Kinetics of the Staebler-Wronski effect

M. Cutrera, R. R. Koropecki, A. M. Gennaro, and R. Arce
Instituto de Desarrollo Tecnológico para la Industria Química, Casilla de Correo 91, 3000 Santa Fe, Argentina
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An extension of the model proposed by Stutzman, Jackson, and Tsai [Phys. Rev. B **32**, 23 (1985)] for the kinetics of light-induced metastable defect creation in *a*-Si:H is presented. We assume a limited density of defect centers and take into account the attenuation of the incident light into the sample. The experimental data of the work mentioned above are well fitted with our modified model. This fit allows for a quantitative estimation of the number of defect centers related to the Staebler-Wronski effect.

Many experimental works have been done in order to clarify the origin of the Staebler-Wronski effect (SWE) (Refs. 1–8), in *a*-Si:H. Among them, one of the most complete sets of measurements is that presented, in recent papers,[7,8] by Stutzmann, Jackson, and Tsai (SJT). According to the SJT microscopic model for the SWE, the light-induced defects are assumed to be single dangling bonds, and consequently the density of light-induced metastable defects can be measured through the induced spin density. The kinetic model proposed by SJT (Refs. 7 and 8) predicts that the density of light-induced defects is a sublinear function of illumination time and light intensity. This prediction is in agreement with their experimental data for the time evolution of spin density[7–9] and photoconductivity.[7,8] However, this model is not able to predict the saturation behavior physically expected at long times. As mentioned by SJT, saturation could take place due to the depletion of accessible metastable sites. In spite of the fact that the typical increase in the spin density ($\cong 10^{17}$ cm^{-3}) measured by different authors is well below the value estimated for saturation ($\cong 10^{18}$ cm^{-3}),[8] it is not obvious whether or not the existence of a limited number of centers could affect the kinetics of spin generation for relatively short times of exposure.

In this work, we have added two hypotheses to the SJT kinetic model. (a) In the annealed state, only a limited number N_m of defect centers are able to be transformed into metastable centers by illumination. Thus, the limiting condition is not only that the induced defects provide alternative paths for electron-hole recombination, but also that the number of centers available is depleted with time. (b) The N_m centers available in the annealed state are homogeneously distributed through the sample. Light attenuation into the sample is taken into account, instead of assuming a two-phase model as proposed by SJT. These hypotheses allow for a good fitting of the SJT experimental data, which in turn provides a quantitative estimation for N_m, a useful magnitude to investigate in order to clarify the microscopic origin of the SWE and to know more about the material structure.

Starting from the equation given by SJT for the spin-generation rate,[8] and assuming that this rate is proportional to the number of centers available to be transformed in metastable centers after the time t of illumination, we get

$$\frac{dN_s}{dt}=\frac{CI^2}{N_s^2(t)}[N-N_s(t)]\ , \tag{1}$$

where $N=N_s(0)+N_m$ is the total density of dangling bonds for $t\rightarrow\infty$, and $N_s(0)$ is the spin density in the annealed state ($t=0$); C includes the different constants involved in the process and I is the intensity of the incident light. Considering the attenuation of light in the sample, I is given by $I=I_0e^{-\alpha x}$, where I_0 is the intensity of the incident light at the sample surface, α is the absorption coefficient, and x varies from $x=0$ to $x=a$, a being the sample thickness.

Equation (1) is integrated to obtain

$$\tfrac{1}{2}[N_s^2(x,t)-N_s^2(0)]+N[N_s(x,t)-N_s(0)] + N^2\ln\left[\frac{[N-N_s(x,t)]}{[N-N_s(0)]}\right]+CI_0^2e^{-2\alpha x}t=0\ . \tag{2}$$

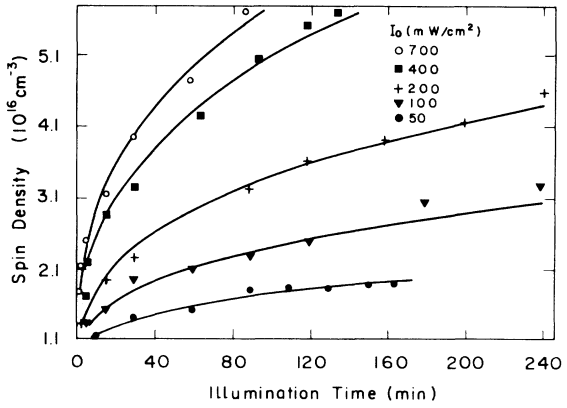

FIG. 1. Effective dangling-bond density as a function of illumination time, for various light intensities. The experimental points are taken from Ref. 8. Solid lines correspond to a fit using Eq. (2).

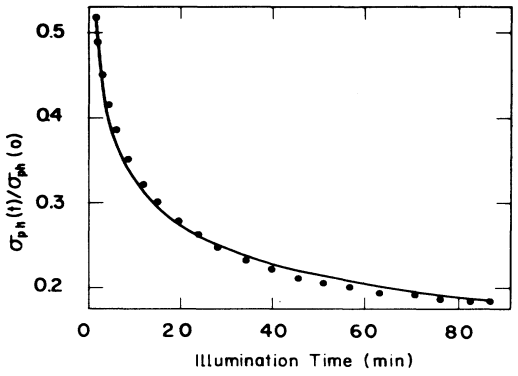

FIG. 2. Experimental decay of the normalized photoconductivity as a function of illumination time for $I_0=170$ mW/cm^2 (data from Ref. 8). The solid line corresponds to a fit using Eq. (3). The resulting parameters are $\alpha a=10$ (a=sample thickness), $C=6.4\times10^{-5}$ cm^{-2}mW^{-2}min^{-1}, and $N=3.4\times10^{18}$ cm^{-3}.

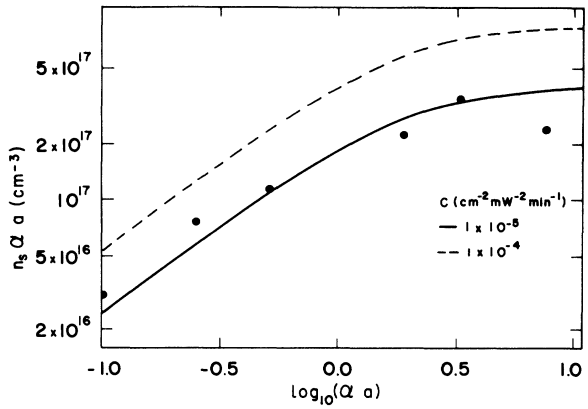

FIG. 3. Variation of the dangling-bond density with sample thickness for $I_0=500$ mW/cm^2 and $t=420$ min (experimental points obtained from Ref. 8, see text). The dashed line was obtained employing Eq. (2) and using an average of the parameters N and C of Table I. The solid line corresponds to the best fit using Eq. (2) with the same N as before, and leaving C as a free parameter.

Equation (2) can be solved only by numerical methods. Once $N_s(x,t)$ is known for all x, it is averaged over the sample volume to obtain the value of the effective spin density $n_s(t)$, defined as the ratio between the total number of spins and the sample volume, $n_s(t)=(1/V)\times\int_V N_s(x,t)dV$.

In order to get the unknown parameters N, α, and C, we made a fit with the SJT experimental data for the effective spin density versus illumination time, using a finite-difference Levenberg-Marquardt algorithm.[10] As the SJT data were obtained for different values of I_0, this procedure allows for a self-consistent check of the estimated parameters. The best fits are shown in Fig. 1, and the corresponding parameters in Table I. We found that the fit for short times is sensitive to the asymptotic value N_m for fixed values of C. For example, if deviations in the adjusted value N_m are imposed, relative variations of the same order result for the calculated induced spin density, at least within the typical exposure times used in the SJT experiments. However, as discussed below, this behavior is not enough to determine N_m independently from C under these conditions.

Starting from Eq. (2), it is possible to make a similar analysis for the photoconductivity, following the assumption of SJT, in which the neutral dangling bonds are assumed to be the most effective recombination centers. The light which generates carriers is attenuated as depth increases, so the contribution to the photoconductivity of each layer of thickness dx must be weighted with the intensity of the incident light at such layer. Under these conditions, the photoconductivity after the sample has been exposed for a time t, normalized by that at $t=0$, can be written as

$$\frac{\sigma_{ph}(t)}{\sigma_{ph}(0)}=\frac{N_s(0)\alpha a}{(1-e^{-\alpha a})}\int_0^a\frac{e^{-\alpha x}}{N_s(x,t)}dx\ . \tag{3}$$

Here, α is the same as that used in the evaluation of $N_s(x,t)$, provided that the wavelength of the light used in the photoconductivity measurements is the same as that used in the generation of the SWE.

We applied the above mentioned algorithm to fit the results from our model with the photoconductivity data of SJT, with α, C, and N as free parameters. The best fit is shown in Fig. 2, and the obtained parameters are $\alpha=3.3\times10^4$ cm^{-1}, $C=6.4\times10^{-5}$ cm^{-2}mW^{-2}min^{-1} and $N=3.4\times10^{18}$ cm^{-3}.

Equations (2) and (3) were used to check the behavior of the effective spin density and photoconductivity as a func-

TABLE I. Parameters resulting from the fit shown in Fig. 1.

I_0 (mW/cm^2)	N (cm^{-3})	α (cm^{-1})	C (cm^{-2}mW^{-2}min^{-1})
50	5.5×10^{18}	3.1×10^4	1.1×10^{-4}
100	5.5×10^{18}	2.9×10^4	1.1×10^{-4}
200	5.5×10^{18}	3.2×10^4	1.1×10^{-4}
400	5.5×10^{18}	3.2×10^4	1.1×10^{-4}
700	4.9×10^{18}	3.8×10^4	1.0×10^{-4}

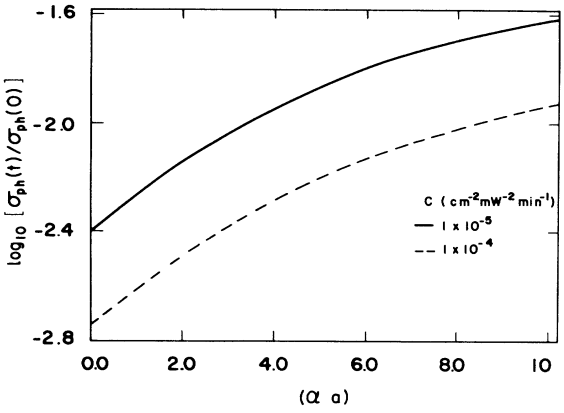

FIG. 4. Variation of photoconductivity with sample thickness, theoretical results. The parameters are the same as in Fig. 3.

tion of the sample thickness, for a given exposure time. Using the values given in Table I, we have plotted the computed effective spin density and photoconductivity as a function of αa in Figs. 3 and 4. The experimental SJT values for the spin density as a function of the sample thickness are also included in Fig. 3 (note that the energy of the light for these data, $\hbar\omega = 1.8$ eV, is different from that used in Fig. 1, $\hbar\omega = 1.9$ eV). We assumed $\alpha = 1 \times 10^4$ cm^{-1} for the representation of these data, considering the α obtained from the fit of N_s versus t and typical α versus $\hbar\omega$ dependences.[11] It is possible to see that the experimental data do not fit well with our model when we use the parameters of Table I. This discrepancy is not surprising because each experiment was carried out with light of different energy and C is expected to depend on the energy through α dependence of the incident light. So, if we take N from Table I, and leave C as a free parameter, the best fit is obtained for $C = 1 \times 10^{-5}$ $cm^{-2} mW^{-2} min^{-1}$. In Fig. 3 it can be observed that, in spite of the experiment mentioned by SJT,[8] their experimental data of induced spin density as a function of sample thickness can be reproduced taking into account the absorption coefficient without any reference to an inhomogeneity present in the distribution of the defect centers. We think that it would be of much importance to make a deeper study in order to clarify this point. Moreover, if the two-phase model is adopted, the dimension proposed by SJT for the active phase is not far from the penetration depth expected for the light used in the experiment. We then conclude that, whatever the origin of the thickness dependence be, the attenuation of light should be considered.

In spite of the relatively high number of free parameters used, it is remarkable the uniformity in the values shown in Table I. On the other hand, the parameters obtained from the photoconductivity data are quite similar to those obtained from the fitting of the spin density. It is worth noting that the values of α obtained from the fitting are close to those reported in the literature at the same energy of the incident light.[11] Starting from the experimental data, and using our extension to the model for the kinetics of defect generation, we obtained $N_m \cong 5.0 \times 10^{18}$ cm^{-3}, which is in agreement with the number of centers which are able to be transformed in metastable centers estimated by SJT on the basis of their microscopic model.

In this work we have shown that under the hypothesis of a limited number of defect centers homogeneously distributed, and taking into account the attenuation of the incident light, the experimental results can be well fitted. The proposed model has the correct asymptotic behavior, and allows for the determination of the number of the SWE related defect centers. However, none of the data ever approach the saturation region, since $N_s(t) < 0.01 N_m$. Therefore, taking into account Eq. (1), it could be possible that variations in C compensate for deviations of N_m in producing the fitting of the experimental data. Indeed, we found that it is possible to fit the data with different values of C by fixing different values of N_m. In this case, the fitting yields results for the product $N_m C$ which tend to a constant value. As a consequence further experiments should be performed in order to determine N_m (and its very existence) more accurately.

On the other hand, the existence of an illumination profile makes the average value $n_s(t)$ much lower than the values of the spin density in the surface layer ($x < 1/\alpha$). Therefore, for these values of x, Eq. (1) must be integrated without the approximation $N_s(t) \ll N_m$. This allowed us to propose and experiment on the basis of a numerical simulation with Eq. (2), assuming thinner samples and larger exposition times. We found that a set of $n_s(t)$ measurements performed on samples of 0.3 μm in thickness, during 50 hs of illumination with 1.9-eV light and 400 mW/cm^2 in intensity, would allow us to determine N_m within an error of 25%, assuming typical values in the order of 10^{18} cm^{-3} for N_m.

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