A critical assessment of different models of the metastability in a-Si:H.

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We have studied the light degradation and the thermal annealing of a-Si:H at different light intensities and temperatures monitoring both the defect density and the photoconductivity. This large set of data is used as a benchmark for the models of the metastability in a-Si:H. We show that none of the existing models can give a full account of them and we point out some mathematical and conceptual errors that could explain these failures. We find that an accurate description of annealing processes is important to select the right form for the creation rate and to improve the agreement between theory and experiments. We show that our data are in good agreement with a model which possesses the following three features: i) the creation rate is proportional to product of the free carrier concentrations ii) the annealing rate is computed considering a broad distribution of energy barriers iii) the energy barrier for the annealing of a metastable defect can be decreased (for a time of the order of 1ps) of an energy of the order of half gap a the monomolecular trapping events at the defect itself.

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I. INTRODUCTION

The light-induced metastability of a-Si:H is a topic that has received a lot of attention in the last 15 years [1,2]. It shows many anomalous characteristics that have so far precluded a satisfactory explanation. The first one is that the growth in the defect number is sublinear in the photon dose Φt (where Φ is the photon flux and t is the exposure time) even at low temperatures and far from saturation [3,25,31]. The time dependence can be approximated by a power law or by a stretched exponential both characterized by an exponent less than 0.5. The second one is that a saturation value can be reached at high temperatures [4]. This saturation value depends on Φ and can be raised (using pulsed light [5]) to a level incompatible with the association of the metastable defects with any impurity [6] (apart from the hydrogen). Finally the annealing of the defects is strongly non-exponential [7] and can be accelerated by the presence of a low light level [8]. All the models proposed to explain these phenomena are largely ad hoc and are unable to explain at least some of the experimental results. In this work we present a large set of data obtained in many different conditions on a single sample. This set of data is used as a benchmark for almost all the models proposed in the literature.

II. EXPERIMENTAL

The experiments were performed on an a-Si:H sample 2 μm thick, grown by Glow-Discharge on a Corning glass substrate (substrate temperature=210 $°C$, chamber pressure= 700 mTorr, grow rate 1.7 Ås^{-1}). The experimental setup was planned to monitor the defect density evolution during the degradation and the annealing for a long time. The light source was initally an halogen lamp. The white light was filtered leaving only the wavelengths in the interval 650-850 nm obtaining a light intensity of about 250mW/cm^2. Later we substituted the lamp with a Kr Laser (λ=647.5 nm). The laser beam was slightly expanded using a cylindrical lens to obtain a power density up to 1400 mW cm^{-2} nearly uniform on a 2×1 mm^2 area. A cryostat connected with a temperature controller allowed to control the sample temperature in the range 10-475 K, with good accuracy (0.1K). All the experiments were performed in vacuum obtained with a turbo molecular pump. A typical problem is the quantification of the temperature increase ΔT of the sample under illumination. A rough theoretical estimate of ΔT can be obtained by the thermal diffusion formula neglecting the heat transmission in the film:

$$\Phi = K\frac{\Delta T}{S} \tag{1}$$

where Φ is the light power density (mW cm^{-2}) absorbed by the film, K the Corning glass thermal diffusion coefficient (14 mW cm$^{-1}K^{-1}$ at RT) and S the substrate thickness (0.13 cm). The ΔT between the holder and the a-Si:H film in the case of illumination by the Kr laser can be evaluated to be about 10 K at RT. A measurement of the actual temperature of the sample is important to confirm experimentally this estimate but it is not an easy task. Since a temperature rise should induce a rise in the sample photoconductivity, we can gain some information measuring, by an oscilloscope, the photocurrent transients. To avoid stability problems we used a degraded sample and monitored the first second of illumination (at 1.4 W/cm^2), at the three temperatures of our investigation (173K, 273K, 373K). Comparing these data with the dependence of the photocurrent on the sample holder temperature at the steady state, we deduced for the temperature increase ΔT an upper limit of 5K at T 273 K and 20 K at 173K. The higher value of Δ T at low T could be due to a temperature dependence of the thermal diffusion coefficient and was taken into account in the analysis of the experimental data. The light soaking were carried out in vacuum after a careful annealing of the sample which was held at 473 K for two hours and than cooled at 4 K min^{-1} until 413 K and at 0.5 K min^{-1} until room temperature. In order to quantify the defect density (N_d) of the annealed state a measurement of the absorption coefficient spectrum by the Constant Photocurrent method (CPM) was carried out after every annealing.

During all the experiments we monitored the defect density measuring the absorption coefficient at 1.2 eV again using the CPM and a mobility-lifetime product ($\mu\tau$) for a constant value of the photocurrent. We measured also the degradation photocurrent during the light soaking experiments. The whole experimental setup was completely controlled by a P.C. so that all the measurement were automatically carried out. Different cycles of degradation and annealing were performed under different experimental conditions of light intensity and temperature as described in table I. In four cases the density of states kinetic was followed also during the subsequent annealing.

During the first seconds of degradation at 373K we observed a large increase of density of states (DoS). Since this effect is not easily reproduced by the models we suspected that it could be due to a fast decay of the photocurrent not resolved by our setup. A more careful investigation on the photocurrent in this range of time was therefore carried out using an ad-hoc experiment. The photocurrent transient during the first four seconds of light degradation was monitored using a digital oscilloscope. The data of this experiment, compared with the photocurrent obtained with one seconds step measures, are reported in Fig. 1. A smooth behaviour is evident in this region but anyway the experimental data sets were improved taking into account the results of this investigation. In fig. 2 and 3 is shown the defect density behavior during degradation at different temperatures and under a light intensity corresponding to a generation rate of 7×10^{20} and 1.56×10^{22} cm^{-3} s^{-1} respectively. It can be seen that the creation rate increases with increasing temperatures and light intensity. A clear saturation is reached only for the degradations at 373K. The data at 173K and low intensity show an anomalous long time decrease. This behavior was already reported in a previous work [12] and was confirmed by a repetition of the experiment. In fig 4 are reported the defect densities of the sample degraded at 373K at the high light intensity, during the dark annealing at different temperatures (403K, 423K, 443K). The annealing rate increases increasing annealing temperature.

The comparison between the dark annealing performed at the same condition (T_{ann}=403K) on sample degraded at two different temperatures is reported in fig. 5. The annealing rate is clearly influenced by the degradation conditions.

As reported earlier by us [12] and others [24–26] we find that the simple linear dependence between the photocurrent and $(N_d)^{-1}$ is far from being verified (fig. 6). Moreover the relationship between the $\mu\tau$ product and N_d is not single-valued and shows an hysteresis effect during the degradation-annealing cycles. This is generally explained [25,26] considering a distribution of capture coefficient and of annealing activation energies of the new metastable states. The states with the higher capture coefficient possess the lower annealing activation energy and therefore are the first to be created and annealed out. This ad-hoc explanation seem to be consistent with the experimental results shown in fig.6 obtained with different degradation temperatures. The states created at low temperature (circles) show a greater capture coefficient and a lower annealing activation energy. Very similar data are shown in ref [27] where the hysteresis loops in a sample degraded at 77K and at RT are reported while the data contained in ref [26] (sample degraded at 4.2 K and RT) are somewhat different. Further support for the existence of a distribution of capture coefficients comes from a close examination of the experimental data collected during the α(1.2eV) CPM measurements which give, as a by-product, a set of photocurrent values obtained under a constant flux of photons of 1.2 eV for different values of defect density. If all the defects were equal this photocurrent should not vary with N_d since the rise in the recombination rate should be compensated by the rise in the defect optical absorption. The photocurrent shows instead large variations and, more interestingly, if we plot $\mu\tau$ versus N_d/I_{ph}(1.2eV) the hysteresis is removed and we recover a nearly linear relationship between the two quantities.

III. RECOMBINATION INDUCED BOND BREAKING MODELS.

As a first step in the data analysis it is often proposed to neglect the effect of annealing. The first of these models is the recombination induced weak bond breaking model of Stutzmann et al. [3], which can be summarised in the following rate equation:

$$\frac{dN_d}{dt} = C_{sw}np \tag{2}$$

where n and p are the free electron and hole concentrations. Supposing that the free carriers lifetimes are limited by the recombinations through the deep defects we have that $n \propto p \propto G/N_d$ and therefore:

$$\frac{dN_d}{dt} = C_{sw}(\frac{G}{N_d})^2 \tag{3}$$

the equation can be easily integrated giving :

$$N_d^3(t) - N_d^3(0) = 3C_{sw}G^2t \tag{4}$$

We have also considered two variations of the basic bond breaking model. The first one was proposed by Stradins and Fritzsche [26] which report that a better fit can be obtained if we use:

$$\frac{dN_d}{dt} = C_{sw}(\frac{G}{(N_d - N_d(0)})^2 \tag{5}$$

which gives:

$$(N_d(t) - N_d(0))^3 = 3C_{sw}G^2t \tag{6}$$

This change is justified by the fact that the metastable states seems to be more efficient in reducing the a-Si:H photoconductivity. On the other hand it was already pointed out that the existence of the hysteresis effect (Fig. 6) imply that the metastable states have a distribution of free carriers capture cross sections. Since the photoconductivity value was also monitored during the degradation process we can examine a third possibility: we can take for granted that the electron density is proportional to the photoconductivity and we can assume that this is also approximately true for the hole density. Under this hyphotesis we have:

$$\frac{dN_d}{dt} = C_{sw}(\Delta\sigma)^2 \tag{7}$$

To check if these simple theories are confirmed by our data we have fitted the values of dN_d/dt, correponding to the initial part of the degradation, with an arbitrary power of N_d^{-1}, $(N_d - N_0)^{-1}$ or $(\Delta\sigma)^{-1}$. The values of the exponents m found in this way are reported in Table II.

It can be seen that all the m values are very scattered and generally greater than 2 (which is the expected value) and that the case in which the creation rate is proportional to $C_{sw}(\Delta\sigma)^2$ gives the worst results. This is due, at least in part, to the fact the annealing processes are completely neglected. We will show later that properly including the annealing effects the best results are instead obtained using a creation rate proportional to $C_{sw}(\Delta\sigma)^2$ showing that these simple rate equations give a description of the data too rough to discriminate between different models.

IV. STRETCHED EXPONENTIAL MODELS

Let us consider first the annealing curves (Figs. 4,5). It has been already shown that the annealing of metastable defect density in a-Si:H follows a monomolecular kinetics [7] since the shape of the curves does not depend on the starting point value. On the other hand these curves are not simple exponential decays but can be fitted quite well by a "stretched exponential" function:

$$N_d(t) = N_S - (N_S - N_0)\exp((-t/\tau)^\beta) \tag{8}$$

where N_S and N_0 are the saturation and the starting defect density values respectively. It is often claimed that the stretched exponential dependence originates from an exponential distribution of activation energies for the annealing [13–15] and that the exponent β is given by $\beta = T/T_0$ where T is the temperature and kT_0 is the characteristic energy of the exponential distribution. Since the stretched exponential fits fairly well also the degradation curves it was proposed [14,15] that also the creation of the new defects is a thermally activated process and that the creation energies are exponentially distributed.

A different hypothesis that leads to the stretched exponential is that the creation and the annealing of the metastable defect are due to the hydrogen movement [16]. The hydrogen diffusion coefficient D_H shows an anomalous "dispersive" behavior since it is not a constant but depends on time as $t^{\beta-1}$. The first data were obtained in doped samples [17] and seem to suggest that β is equal to T/T_0 with $T_0 = 600K$. The dispersive D_H and the temperature dependence of β were explained supposing that the hydrogen movement is limited by the existence of an ensemble of traps with an exponential distribution of activation energy for the H atom reemission. Since in this model both the creation and the annealing rates must be multiplied by a factor proportional to D_H the rate equation becomes:

$$\frac{dN_d}{dt} = D_{00}(R_0 t)^{\beta-1}[(C_1 G + \nu_1)(N_T - N_d) - (C_2 G + \nu_2)N_d] \tag{9}$$

where ν_1 and ν_2 are the thermal creation and annealing rates while C_1G and C_2G are the light induced creation and annealing rates respectively [20]. The solution of this equation is again given by a stretched exponential.

In Tab. III we report the stretched exponential parameters obtained fitting the experimental data. We can see that the β values are nearly independent of T and are much lower than the values found extrapolating the D_H data to lower temperatures [16].

A first comment to these data is that the mathematical derivations [13–15] that lead to the stretched exponential starting from an exponential distribution of barriers are wrong. In ref. [13] the authors define a wrong rate of trap emptying $\tilde{t}_e$ (their equation 8) after they have already calculated the correct result ($\Psi(t)$ reported in their eq. 7). In refs. [14,15] instead the error consists in the confusion between the normalization constant of the initial defect distribution and the total number of defects which is obviously time dependent (see for example eq. 5 in ref. [15]). Moreover it is well known from the theory developed to interpret the transient photoconductivity experiments that the long time decay of the number of electrons trapped in an exponentially decreasing density of states follows a power law ($t^{-\beta}$) [21] and not a stretched exponential. The error could be caused by the fact that if we cut the distribution to a maximum annealing energy (and this is necessary if the supposed exponential distribution has an increasing number of states with increasing annealing energy as often happen in the studies on degradation [14,15]) the time decay does not follow any more a power law and can be confused with a stretched exponential (see the appendix). It could be also shown that fitting the data with a stretched exponential would give a β weakly dependent on T.

While it is anyway reasonable to use a distribution of activation energy to model the annealing process (but the growth and the decay of the defect number must be computed in a numerical way as will be shown in the following paragraph) it is much less plausible that a distribution of creation energy could play a role in the degradation kinetic considering the weak temperature dependence of the creation efficiency.

Even the rate equation based on the dispersive hydrogen diffusion seems not correct to us since it assumes that the hydrogen diffusion is maximum at the starting of the annealing or of the degradation experiment and then slows down as the H atoms are trapped in deeper and deeper traps. This is not a realistic description since the H atoms excitation (by the light or the temperature rise) to a transport state takes place for the whole experiment duration and not only at its beginning. The same criticism was also previously applied [9] to the analysis of hydrogen diffusion which constitutes the basis of the degradation rate equation. It must be also noted that measurements of the time dependence of D_H performed in undoped samples showed a very complex behavior and a strong dependence on the sample characteristics [18,19].

In any case the H diffusion based model cannot explain the differences in the annealing behavior of samples degraded at different temperatures (see table III).

It has to be noted that very recently Van de Walle [10] proposed a model in which a time dependence very similar to the stretched exponential can be obtained without invoking a statistical distribution for the annealing energies. In this model the defects are created when a moving H atom is trapped at a weak bond. The energy necessary to anneal the defect is therefore that required to release the H atom and is taken equal for all the weak bonds. The deviation from the exponential behaviour stems from the possibility of retrapping for the H atoms in the interstitial position. Anyway a limited number N_T of weak bonds is assumed and the anomalous behaviour disappear for defect densities much lower than N_T. This is inconsistent with the experimental fact that the site number at which the defect can be created is much larger than the typical saturation values and with the independence on the starting point of the shape of the annealing curves. Removing the assumption of a limited N_T a different solution (composed of two exponential) is obtained. Even this solution can fit some curves for a well defined set of parameters but is unable to give a consistent explanation of all the data.

V. NUMERICAL ANALYSIS.

We have seen in the previous paragraph that the comparison between the prediction of a rate equation like that proposed by Stutzmann and the experimental data does not give sensible results if we do not introduce the effect of the annealing. On the other hand the data show that the defects do not have the same annealing rate. We cannot therefore write down a single rate equation for the total numer of defects. We can set up a more general approach considering a pool of potential defects with a distribution of annealing energies given by an arbitrary function P(E). Indicating with $f(E,t)$ the fraction of potential defects with annealing energy E actually present at time t we can write:

$$\frac{df}{dt} = (1-f)C(E) - fR(E) \tag{10}$$

where C(E) and R(E) are the creation and the annealing rate respectively. The total number of defects $N_d(t)$ is given by:

$$N_d(t) = \int f(E,t)P(E)dE \tag{11}$$

For the annealing term we assume a monomolecular annealing mechanisms which give an annealing rate dependent on energy but independent of N_d. For the thermal annealing rate we use the standard form $\omega_0 \exp(-E/kT)$. To determine the value for ω_0 we have followed the procedure used in [7] that is we have plotted the annealing curves obtained at different temperatures versus $KT\ln(\omega_0 t)$ (Fig. 7). The correct value of ω_0 is that which gives the best overlap between the curves. The method is not very accurate due to the presence of the distribution but we obtain in this way a value much greater (around $10^{13}s^{-1}$) than that ($10^{10}s^{-1}$) obtained in [7]. Anyway our value is near the typical network vibration frequencies and therefore we will use it in the following.

We have to introduce the effect of the light induced annealing (LIA) also. To this aim we have to add to R(E) another term whose mathematical form depends on the microscopic mechanisms ipotized for the LIA process. In the most common picture the capture of a carrier at the defect release some excess energy ΔE which aid the barrier jump. The excess energy can be subtracted from the barrier height [11] or converted to an effective temperature [12]. After a comparison to similar processes which take place in crystalline material [22,23] we reverted to the first approach. The prefactor is directly connected with the rate of carrier capture and can be written as:

$$R(E) = \omega_0 \exp(-E/kT) + v\sigma_c n\tau_{th}\omega_0 \exp(-(E-\Delta E)/kT) \tag{12}$$

where v is the electron thermal velocity, σ_c is the metastable defects electron capture cross section and τ_{th} is the time necessary to network vibrations to relax to the thermal equilibrium state. For our numerical simulations we have supposed that the electron density is proportional to $\Delta\sigma$ and therefore:

$$R(E) = \omega_0 \exp(-E/kT)(1 + C_{LIA}\Delta\sigma) \tag{13}$$

with:

$$C_{LIA} = \frac{v\sigma_c\tau_{th}}{q\mu}\exp(\Delta E/kT) \tag{14}$$

Written in this form the light induced annealing process is still a thermally activated process. This characteristic is needed to explain the experimental data [8] since the LIA is not observed at temperatures lower than room temperature. Since the form of P(E) and C(E) and their dependence on other parameters (like temperature, hole and electron concentration, total number of defect etc.) are not precisely known we have still many possible forms for the rate equation. Let us discuss the different forms of these two functions that we have tried to fit our experimental data.

The pool function: A first constraint of this function is that its integral must be higher than 10^{18} cm^{-3} to be able to accomodate the large number of defect generated under pulsed illumination. Moreover the pool should not contain states of annealing energy higher than the gap since this is probably the maximum energy available for their creation and therefore we use a parameter to establish a maximum annealing energy. To minimize the number of free parameters we have used only one-modal functions and we will show the results for the following four choices: exponential ($A\exp(-E/E_0)$), gaussian ($A\exp(-((E-E_0)/\sigma)^2/2$), power ($A(E-E_m)^n$), Fermi-Dirac ($A/[1+\exp(-((E-E_F)/E_0)]$). For all the four functions the density of states is taken to be zero above a certain energy E_m and the normalization constant A was calculated to give the wanted total number of states taking into account this high energy cut.

The generation term: its dependence on G or $\Delta\sigma$ must be stronger than that of the light induced annealing term to obtain a saturation value which depends on G even when the thermal annealing rate is negligible and to reproduce the fact that the light induced annealing rate is initially faster than the thermal annealing one. To simplify the fit we have used a term independent of E and we have tried four different expressions:

1) A creation rate equal to that used in ref [3]:

$$C = C_{sw}(G/N_d)^2 \tag{15}$$

Obviously our calculations give better results since they contain the annealing rate

2) Same as 1 but using the photoconductivity $\Delta\sigma$ instead of G/N_d:

$$C = C_{sw}(\Delta\sigma)^2 \tag{16}$$

3) We suppose that the defect creation process is due to the recombination between a free electron and an hole trapped in the valence band tail. A simple expression for the density of trapped holes (p_T) can be obtained (following Ref. [29]) approximating the trapped holes quasi Fermi level with the free hole quasi Fermi level E_f^p defined by: $p = N_v \exp(-E_f^p/kT)$

Writing the density of states in the valence band tail as $N_0 \exp(-E/kT_v)$ we obtain: $p_T = N_0 kT_v(p/N_v)^{T/T_v}$ Finally C can be written as:

$$C = C_{sw}(\Delta\sigma)^{1+T/T_v} \tag{17}$$

4) Lastly we consider an Auger recombination mechanism in which a free electron recombine with a trapped hole and gives its excess energy to a trapped electron. In a way similar to the case 3 we can write:

$$C = C_{sw}(\Delta\sigma)^{1+T/T_v+T/T_c} \tag{18}$$

where kT_c is the conduction band tail slope.

The free parameters contained in the rate equations are twelve: three values for C_{sw} and three for CLIA at the three different temperatures, three parameter to describe the pool function and three values of ΔT to describe the rise in the sample temperature under the high illumination intensity. We know that this temperature rise is not large and is therefore not important for C_{sw} and C_{LIA} but it must be introduced in the exponential of the annealing term. To find the best set of parameters for the various forms of the rate equation we have minimized (using the MINUIT program from a CERN Library) the χ^2 calculated over all the data considered and the corresponding numerical solutions of the rate equation. The best results were obtained using an exponential P(E) and $C(E) = C_{sw}(\Delta\sigma)^2$.

Let us show how the different forms of C(E) and P(E) change the χ^2 value. In table IV we report the χ^2 values that are obtained using $C_{sw}(\Delta\sigma)^2$ as creation term and one of the four distributions previously described as P(E).

We can see that the results depend very weakly on the exact shape of P(E). This can be easily understood looking at fig. 8 where the four optimal distributions are drawn. They are very similar in the energy interval between 1 and 1.5 eV where most of the metastable defects are created (see fig. 11 later on).

In table V are reported instead the values of χ^2 obtained using an exponential P(E) and each of the four generation rates described above.

The best results are obtained using $C_{sw}(\Delta\sigma)^2$ indicating that the creation rate is proportional to the product of the free carriers concentrations. If we use instead C_{sw}/N_d^2 the results are worse probably because there is a better correlation between the free carrier concentrations and $\Delta\sigma$ with respect to $1/N_d$. We can see also that if we write the creation term using the trapped carriers (as suggested by Stutzmann et al. [3]) we obtain an higher χ^2. In other words the creation rate must contain a power of $\Delta\sigma$ not lower than two. We can improve the χ^2 value using the trapped carriers and an Auger process in which three carriers are involved but the simpler hypothesis of the bimolecular recombination still gives better results. This table also imply that a creation term which reflect the simple capture of a carrier by a charged defect (as proposed by Adler in ref [30]) would give still worse results beeing simply proportional to the carrier density.

The optimal parameter set for the best case (exponential pool and $C = C_{sw}(\Delta\sigma)^2$) are reported in Table VI. The parameters E_m, E_0, e N_{max} describe the pool and are the maximum energy in the pool, the exponential slope and the total number of the defects respectively. It should be pointed out that the high value of N_{max} is due to the large number of precursors with very low annealing energy which are not relevant for our fits. ΔT is the temperature rise present at high light intensity. The theoretical curves obtained with these parameters are shown in fig 2, 3, 4 and 5 as solid lines.

Figures 9 and 10 show the values obtained for the parameters C_{sw} e C_{LIA} as a function of temperature.

We can see that C_{LIA} exhibits a clear activated behavior with an activation energy of 0.68 eV which corresponds to the ΔE appearing in the light induced annealing term. Since the defects are located near midgap this value is quite reasonable.

The prefactor of C_{LIA} is $6 \times 10^{-3} Wcm$. Using the expression 14 for C_{LIA}, with $\mu = 10cm^2(Vs)^{-1}$, $v = 10^7 cms^{-1}$, $\sigma_c = 10^{-15}cm^2$, we obtain $\tau_{th} \simeq 10^{-12}s$ which is also a reasonable value beeing about a factor of ten greater than ω_0^{-1}. A relaxation time of the amorphous silicon network vibrations of the order of one picosecond is also in agreement with recent numerical calculations [28]. As for C_{sw} we can see that it is not temperature independent. This could derive from a temperature dependence of the cross section for the bimolecular recombination. If we try to extract an activation energy from our data we obtain a value of 0.13 eV.

Figure 11 shows the distribution of annealing activation energies of the new metastable defects. The lower the degradation temperature the lower the mean annealing activation energy and therefore the lower the annealing temperature required to remove the defects. It must be pointed out anyway that using $\omega_0 = 10^{13}s^{-1}$ we obtain high annealing activation energies and as a consequence a large amount of energy is also required to create a new defect (an energy larger than 1.6eV since otherwise the defects shoould be present also in the "equilibrium" state). Such a large energy imply the need of a very peculiar recombination event in agreement with the initial proposal made by Stutzmann et al. [3]. This conclusion is independent from the details of the model but depends only on the value of ω_0 and on the hypothesis that the thermal annealing process is completed in only one step.

VI. DISCUSSION

Models similar to that developed in the last section of this paper were presented in other two works [11,33] and therefore a comparison of the results is in order. The main differences between the model developed by Caputo et al. [11] and our model are: i) The free carrier concentrations are calculated from a numerical model of the photoconductivity of a-Si:H . Since the photoconductivity shows a complex behavior which cannot be reproduced by a numerical model we have derived the carriers concentrations from the measured values of $\Delta\sigma$. ii) The annealing energy distribution was assumed to be a gaussian and its total number was varied for different generation rates. iii) The light induced annealing effect was described by a simple reduction of the annealing activation energies of an amount ΔE which does not vary during each run. ΔE must reproduce therefore the effects due to the product $C_{LIA}\Delta\sigma$. This explains the very low absolute value of ΔE (around 0.1 eV compared to our 0.68 eV) and the correlation between ΔE and the photoconductivity quasi Fermi level found in Ref. [11]

The model of Zhang et al. [33] remove the first difference since they used the measured values of $\Delta\sigma$ to calculate the trapped carrier concentrations. The annealing energy distribution is a gaussian with an high and a low energy cutoff and the total number of precursor was kept fixed. The light induced annealing effect was modeled (in their rate equation II) exactly in the same way as in Ref. [11] that is the proportionality to $\Delta\sigma$ is not explicitly pointed out. As a result a low value of ΔE is again obtained but the authors did not observe any correlation between ΔE and the photoconductivity quasi Fermi level. This is due to the fact that they compared values of ΔE and obtained at different temperatures while in ref [11] were used values obtained at different generation rates. Finally even in ref [33] the saturation behavior is not correctly described since it takes place exhausting the precursors.

A very important point to verify is if our model is able to explain the behavior observed in the degradation experiments performed at very low temperatures. To this end we have tried to fit the data obtained by Stradins and Fritzche at 20K [31]. At this low temperature the photoconductivity stays almost constant during the experiment suggesting that the defect concentration should rise linearly with time. Can the distribution of annealing energies give rise to the sublinear time dependence that is instead observed in the experiments? It turns out that it can and that it is possible to obtain a very good agreement with the experimental data. Unfortunately the agreement is obtained only if we assume a very narrow distribution of annealing energies. The slope of the exponential distribution (E_0) should be of only 2.5meV compared to the 94 meV needed to obtain a good fit of the high temperature data. This contrasts with the experimental result [26] that a large fraction of the defects created even at 20K survive even when the sample is heated to room temperature (this is not compatible with annealing activation energy of the order of few meV) and with the hyphotesis that the existence of the distribution is due to the disorder which produces many different configurations of the network around the metastable defects. If this is true the distribution shape cannot depend on temperature. If we try to fit the low temperature data togheter with our data keeping constant the parameters of P(E), the agreement betwen the theory and the experimental data at 20K is very bad.

These results, obtained from the numerical simulations, can be understood in term of a simple analitical calculation. It can be shown (see the appendix) that a rate equation with a constant creation rate and an annealing rate deriving from an exponential distribution of annealing energies (with a characteristic energy E_0) has an approximated analitical solution which follows a power law of the time with an exponent m given by $(1 - kT/E_0)$. To obtain $m = 1/3$ the slope E_0 should be equal to $3/2kT$.

It is interesting to note that if E_0 depends linearly on T the annealing lifetime distribution $P(\tau)$ is independent of T and is proportional to $\tau^(- 1 - kT/E_0)$. Restated in term of the annealing lifetimes our results are very similar to that obtained by Stradins et al. [32] which suggested that to obtain a power law (with an exponent m) for the defect creation kinetic we need a distribution of the annealing times of the form $P(\tau) = \tau^{m-2}$. A possible hypothesis is therefore that at low temperatures the annealing of the metastable defects does not proceed exciting thermally the network to overcome the barrier but by quantum mechanical tunneling.

VII. CONCLUSIONS

In this work we have presented a large body of experimental data on the temporal behavior of the defect density in a-Si:H during the light induced degradation and the following thermal annealing. We have used these data to test some well known theoretical models of the Staebler-Wronski effect. In some of these models the kinetic is explained starting from the anomalous behavior of the hydrogen diffusion in a-Si:H. They predict a defect density that depends on time as a stretched exponential with an exponent β that should depend linearly on the temperature. Although our data can be fitted quite well by stretched exponentials the exponent β does not show the expected T dependence and its value does not seem compatible with that deduced from H diffusion experiments. Even if it is not possible to definitely exclude a role of the hydrogen in these phenomena it seems clear that these theories are to be rejected.

We are therefore forced to explain the non-exponential behavior of the annealing kinetic with the usual hypothesis of the existence of a distribution of annealing energies. We have then analyzed our data fitting them with the numerical solution of some different rate equations. The best results are obtained using a creation rate that is proportional to the square of the photoconductivity of the material as measured under the degradation light. A creation rate proportional to a power lower than two gives invariably worse results. This fact together with the high absolute value of the annealing activation energy seem to support the proposal initally advanced by Stutzmann, Jackson and Tsai that the creation of the new metastable defects is triggered by specific non-radiative bimolecular recombination events in which there is a large release of vibrational energy. We have also found that it is necessary to introduce a light induced annealing term to reproduce correctly the saturation in the metastable defect density observed (at room temperature and above) for long exposure time. Our calculations show that this term is probably due to the energy release that takes place in the standard monomolecular recombination events via deep defects. We must anyway admit that in spite of our effort the global fit of our data is not completely satisfactory even if it is one of the best ever obtained. Even the low temperature behavior (observed by other researchers) remain a puzzle that cannot be explained by our model. The only possible explanation of these data is the existence of an addictional temperature independent distribution of annealing rates due for example to tunneling phenomena.

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APPENDIX

In this appendix we present two approximate calculations that clarify two important points although they cannot substitute the numerical calculations beeing of no general validity.

We start deriving the time decay of defect total number ($N_d(t)$) for an ensemble of defects which at t=0 possess an exponential distribution of annealing activation energies:

$$n_d(E, t = 0) = Ae^{-E/E_0} \tag{A1}$$

where A is a normalization constant:

$$A = N_{max}/[E_0(1 - e^{-E_m/E_0})] \tag{A2}$$

N_{max} is the total defect concentration at t=0 and E_m is the maximum annealing energy. The rate equation is:

$$\frac{dn_d(E,t)}{dt} = -\frac{n_d(E,t)}{\tau(E)} \tag{A3}$$

For a thermal annealing the defect lifetime can be written as $\tau(E) = \omega_0^{-1}e^{E/kT}$. The solution of the rate equation is trivial and gives for the total number of defects:

$$N_d(t) = A\int_0^{E_m} e^{-E/E_0}e^{-t/\tau(E)}dE \tag{A4}$$

defining:

$$\tau_{max} = \omega_0^{-1} e^{E_m/kT} \tag{A5}$$

we can write:

$$e^{-t/\tau(E)} = e^{-t/\tau_{max}} \exp[-t(\frac{1}{\tau(E)} - \frac{1}{\tau_{max}})] \tag{A6}$$

the latter exponential can be well approximated by a Θ function:

$$e^{-t/\tau(E)} = e^{-t/\tau_{max}} \theta(E - E^*) \tag{A7}$$

with

$$E^* = kT \Big[\ln \big(\frac{\omega_0^{-1} t \tau_{max}}{t + \tau_{max}} \big) \Big] \tag{A8}$$

a simple integration then gives:

$$N_d(t) = A e^{-t/\tau_{max}} E_0 \Big[e^{E_m/E_0} - \big(\frac{\omega_0^{-1} t \tau_{max}}{t + \tau_{max}} \big)^{kT/E_0} \Big] \tag{A9}$$

This solution is reported in Fig. 12 together with the exact numerical solution and the often proposed stretched exponential with $\beta = kT/E_0$. It is evident that the stretched exponential is not a good approximation of the decay shape and that our formula gives a much better agreement.

The utility of Eq. A9 is limited from the fact that the in real cases the annealing energy distribution at the beginning of the annealing process is not known since it depends on the details of the degradation process (see fig. 11). The actual defect distribution must be calculated numerically following the approch developed in section V. The only case amenable to an approximated analitical treatment is that in which the creation rate is a constant C_{sw} independent of the defect density. Using the same notation of section V we want now to show that using an exponential pool of precursors $P(E)$ a power law rise of $N_d(t)$ is obtained even if the creation rate is constant. The rate equation can be written as:

$$\frac{df(E,t)}{dt} = C_{sw}(1 - f(E,t)) - \frac{f(E,t)}{\tau(E)} \tag{A10}$$

The solution is:

$$f(E,t) = \frac{\tau(E) C_{sw}}{1 + \tau(E) C_{sw}} [1 - \exp\big(- t \frac{1 + \tau(E) C_{sw}}{\tau(E)} \big)] \tag{A11}$$

Let us consider the initial part of the degradation for which $C_{sw} t \ll 1$.In this case it can be seen that a first order approximation for f(E,t) is $\tau(E) C_{sw}$ for $t > \tau(E)$ and $t C_{sw}$ for $t < \tau(E)$.

The boundary between the two approximations is given by $E_d = kT \ln(\omega_0 t)$.

The total number of defects :

$$N_d(t) = A \int_0^{E_m} e^{-E/E_0} f(E,t) dE \tag{A12}$$

can therefore be calculated as:

$$N_d(t) = A \int_0^{E_d} e^{-E/E_0} C_{sw} \tau(E) dE + A \int_{E_d}^{E_m} e^{-E/E_0} C_{sw} t dE \tag{A13}$$

which gives:

$$N_d(t) = \frac{C_{sw}}{\omega_0 (\frac{1}{kT} - \frac{1}{E_0})} \Big[(\omega_0 t)^{1 - \frac{kT}{E_0}} - 1 \Big] + \frac{C_{sw}}{\omega_0} \Big[(\omega_0 t)^{1 - \frac{kT}{E_0}} - e^{-E_m/E_0} \Big] \tag{A14}$$

The two constants inside the square brackets are generally negligible with respect to $(\omega_0 t)^{1 - \frac{kT}{E_0}}$ and therefore we obtain the anticipated power law.

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FIG. 1. Light degradation photocurrent transient measured at 373K. Solid line refers to oscilloscope continuum acquisition, symbols to single point one second step acquisition.

FIG. 2. Experimental defect density vs illumination time for the degradation performed at light intensity of $7 \times 10^{20} cm^{-3} sec^{-1}$ at different temperatures; squares T_{deg}=373K, circles T_{deg}=293K, up triangles T_{deg}=173K. The solid lines are the fits obtained with the model described in the text.

FIG. 3. Experimental defect density vs illumination time for the degradation performed at light intensity of $1.56 \times 10^{22} cm^{-3} sec^{-1}$ at three different temperatures; squares T_{deg}=373K, circles T_{deg}=298K, up triangles T_{deg}=173K. The solid lines are the fits obtained with the model described in the text.

FIG. 4. Experimental defect density vs annealing time for dark annealing experiments performed at three different temperatures; T_{ann}=403K (circles), T_{ann}=423K (squares), T_{ann}=443K (triangles). The sample was degraded at T_{deg}=373K with a light intensity of $1.56 \times 10^{22} cm^{-3} sec^{-1}$. The solid lines are the fits obtained with the model described in the text.

FIG. 5. Experimental defects density Vs annealing time for the dark annealing performed at T_{ann}=403K of the samples degraded at T_{deg}=373K (circles), T_{deg}=173K (triangles), at high light intensity. The solid lines are the fits obtained with the model described in the text.

FIG. 6. Mobility-lifetime product versus the defect density during degradation-annealing cycles at two different degradation temperatures: circles T_{deg}=173K (T_{ann}=403K), squares T_{deg}=373K (T_{ann}=443K).

FIG. 7. Normalized metastable defect density after an annealing time t as function of $kT\ln(\omega_0 t)$ for different annealing temperatures. The ω_0 values are reported near the curves.

FIG. 8. Optimal annealing activation energy distributions: Gussian (solid line), power (dotted line), exponential (dashed line), Fermi-Dirac (dotted-dashed line).

FIG. 9. Values of the parameter C_{sw} obtained from the fits as a function of temperature.

FIG. 10. Values of the parameter C_{LIA} obtained from the fits as a function of temperature.

FIG. 11. Defect density distribution calculated for degradations performed at three different temperatures :173K (solid line), 293K (dotted line), 373K (dashed line)

FIG. 12. Numerical solution of the time decay (at $T_{ann} = 465K$) of defect total number for an ensemble of defects which at t=0 possess an exponential distribution of annealing activation energies with $E_0 = -0.1eV$ (symbols) and with an high-energy cutoff at $E_m = 1.5eV$. The approximated formula derived in the appendix (solid line) and the stretched exponential with $\beta = kT/E_0 \simeq= 0.4$ (dashed line) are also reported.

TABLE I. Experimental conditions of the degradation (and annealing in four cases) cycles considered in this work: degradation and annealing temperature, first and last value of the density of defects, first and last value of photoconductivity under the degradation light and generation rate due to the degradation light. The generation rate value reported for the first three runs is due to the halogen lamp and is therefore only an approximate value calculated supposing an uniform power density in the energy interval selected by the filters (1.46-1.92eV) and using the measured absorption coefficient of the sample.

T_d(K)	T_a(K)	N_0(cm^{-3})	N_{LS}(cm^{-3})	σ_0 $((Wcm)^{-1})$	$\sigma_{LS}((Wcm)^{-1})$	G(cm$^{-3}s^{-1}$)
173	*	4.1×10^{15}	1.8×10^{16}	5.3×10^{-5}	6.9×10^{-6}	7×10^{20}
293	*	4.1×10^{15}	3.7×10^{16}	2.7×10^{-4}	9.6×10^{-6}	7×10^{20}
373	*	4.6×10^{15}	3.0×10^{16}	2.1×10^{-4}	5.2×10^{-5}	7×10^{20}
373	423	5.0×10^{15}	4.9×10^{16}	1.27×10^{-3}	3.5×10^{-4}	1.56×10^{22}
373	403	5.2×10^{15}	4.3×10^{16}	1.16×10^{-3}	2.9×10^{-4}	1.56×10^{22}
373	443	5.0×10^{15}	5.1×10^{16}	1.19×10^{-3}	3.1×10^{-4}	1.56×10^{22}
173	403	4.4×10^{15}	7.4×10^{16}	3.7×10^{-4}	2.0×10^{-5}	1.56×10^{22}
293	*	5.9×10^{15}	9.1×10^{16}	8.3×10^{-4}	8.6×10^{-5}	1.35×10^{22}

TABLE II. Values of the power m obtained fitting the degradation curves with three simple rate equations containing only a creation rate inversely proportional to the m-th power of the quantities shown in brakets.

G$(cm^{-3}s^{-1})$	$T_d(K)$	m(N_d)	m($N_d - N_0$)	m($\Delta\sigma$)
7×10^{20}	173	2.9	1.7	4.4
1.56×10^{22}	173	3.3	2.6	3.5
7×10^{20}	293	3.1	2.2	2.0
1.35×10^{22}	293	3.4	2.6	2.6
7×10^{20}	373	3.5	3.2	1.6
1.56×10^{22}	373	3.5	3.8	8.4
1.56×10^{22}	373	4.3	3.1	10
1.56×10^{22}	373	4.3	4.8	10

TABLE III. Values of the parameters β and τ obtained fitting the degradation and the annealing curves with stretched exponentials.

G$(cm^{-3}s^{-1})$	T_d(K)	β_d	$\tau_d(s^{-1})$	T_a(K)	β_a	τ_a (s^{-1})
0.7×10^{21}	173	0.49	3.7×10^6	-	-	-
1.56×10^{22}	173	0.33	6.1×10^5	403	.22	600
0.7×10^{21}	293	0.46	1.1×10^5	-	-	-
1.35×10^{22}	293	0.33	7091	-	-	-
0.7×10^{21}	373	0.45	3300	-	-	-
1.56×10^{22}	373	0.30	123.5	403	.41	2.4×10^5
1.56×10^{22}	373	0.31	94.4	423	.35	3.0×10^4
1.56×10^{22}	373	0.32	161.2	443	.38	6.5×10^3

TABLE IV. χ^2 values obtained using $C_{sw}\Delta\sigma^2$ as creation term and four different distributions for P(E)

P(E)	χ^2
exponential	8992
gaussian	9776
power	9484
Fermi-Dirac	9004

TABLE V. χ^2 values obtained with different creation rates and an exponential pool for the metastable defects.

C(E)	χ^2
C_{sw}/N_d^2	15632
$C_{sw}(\Delta\sigma)^2$	8992
$C_{sw}(\Delta\sigma)^{1+T/T_v}$	22268
$C_{sw}(\Delta\sigma)^{1+T/T_v+T/T_c}$	11120

TABLE VI. Optimal parameter set corresponding to the theoretical fits shown as solid lines in fig. 2,3, 4,5

C_{sw} (173K)	183
C_{sw} (293K)	3020
C_{sw} (373K)	21700
ΔT (173K)(K)	20
ΔT (293K)(K)	3.5
ΔT (373K)(K)	3.1
C_{lia} (173K)	4.55×10^{17}
C_{lia} (293K)	2.47×10^9
C_{lia} (373K)	1.05×10^7
E_m (eV)	1.663
E_0 (eV)	0.0936
N_{max} (cm^{-3})	1.4×10^{23}