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Influence of illumination during annealing of quenched defects in undoped amorphous silicon

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Measurements of isothermal relaxation of metastable defects induced by thermal quenching in undoped *a*-Si:H films are reported in the high-temperature range. During the relaxation studies following successive quenches from 250 °C, a white-light illumination corresponding to various photoexcitation rates G was applied. Increasing G first increases the rate of annealing of defects to a maximum value, then decreases it and for higher G the annealing rate becomes lower than the dark annealing rate. The implications for kinetic models of creation and recovery are discussed. A model including both nondispersive and dispersive behaviors and a term $-GN$ (defect density) to take account of light-induced recovery fits the present experimental data as well as a set of other experiments.

Despite the enormous amount of work and literature devoted to elucidate the thermal and light-induced instability and degradation of the properties of hydrogenated amorphous silicon (*a*-Si:H), the situation in the field of proposed models,[1–9] as well as that of experimental results,[10–14] is far from clear. In their pioneering work on the kinetic analysis of generation of light-induced metastable defects, Stutzmann, Jackson, and Tsai[1] proposed a model along with a rate equation with two terms that describes light-induced creation and thermal annealing of defects. Redfield[2] then introduced a third term to take into account light-induced recovery of defects. Smith and Wagner[3,4] identified three defect processes: light-induced defect generation, thermal annealing, and thermal defect generation; however, they found that the third term introduced by Redfield[2] does not need to be invoked to explain their observed data up to 150 °C. Finally Redfield[5] and Bube and Redfield[9] suggested that symmetry imposes a kinetic equation exhibiting dispersive or nondispersive behavior with four terms, namely,

$$dN/dt = C_1 R(N_t - N) - C_2 RN - \nu_2 N + \nu_1 (N_t - N)\,. \quad (1)$$

The meanings of the parameters are given in the above quoted papers;[5,9] we just recall here that the two first terms on the right-hand side refer to optical formation and annealing of defects N and the two others are for thermal annealing and production of defects. N_t is the maximum density of sites that can be converted to metastable defects. For nondispersive processes C_1 and C_2, ν_1 and ν_2 are independent of time and $\nu_1 = 10^{11}\exp(-1.14\ \mathrm{eV}/kT)\ \mathrm{s}^{-1}$, $\nu_2 = 10^{11}\exp(-1\ \mathrm{eV}/kT)\ \mathrm{s}^{-1}$, whereas for dispersive processes they are time dependent. Depending on the recombination mechanism considered, the rate R of the recombination process can be written $R = G$ or $R \propto G^2/N^2$, G being the volume photoexcitation rate.

Let us now consider the experimental results: While some researchers[10] reported that the room-temperature saturated defect density measured after light soaking has no dependence on light intensity, others[11,12,14] claimed that it has; if this is the actual result it is clear that it invalidates Eq. (1). The aim of this paper is to present new experimental results about annealing of quenched defects with special emphasis on the role of illumination. Though the validity of the separation of the defect processes into four independent terms such as those in Eq. (1) remains questionable,[15] for the sake of simplicity we chose to discuss our results using an equation of that type in order to define the possible form of the four right-hand-side terms.

The electronic-grade ~5-μm-thick undoped *a*-Si:H samples were made by the standard plasma-enhanced chemical-vapor deposition technique with deposition conditions described elsewhere.[16] All details concerning experiments have been given in the same paper. Let us first consider the situation in the dark in order to check the validity of the two thermal terms in Eq. (1). The equilibrium defect density derived from the constant photocurrent method (CPM) versus temperature[16] is given in Fig. 1. According to Eq. (1) and the expressions for ν_1 and ν_2, one expected that $N = N_t \exp(-0.14\ \mathrm{eV}/kT)$ with[9] $N_t = 1\text{–}2\times10^{17}\ \mathrm{cm}^{-3}$ in good agreement with the data in Fig. 1. Let us now consider the effect of illumination on the isothermal relaxation observed after a quench from 250 °C. First of all it is shown in Fig. 2 that after quenching and stabilizing the temperature, the conductivity $\sigma(t)$ increases monotonically to the final value σ_f, a consequence of the decrease of the density of metastable defects N during annealing.[16] After successive identical quenches, the relaxation has been studied at different tem-

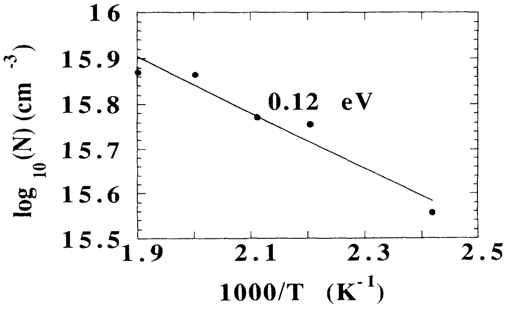

FIG. 1. The equilibrium defect density in undoped *a*-Si:H derived from CPM vs temperature. The straight line is a fit to the data using $N = 1.2\times10^{17}\exp(-0.12\ \mathrm{eV}/kT)$.

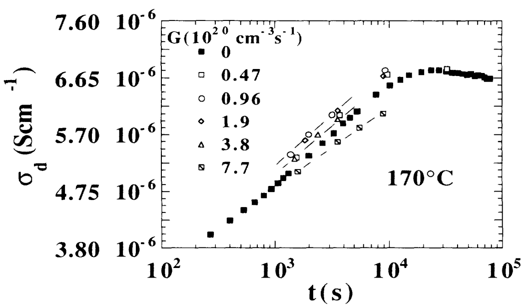

FIG. 2. The time dependence at 170 °C of the dark conductivity of an undoped *a*-Si:H sample after quenching from 250 °C. Illumination corresponding to various photoexcitation rates G is applied since $t = 0$ and it is suppressed during the dark conductivity measurements.

peratures under water-filtered white-light illumination of various intensities given by an iodine lamp. It is seen in Fig. 2 that increasing G first increases the rate of annealing to a maximum value, then decreases it and even, for high G, makes it lower than that observed in the dark. Such a behavior is clearly incompatible with Eq. (1) and the possible expressions for R. Then following Delahoy and Tonon[17] and Wu, Siefert, and Equer,[12] we suggest that Eq. (1) should be replaced by

$$dN/dt = G^2/\gamma N^2 - \lambda N G - \nu_2 N + \nu_1 (N_t - N) . \qquad (2)$$

It is then seen that, for any given temperature, low-intensity illumination corresponding to $G < G_t = \gamma \lambda N(0)^3$ increases the rate of annealing with respect to the dark annealing rate, whereas higher G decreases it. $N(0)$ is the quenched defect density at the beginning of the relaxation. Furthermore with $V = -dN/dt$ being the rate of annealing, V reaches its maximum value for $G_M = G_t/2$. The relaxation times τ_G [times corresponding to the same $\sigma(t)$ obtained at half evolution of the dark conductivity] measured under illumination and normalized to dark relaxation times τ_d are shown in Fig. 3. We observe a rather good agreement between experimental data and the expected relation $G_M = G_t/2$.

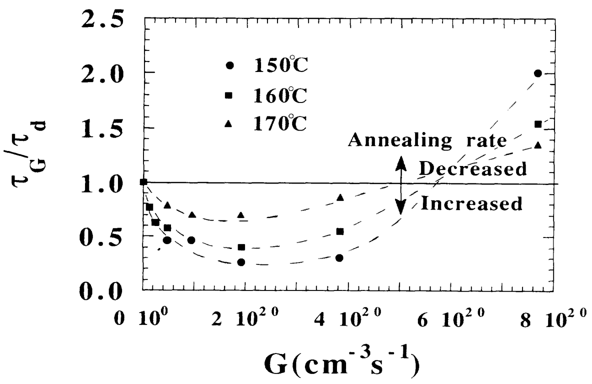

FIG. 3. Relaxation times τ_G of the annealing process measured under illumination, normalized to the relaxation time τ_d measured in the dark, vs photoexcitation rate G. The dashed lines are guides to the eye.

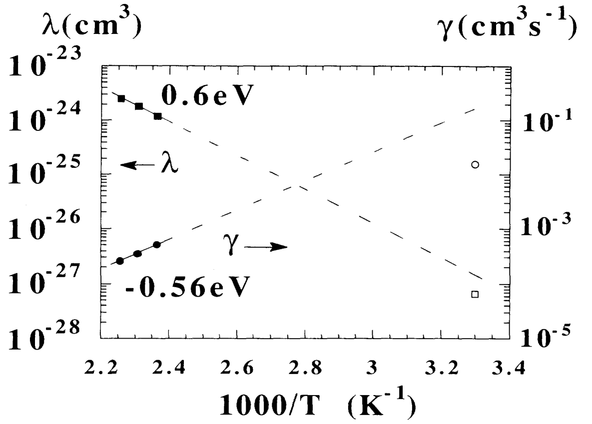

FIG. 4. The parameters λ and γ in Eq. (2) vs temperature (solid symbols). the values measured at room temperature by Wu, Siefert, and Equer (Ref. 12) are also shown (open symbols).

Let us now examine the values of parameters γ and λ and their variation with temperature. The relaxation times deduced from Eq. (2) are $\tau_d = (\nu_1 + \nu_2)^{-1}$ in the dark and $\tau_G = (\nu_1 + \nu_2 + \lambda G)^{-1}$ for low G. Then $\tau_G^{-1} - \tau_d^{-1} = \lambda G$ from which λ can be derived at different temperatures. With $G_t = \gamma \lambda N(0)^3$, λ, and $N(0) \sim 10^{16}$ cm^{-3} (Fig. 1) being known, γ is then derived. The results are given in Fig. 4 which shows that λ is thermally activated with an energy of 0.6 eV; the value of 0.56 eV obtained for the activation energy of γ^{-1} leads to an activation energy of 0.04 eV for $\gamma\lambda$, in good agreement with the value of 0.046 eV given by Wu, Siefert, and Equer.[12] Concerning the activation energy of γ^{-1} let us use experimental data recently published,[18] which show that during light soaking, as the defect density roughly increases as $G^{2/3} t^{1/3}$, for any time, the defect density is thermally activated with an energy of $\sim$0.2 eV. From Eq. (2) it is immediately seen that this activation energy corresponds to that of $\gamma^{-1/3}$, again in good agreement with our result. It is observed in Fig. 4 that extrapolation of our data up to room temperature gives a good agreement with the value of λ given by Wu, Siefert, and Equer.[12] Our value of γ at room temperature is somewhat higher than theirs; however, if one considers the term expressing the optical formation of metastable defects at low temperature given in Eq. (9) in the paper of Bube and Redfield[9] and the numerical values of the parameters used in their calculations, one obtains $\gamma = 0.1$ cm^{3}s^{-1} in good agreement with our extrapolated value.

Up to now, for the sake of simplicity, we only considered the nondispersive case [Eq. (2)], however, introducing dispersive behavior in λ, ν_1, and ν_2,[9] and in the light-induced defect generation[19] immediately leads to

$$dN/dt = t^{\beta-1} [(\gamma')^{-1} (G^2/N^2)^{\beta} - \lambda' N G - \nu_2' N + \nu_1' (N_t - N)] , \qquad (3)$$

where $\beta = T/T_v$, $(kT_v)^{-1}$ is the slope of the exponential valence-band tail. G_t and G_M have the same meanings as before, and it is seen immediately that

$$G_t = (\gamma\lambda)^{1/(2\beta-1)} N(0)^{(2\beta+1)/(2\beta-1)}$$

and $G_M = G_t/(2\beta)^{1/(2\beta-1)}$ from which one has $G_M < G_t/2$ since $\beta < 1$, and the agreement with the data in Fig. 3 is even better.

In summary, we have shown that low-intensity illumination of undoped *a*-Si:H films during annealing at high temperature of thermally quenched defects increases the annealing rate, whereas higher-intensity illumination decreases it. In order to explain our results we proposed to describe the kinetic behavior using a model leading to Eqs. (2) and (3). This model has many other advantages: (i) it fits the observed kinetics of light-induced defects well,[12] (ii) it explains the light-intensity dependence of the room-temperature saturated defect density,[11,12,14] and (iii) it gives a unified description of light-induced and current-induced defect mechanisms for which a current-induced defect annihilation and a dependence of the saturated defect density on the inducing current have also been observed.[20]

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