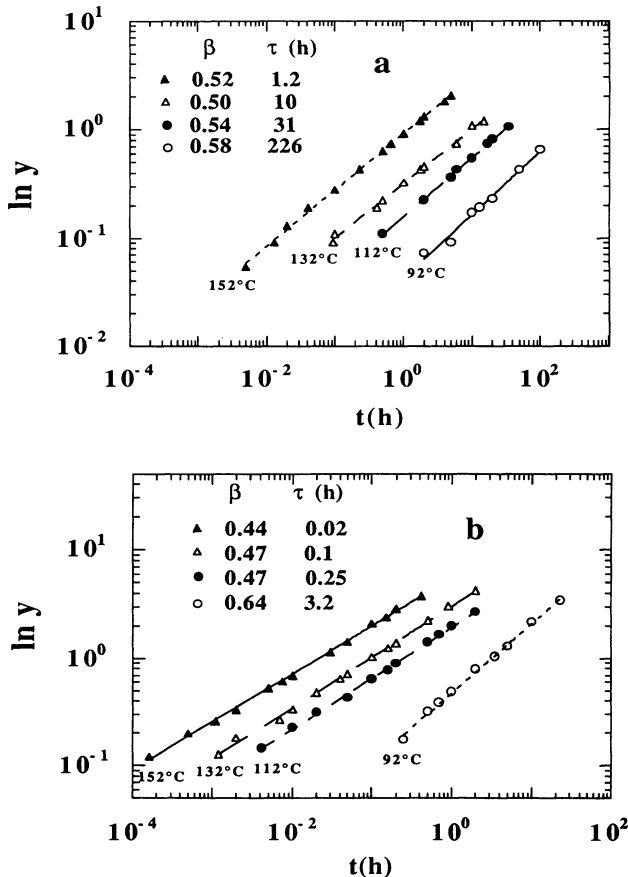Figure 2 shows that Eq. (5') works slightly better than Eq. (6') at low temperature while the opposite situation
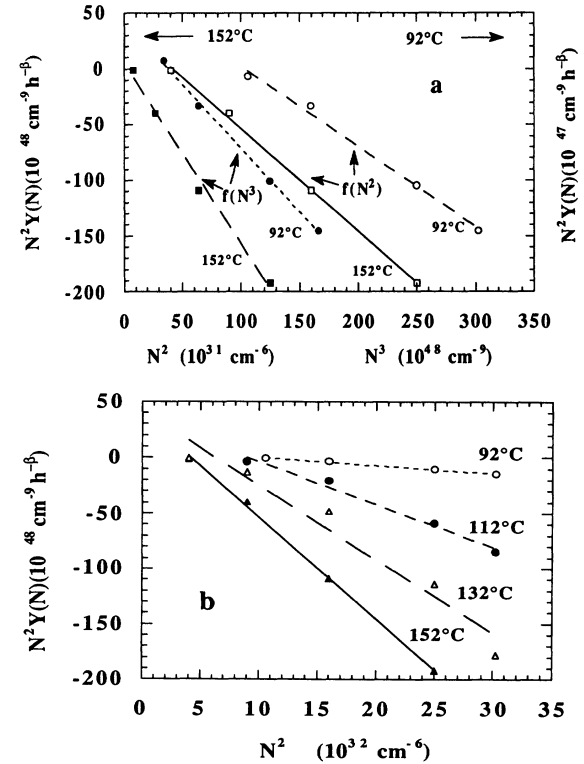

FIG. 1. Time dependence of the normalized defect density $y = [N(0) - N(\infty)]/[N(t) - N(\infty)]$ during annealing in the dark (a) and under illumination 0.34 W/cm² (b) at different temperatures. $N(0)$ and $N(\infty)$ are the defect densities at the beginning and at the end of the relaxation, respectively. The data have been taken from Ref. 5. The lines are fitted to the data using the function $y = \exp[(t/\tau)^\beta]$ with $\beta = 1 - \alpha$ and τ values given in the figure.

FIG. 2. (a) Plots of $N^2 Y(N)$ vs N^2 and N^3 derived from experimental data (Ref. 5) at two temperatures. The function $Y(N)$ is defined in the text. A better agreement with Eq. (5') as compared to Eq. (6') is obtained at low temperature while the opposite is observed at high temperature: the values of the regression coefficient of the fits are ■, 0.995; ●, 0.999; □, 0.999; ○, 0.996. (b) Plots of $N^2 Y(N)$ vs N^2 at different temperatures.

prevails at high temperature. It is then difficult to choose between Eqs. (5') and (6'); at this point neither equation can be excluded. However, interpretation of these data using Eq. (6') is more consistent with the results of other works, as we now show. From Eq. (6') and Fig. 2 it is easy to obtain the behavior of C_d and λ as a function of temperature. This is shown in Fig. 3. C_d is thermally activated with an activation energy of 0.1 eV, in good agreement with that (0.12 eV) given in Ref. 9. If the behavior of λ is analyzed in terms of a single activated process, a value of 0.45 eV is derived for the activation energy. However, the data $\log_{10}\lambda$ vs T^{-1} show a systematic deviation from a straight line, suggesting either large changes in the activation energy within a narrow temperature range or that the assignment of an activation energy to the optical anneal term is not the appropriate approach. The precedent activation energies are lower than those derived for C_d and λ' by Gleskova, Morin, and Wagner[7] *from the same experimental data* but without taking into account the dispersive behavior and assuming that the annealing term was of the form $-\lambda'NG$. It is worth noting that Graeff, Buhleier, and Stutzmann,[6] in their analysis of light-induced annealing experiments, again assuming nondispersive kinetics, found a better agreement with the experimental data when the annealing term was taken as $-\lambda Nc$; no value was given for the activation energy of λ.

Let us now draw other inferences from Eqs. (3) and (4). First we consider the value of the steady-state defect density N_S under illumination. Equation (4) shows that

$$N_S \propto G^{1/2} . \tag{7}$$

The experiments leading to N_S are difficult and tedious to carry out, particularly at room temperature,[11] so we took advantage of the thermally activated processes appearing in Eqs. (3) and (4) to get quickly and precisely the values of N_S by using light soaking at high temperature. Our results are given in Fig. 4, along with the data obtained by other groups. A reasonable agreement with Eq. (7) is observed. Hata, Ganguly, and Matsuda[12] recently
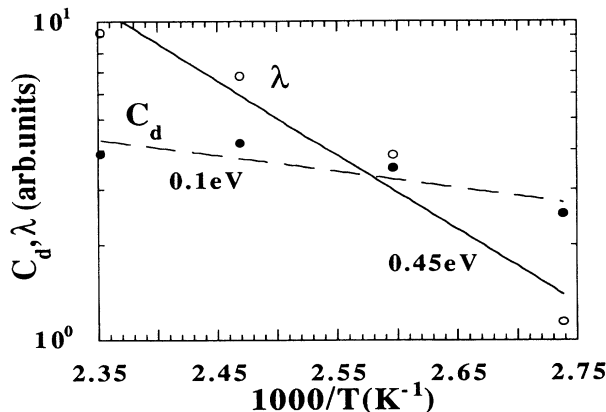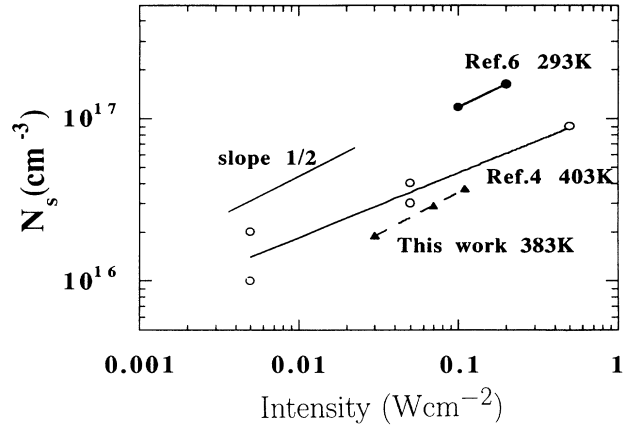

FIG. 4. The steady-state defect density as a function of light-soaking intensity obtained in the present work as well as taken from the literature. The temperature 383 K means that after equilibrium has been reached at 383 K under illumination, the sample is rapidly cooled in the dark to 303 K where the defect density is then measured by the constant photocurrent method (Ref. 14).

fitted their data obtained under cw illumination using $N_S \propto G^{\gamma'}$ with $\gamma'=0.45-0.54$. Other groups cited in Ref. 12 measured lower values for γ'. It must be noted that for the sake of simplicity, under illumination n and p have been put in the form given above. However, in light-soaked electronic-grade a-Si:H it has often been found that $n \sim p \sim G^{\gamma}/N^{\delta}$ with $\gamma \sim 1$ and $\delta > 1$. For example, Merten et al.[13] measured $\gamma \sim 0.8-0.9$ and $\delta \sim 1.6$ while Zhang, Kumeda, and Shimizu[14] measured $\gamma \sim 0.7-0.8$ and $\delta \sim 1.2$ Equation (3) then leads to $N_S \propto G^{\gamma'}$ with $\gamma'=\gamma/(1+\delta) \sim 0.31-0.37$. It is then essential to note that, by taking into account these considerations, it is always possible to get from Eq. (3) γ' values in the range 0.3–0.5, as experimentally observed while this is not possible with Eq. (2), which gives γ' values significantly lower than 0.5. The light-induced annealing term given in Eq. (3) is then favored with respect to that given in Eq. (2).

Let us finally mention another experimental observation which leads to the same conclusion. Prolonged illumination with pulsed laser light [τ pulse $=10$ ns, repetition rate 10 s^{-1}, energy per pulse U in the range $(2.5-33)\times10^{-3}$ J cm^{-2}] leads to rapid saturation of the defect density,[15,16] with a saturated defect density which depends linearly on U and a rising time depending slightly on U.[16] Again by using Eq. (3) and by discretizing it in terms of individual pulses we have been able to explain these results while Eq. (2) has been shown to be inadequate.[16]

In summary, light-induced annealing of metastable defects in a-Si:H has been analyzed in terms of a dispersive model. These results as well as others, and in particular the measurement of the steady-state defect density as a function of the photocarrier generation rate G, can be explained by adding to the defect creation equation proposed by Stutzmann, Jackson, and Tsai[9] an annealing

FIG. 3. The temperature dependence of C_d and λ derived from Fig. 2(b) and Eq. (6').

term which is proportional to the product of defect density and the carrier density rather than the product of the defect density and G as sometimes assumed in earlier works in the field. The creation prefactor C_d exhibits a weak temperature activation energy, as is often observed. The activation energy of the light-induced prefactor λ is about 0.45 eV, however further experimental work is needed to check that the assignment of an activation energy to the optical annealing term is the appropriate approach.

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