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A F Meftah[1], A M Meftah and A Merazga

Faculté des Sciences, Laboratoire des Matériaux Semi-conducteurs et Métalliques,
Université Mohammed Khider, BP 145, Biskra 07000, Algeria

E-mail: afak_meftah@hotmail.com

Abstract

This work is a theoretical study of the defect creation and annealing, and of the photoconductivity degradation of an intrinsic a-Si:H film under continuous illumination. A new model is developed for the Staebler–Wronski effect (SWE). In this model, we consider that a defect of the SiHD type is locally created by a non-radiative recombination at a weak bond close to a SiHHSi configuration. Also, it is considered that the light induced defect (LID) annealing requires a hydrogen diffusion motion. Using the fact that the areas of defect Gaussians increase with illumination time while their positions and widths remain unchanged, we present the evolution of the gap state defect density, calculated by the defect pool model, with illumination time. This density of states, which varies during illumination, is introduced in the simulation of the photoconductivity to obtain its degradation. In addition, the validity of the proportionality of the photoconductivity to the illumination intensity G and to the inverse dangling bond density is assessed. Our investigations show a monomolecular behaviour of the photoconductivity ($\sigma_{ph} \propto N_d^{-\gamma}$, $\gamma \sim 1$) for moderate intensity. They also show an illumination intensity dependency on G^α, with α varying between 0.5 and 1, in agreement with a large number of similar investigations.

1. Introduction

Light induced defect (LID) creation under continuous illumination, the so-called Staebler–Wronski effect (SWE) [1], is the main problem which limits a-Si:H film applications. There are two typical models to describe LID creation: weak bond breaking by non-radiative

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[1] Author to whom any correspondence should be addressed.

recombination [2] and metastable hydrogen collision [3]. The weak bond breaking model describes the SWE as a local effect, while the hydrogen collision model requires long range hydrogen motion. Both models lead to the same defect dependency on illumination time and intensity but with different SWE efficiencies. The increase in the density of defects leads to a decay of the photoconductivity (σ_{ph}) with the illumination time (t_{ill}) [1]. The evolution of σ_{ph} with t_{ill} is frequently used as a quick estimate of the stability of a given a-Si:H sample.

In this paper, we have developed a new microscopic model for the LID creation and annealing in which we consider the creation as a local effect according to the improved model proposed by Powell *et al* [4]. However, the LID annealing requires a hydrogen diffusion motion. Using the fact that areas of the Gaussian distributions of defects increase with illumination time while their positions and widths remain unchanged [5], we present the evolution of the gap state defect density. This is introduced in the photoconductivity simulation to obtain the photoconductivity degradation during illumination. We also assessed the validity of the proportionality of the photoconductivity to the illumination intensity and to the inverse dangling bond density.

2. Model

It is considered that the metastability phenomenon is related to hydrogen in a-Si:H. The assessment of factors determining the photodegradation in high efficiency a-Si:H solar cells indicated that the non-H-diluted sample (standard sample) with 15 at.% H contains Si–H_2 bonds in addition to Si–H bonds. Further, $\sim$85% H is clustered and the additional metastability is related to the H cluster and/or Si–H_2 bonds [6]. However, the direct breaking of Si–H bonds is unlikely to occur because of energy reasons [7, 8]. The metastability may be related to the doubly hydrogenated SiSi bonds, SiHHSi, when both hydrogen atoms are ejected [7]. These configurations have been emphasized previously in order to explain that device-grade a-Si:H is very little affected by further hydrogenation or limited dehydrogenation, as far as the tail state distribution or the defect density are concerned [4].

Cheong *et al* [9] have presented evidence for long-range hydrogen motion in a-Si:H under room temperature illumination by monitoring the changes in the Raman spectrum of an a-WO_3 overlayer with illumination. They observed that illumination causes hydrogen to diffuse out of the a-Si:H layer into the a-WO_3 layer. This result validates one of the crucial assumptions used in the hydrogen collision model for the SWE.

The role of hydrogen in the stabilization of metastable defects has been recognized for a long time [10]. It has been shown that the observed steady state defect density results from a competition between LID creation and LID annealing [7, 11–13]. It is generally believed that the LID annealing is related to hydrogen [7, 14–16].

Taking into account the experimental features of the SWE presented above, we propose a new approach for modelling metastability in a-Si:H. In this model, the defect creation in a-Si:H under continuous illumination occurs by a non-radiative recombination between optically excited electrons n and holes p at a weak bond which is close to a doubly hydrogenated bond, SiHHSi. This site is energetically favourable for recombination due to the additional stress imposed by the two hydrogen atoms. One of the two hydrogen atoms moves to the site of the broken SiSi bond, forming two adjoining SiHD defects according to the following reaction:

$$\text{SiSi} + \text{SiHHSi} \overset{e+h}{\leftrightarrow} 2\text{SiHD}. \tag{1}$$

This hydrogen atom is located at the tetrahedral site rather than the bond centred site of the broken SiSi bond, and the separation of the dangling bond and hydrogen atom is in the range 4–5 Å, which is consistent with all ESR experiments [4].

The recombination at the SiHD site allows the production and the diffusion of a metastable hydrogen atom through the material. If the dissociated hydrogen atom is inserted in the nearby SiHD defect, this later will be annihilated and, in this case, there is not an SWE. Thus, the hydrogen atom remains mobile until it meets a distant SiHD defect. Therefore, they annihilate to form an SiHHSi bond. The hydrogen atom can also be retrapped by colliding with a second metastable H. In this case, both metastable H are trapped to form an SiHHSi bond again.

Taking into account the processes described above, we propose rate equations governing the kinetics of SiHD and metastable H under illumination as follows:

$$\frac{dN_d}{dt} = R_{SiSi} - R_{SiHD} - C_d^c N_H N_d \tag{2a}$$

$$\frac{dN_H}{dt} = R_{SiHD} - C_d^c N_H N_d - 2C_H^c N_H^2 \tag{2b}$$

where N_d and N_H are the densities of SiHD and metastable H, respectively. $R_{SiSi} = k_d np$, where k_d expresses the light induced creation of SiHD. n and p are the free electron and free hole densities. $R_{SiHD} = k_H np$, where k_H represents the dissociation of a hydrogen atom from an SiHD defect. C_d^c and C_H^c are rate constants for the two trapping processes of the hydrogen atom. The factor of two in equation (2b) is due to the fact that each collision removes two metastable H.

We assume that n and p are determined by the steady state numbers and are, in the case of monomolecular recombination, proportional to illumination intensity G and inversely proportional to the defect density N_d:

$$n = p = \frac{G}{C_c N_d} \tag{3}$$

where C_c (10^{-8} cm^3 s^{-1}) is the capture coefficient of free carriers by dangling bonds. If we assumed at all times that $N_H \ll N_d$ and that the equilibrium of the metastable H is fast compared to any other chemical species, then $dN_H/dt = 0$. Equation (2b) implies $R_{SiHD} \simeq C_d^c N_H N_d$. Substituting $C_d^c N_H N_d$ into equation (2a) yields the SW creation rate:

$$\frac{dN_d}{dt} = \frac{(k_d - 2k_H)}{C_c^2} \frac{G^2}{N_d^2}. \tag{4}$$

Equation (4) has a form identical to that of Stutzmann *et al* [2] and Branz [3], but with a different SW efficiency. The solution of equation (4) is:

$$N_d^3(t) - N_d^3(0) = 3\left(\frac{k_d - 2k_H}{C_c^2}\right) G^2 t. \tag{5}$$

On the other hand, if $k_d \gg 2k_H$, the N_H creation rate as well as the N_H concentration will be much lower than the creation rate and concentration of N_d, a condition which is similar to that previously supposed. Then, one also expects that $N_d(t) \propto G^{2/3} t^{1/3}$. In this case, figure 1 shows the metastable H and SiHD defect densities calculated by the proposed model under continuous illumination of intensity $G = 10^{22}$ cm^{-3} s^{-1}. The initial conditions are $N_d = 10^{16}$ cm^{-3} and $N_H = 0$, and the values of the different constants involved are $k_d = 5 \times 10^{-15}$ cm^3 s^{-1} which is equal to the value given by Morigaki *et al* [15], $k_H = 10^{-18}$ cm^3 s^{-1} to have the condition $k_d \gg 2k_H$, and $C_d^c = 4 \times 10^{-19}$ cm^3 s^{-1} and $C_H^c = 10^{-17}$ cm^3 s^{-1} are in the interval $(2 \times 10^{-17}, 10^{-21}$ cm^3 s^{-1}), as reported by Branz [3]. After 10^2 s, a $t^{1/3}$ increase of the SiHD defect density appears while $N_H(t)$ has little variation with 3×10^{12} cm^{-3} as the maximum at 3–4 $\times 10^2$ s. In this case, the steady state density for long times, reported by numerous experiments [7, 11], is not observed because the metastable hydrogen, which plays the main role in the LID annealing, has relatively small concentration ($\sim 10^{12}$ cm^{-3}). However, if $2k_H \sim k_d$, we can observe in
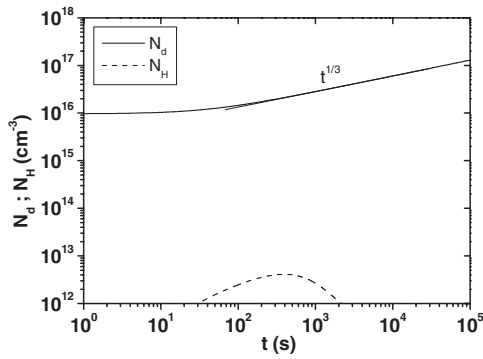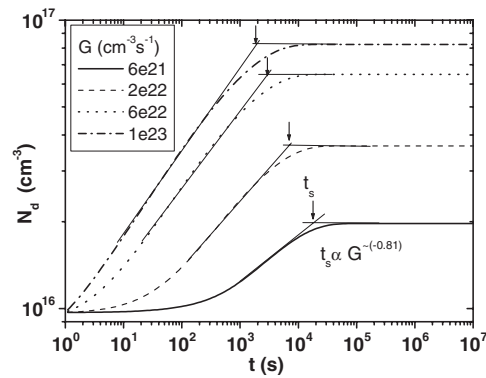
Figure 1. Variation of the LID and metastable H for the case where $k_d \gg 2k_H$.
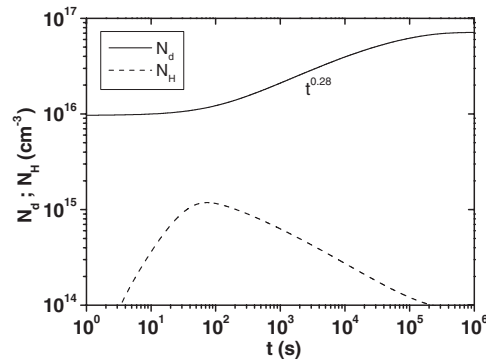
Figure 2. Variation of the LID and metastable H for the case where $2k_H \sim k_d$.
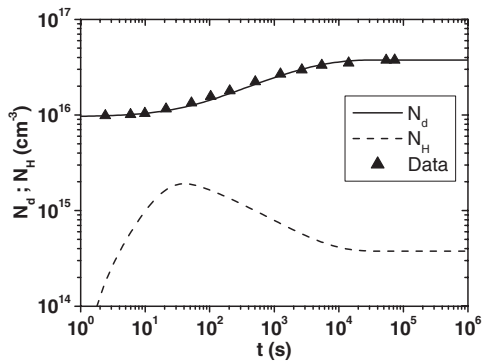

Figure 3. Comparison between the simulated LID creation and experimental data at 100 °C (from [7]).

Figure 4. LID density versus illumination time under several light intensities, calculated from the proposed model.

figure 2 the appearance of a steady state density for long times ($\sim 10^5$ s). An increase of the metastable hydrogen is also observed until 10^2 s ($N_H \sim 10^{15}$ cm^{-3}), when a $t^{-0.28}$ decay results from the $t^{0.28}$ increase in the SiHD density. From the results above, we can consider k_H as a parameter reflecting the hydrogen amount in the material. We attempted to compared the SiHD defect creation kinetics to the observations of Godet [7], who measured the photocreated dangling bond density by a constant photocurrent method for a glow-discharge high-quality (standard) sample. A CW xenon-arc lamp with wavelengths below 570 nm was used for illumination, and then G is 10^{22} cm^{-3} s^{-1}. The results are shown in figure 3. The parameters are those used previously, except k_H, which is taken equal to $C_1 N_{do}$ of Morigaki *et al* [15]: that is, $k_H = 3 \times 10^{-15}$ cm^3 s^{-1}. The dangling bond (SiHD) density increases from 10^{16} cm^{-3} initially to a steady state value of 3.75×10^{16} cm^{-3} for illumination time $> 10^4$ s. The simulated curve is in agreement with the measured points. The metastable hydrogen increases nearly exponentially until 40 s, which delays the increase of the SiHD density. After 40 s, a decrease of the metastable hydrogen occurs parallel to the increase of the SiHD density until 2×10^4 s, after which a steady state is established for the two densities.

We have simulated the behaviour of the defect creation kinetics as a function of the light intensity. Figures 4 and 5 summarize some properties of the proposed model.
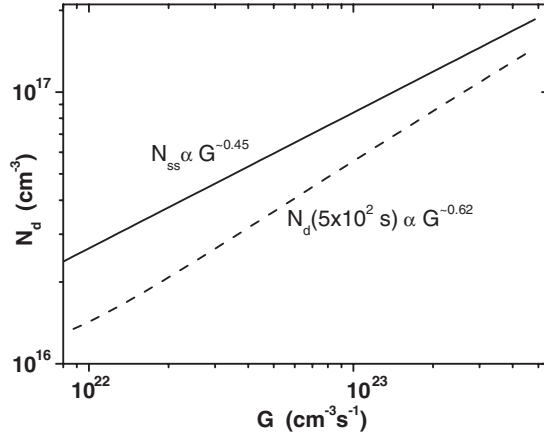
Figure 5. LID increase at 500 s (– – –) and at saturated state (——) as a function of the illumination intensity.

(1) The slope of $\log N_d(t)$ versus $\log(t)$ approaches $1/3$ as generally observed when G increases.

(2) The density of SiHD defects scales nearly with the expected $G^{2/3}$ power.

(3) t_s, the time required to reach the saturation state, decreases as $\sim G^{-0.81}$.

(4) The steady state density, N_{ss}, increases with illumination intensity G and follows a $G^{0.45}$ law which is consistent with [17] but little stronger than the $G^{0.33}$ law found in [2, 11].

3. The evolution of the density of states with illumination time

The defect pool model (DPM) has been proposed for the equilibrium properties of a-Si:H; it can account for a wide range of experimental results [18, 19]. The equilibration mechanism was identified as a conversion of weak bond to dangling bond according to the reaction SiHHSi + SiSi ↔ 2SiHD [19]. The density of state distribution was determined by applying the law of mass action to both reactions: SiHD ↔ SiSi + H and SiHHSi ↔ SiSi + 2H between the weak bond energy in the valence band tail (VBT), assumed to have an exponential distribution, and the energy level in the gap where the defect is formed. The density of state calculated within the framework of the DPM is expressed as follows [19]:

$$D(E) = \gamma \left[\frac{2}{f^0(E)} \right]^{k_B T^*/2E_{v0}} P \left[E + \frac{\sigma^2}{2E_{v0}} \right], \tag{6}$$

with

$$\gamma = \left[\frac{G_v 2 E_{v0}^2}{[2E_{v0} - k_B T^*]} \right] \left[\frac{H}{N_{SiSi}} \right]^{k_B T^*/4E_{v0}} \exp \left[\frac{-1}{2E_{v0}} \left[E_p - E_v - \frac{\sigma^2}{4E_{v0}} \right] \right].$$

$P(E)$ is the defect pool function, assumed to have a Gaussian distribution. σ and E_p are, respectively, the pool width and peak position. G_v and E_{v0} are, respectively, the density of states at E_v and the VBT width. T^* is the equilibrium temperature (freeze-in temperature) for which the density of states is maintained. H is the total hydrogen concentration and N_{SiSi} is the total electron concentration in the material. $f^0(E)$ is the neutral dangling bond state occupancy. The conduction band tail (CBT) is also assumed to have an exponential distribution.
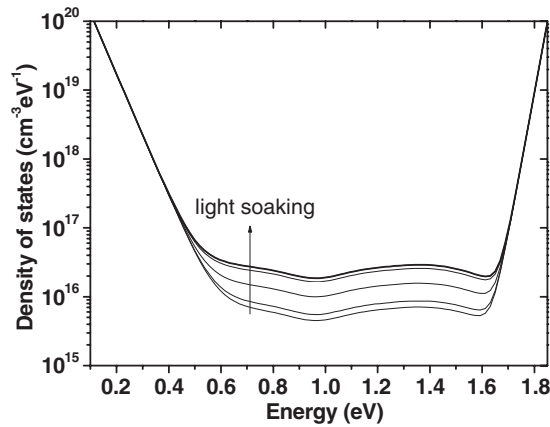
Figure 6. The evolution of the density of states with illumination time.

The density of states is mapped onto an effective one-electron density of states $g(E)$, which relates well to the density of states that is measured in most spectroscopic techniques with thermal transitions [18]. The one-electron density of states was approximated by [18]

$$g(E) \simeq D(E + k_B T \log 2) + D(E - U - k_B T \log 2) \tag{7}$$

and its occupancy is given by the Fermi–Dirac function.

Schmidt *et al* [5] have studied the light induced degradation of an a-Si:H sample by the constant photocurrent method. They have found that the density of occupied states obtained from the deconvolution procedure shows the presence of two peaks within the gap which are fitted with two Gaussians ascribed to the neutral and negatively charged dangling bonds. The areas of both Gaussians increase as $t^{1/3}$ while their positions and widths remain unchanged with the illumination time. The VBT is also found to be practically constant with the illumination time. These observations allow us to propose the following features for the density of states during illumination.

(1) The pool width and peak position remain unchanged.
(2) The pool area increases by the same evolution factor as the defect density, $N_d(t)$.
(3) The CBT and the VBT remain unchanged.

Longeaud *et al* [8] have found that light-soaking results in an increase of the deep defect density and a broadening of the CBT. But this broadening is less important that the deep defect density increase. For this reason, we have supposed as an approximation that the CBT remains unchanged.

Figure 6 shows the evolution of the defect state density with illumination time, taking into account the assumptions above. The parameters used in the defect state density calculation are given in table 1.

4. Simulation of the photoconductivity degradation

In this section, we will use the varying density of states as developed in section 3 to describe the metastable changes of the steady state photoconductivity during illumination. The increase dN_d/dt of the dangling bond density resulting from the SWE occurs on a much longer time scale than the equilibration between the different populations of electrons and holes. Hence the

Table 1. Density of states parameters.

Parameters	Values
σ (eV)	0.19
E_p (eV)	1.27
$E_c - E_v$ (eV)	1.90
E_{Fi} (eV)	0.98
G_c (cm^{-3} eV^{-1})	10^{21}
G_v (cm^{-3} eV^{-1})	10^{21}
T^* (K)	500
T_c (K)	246
T_v (K)	570
H (cm^{-3})	5×10^{21}
N_{SiSi} (cm^{-3})	2×10^{23}

equilibration between the different occupancies will not be disturbed by the slowly increasing number of dangling bonds, and a quasi-steady state approach is possible [2]. Assuming the quasi-steady state condition (the generation rate equals the total recombination rate) and charge neutrality condition, one can write a system of two nonlinear equations:

$$G = R_{CBT} + R_{VBT} + R_D \tag{8a}$$

$$-n + p - n_t + p_t - N_d^- + N_d^+ = 0 \tag{8b}$$

where R_{CBT}, R_{VBT} and R_D are the recombination rates at the CBT, VBT and dangling bonds, respectively. n_t, p_t, N_d^-, N_d^+ are the charge densities in the CBT, VBT and dangling bonds, respectively. The net recombination rates at CBT, VBT and dangling bond are, respectively,

$$R_{CBT} = \int_{E_v}^{E_c} \left\{ n C_n^c(E) \left[1 - f_n(E) \right] - e_n^c(E) f_n(E) \right\} N_{CBT}(E) \, dE \tag{9a}$$

$$R_{VBT} = \int_{E_v}^{E_c} \left\{ n C_n^v(E) f_p(E) - e_n^v(E) \left[1 - f_p(E) \right] \right\} N_{VBT}(E) \, dE \tag{9b}$$

$$R_D = \int_{E_v}^{E_c} \left\{ n C_n^d(E) \left[1 - f_n(E) \right] - e_n^d(E) f_n(E) \right\} N_D(E) \, dE \tag{9c}$$

where C_n^i and e_n^i (i stands for c, v or d) are, respectively, the capture and emission rates for electrons, and $f_j(E)$ ($j = n, p$) is the occupancy function which was determined using the Simmons–Taylor statistics [20]. N_{CBT}, N_{VBT} and N_D are, respectively, the densities of CBT, VBT and one-electron dangling bond states. The charge densities in the band tails and dangling bonds, obeying the charge neutrality condition (8b), are
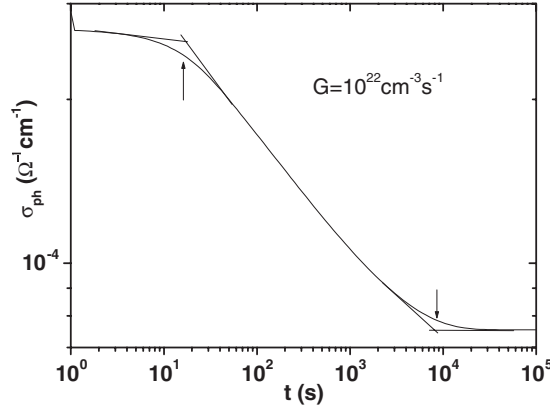
$$n_t = \int_{E_v}^{E_c} N_{CBT}(E) f_n(E) \, dE \tag{10a}$$

$$p_t = \int_{E_v}^{E_c} N_{VBT}(E) f_p(E) \, dE \tag{10b}$$

$$N_d^- = \int_{E_v}^{E_c} N_D(E) f_n(E) \, dE \tag{10c}$$

$$N_d^+ = \int_{E_v}^{E_c} N_D(E) f_p(E) \, dE. \tag{10d}$$

Figure 7. Photoconductivity degradation simulated for $G = 10^{22}$ cm^{-3} s^{-1}.

Table 2. Parameters of the photoconductivity simulation.

Parameters	Values
$C_n^c = C_n^v$ (cm^3 s^{-1})	10^{-8}
μ_n (cm^2 s^{-1} V^{-1})	10
μ_p (cm^2 s^{-1} V^{-1})	1

The system of the two equations (8*a*) and (8*b*) was solved numerically for the unknown concentrations n and p over the range of $N_d(t)$, and the photoconductivity

$$\sigma_{ph}(t) = q\mu_n(n(t) - n_0) + q\mu_p(p(t) - p_0) \tag{11}$$

was calculated. μ_n and μ_p in equation (11) are the mobilities of free electrons and free holes, respectively. Typical values of C_n^c, C_n^v, μ_n and μ_p are given in table 2 [21]. C_n^d has the same value as C_c.

In figure 7, we have presented the simulated photoconductivity degradation. The decrease of the photoconductivity occurs parallel to the increase of the dangling bond density. The times of the beginning and of the saturation of the metastable changes (indicated by arrows in the figure) have almost the same values as those observed in the photocurrent degradation measurement of [8]. Further, figure 8 shows the decrease of the photoconductivity as a function of dangling bond density. It can be seen that $\sigma_{ph} \propto \frac{1}{N_d^\gamma}$, $\gamma \sim 1$, which indicates that the photoconductivity follows the monomolecular behaviour of equation (3). It is also useful to ascertain the validity of the photoconductivity proportionality to the illumination intensity, G. Figure 9 shows that the observed dependences are $\sigma_{ph} \propto G^{0.93}$ in the annealed state, and $\sigma_{ph} \propto G^{0.5}$ in the saturated state. These results are in agreement with a large number of similar investigations reporting the intensity dependency of the photoconductivity as G^α, with α varying between 0.5 and 1. On the other hand, according to the approximation $\sigma_{ph} \propto \frac{G}{N_d}$ used in section 2, one expects that $\sigma_{ph} \propto G$ in the annealed state where $N_d(0)$ is independent of G. However, in the saturated state where $N_{ss} \propto G^{0.45}$, one expects, according to the proposed model, that $\sigma_{ph} \propto G^{0.55}$. Therefore, the two obtained results on the photoconductivity proportionality to the illumination intensity are in agreement with the predictions which arise from the approximation $\sigma_{ph} \propto \frac{G}{N_d}$.
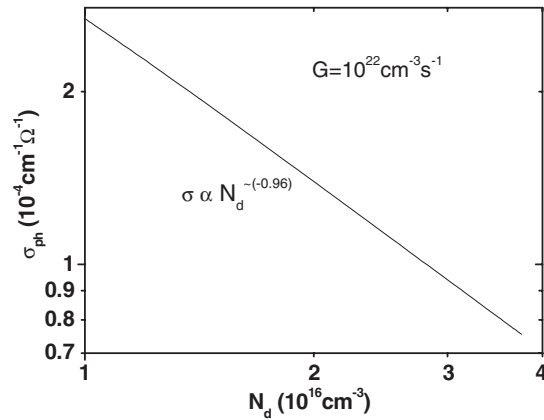
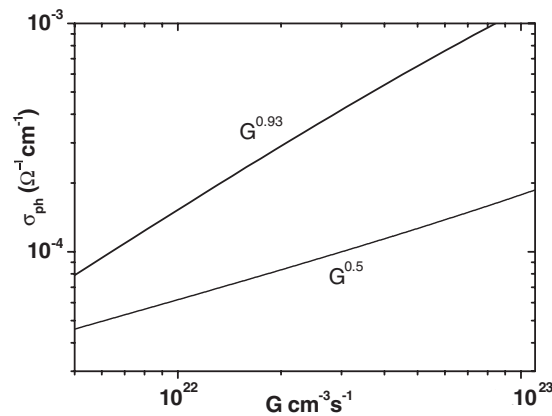**Figure 8.** Photoconductivity degradation versus the LID density during illumination.

Figure 9. The intensity dependence of the photoconductivity in the annealed state ($\sigma_{ph} \propto G^{0.93}$) and the saturated state ($\sigma_{ph} \propto G^{0.5}$).

5. Conclusion

In summary, we have presented a theoretical study of light induced defect creation and annealing, and the resultant degradation of the photoconductivity, in intrinsic a-Si:H. Our results can be summarized as follows.

(1) The observed saturation is considered as an equilibrium between light induced SiHD defect creation, locally created, and light induced defect annealing by hydrogen diffusion. The model fits the observed kinetics of light induced defects well.

(2) The density of defects increases as $t^{\beta} G^{0.62}$, where β approaches $1/3$ when G increases and $G^{0.62}$ is close to the $G^{2/3}$ law.

(3) The saturated density of defects slightly depends on the illumination intensity and is proportional to $G^{0.45}$.

(4) The proportionality of the photoconductivity with $\frac{1}{N_d}$, $\sigma_{ph} \propto \frac{1}{N_d}$, has been verified and the observed photoconductivity dependences on illumination intensity are $\sigma_{ph} \propto G^{0.93}$ in the annealed state and $\sigma_{ph} \propto G^{0.5}$ in the saturated state, in agreement with a large number of similar investigations and with the predictions of the approximation $\sigma_{ph} \propto \frac{G}{N_d}$.

Furthermore, and as a perspective to this work, it is interesting to simulate the temperature dependency of the steady state defect density within the framework of the proposed model. Also, it should be useful to relate the parameter k_H to the structural properties of the film, since this parameter traduces qualitatively the amount of hydrogen in the material.

Acknowledgments

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