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Dependence of the light-induced degradation kinetics of photoconductivity and ambipolar diffusion length as a function of doping level in *a*-Si:H

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Variation of both photoconductivity σ_{ph} and ambipolar diffusion length L_{amb} have been measured during exposure to light on a series of lightly *p*- and *n*-doped *a*-Si:H samples. The observed decay of the photoconductivity with time of exposure has been fitted by a power-law function. The power-law exponent observed strongly depends on doping. On the other hand, ambipolar diffusion length generally remains constant during the observed part of the degradation process, except for a slightly boron-doped sample with the Fermi-level near midgap. In the latter, L_{amb} decreases in accordance with σ_{ph}. The experimental observations can be qualitatively explained taking into account dangling bonds with their three charge states (D^+, D^0, D^-) as main recombination centers.

I. INTRODUCTION

One of the main goals toward which one pursues the investigation of the light-induced degradation process in *a*-Si:H is the achievement of a high stable efficiency in *p-i-n* solar cells. In these devices operating under steady-state conditions, the relative position of the Fermi level with respect to the band, the densities of free carriers as well as the average charge condition of the dangling bonds (D^+, D^0, D^-) will all vary in space. Dangling bonds play a major role in recombination and the preponderant free carrier onto dangling bond transition associated with recombination also varies in space within the device.[1] It has furthermore been shown that recombination is a key mechanism in the degradation process. For these reasons the degradation process in *p-i-n* devices is extremely complex and one needs to study first the behavior of uniform layers in a more complete manner.

In fact, by lightly doping *a*-Si:H samples with gas phase doping levels in the ppm range, one can obtain homogeneous material with an adjustable Fermi-level position. This method has recently been experimentally shown to lead to variations of the steady-state transport properties of both types of free photogenerated carriers over orders of magnitude.[2,3] The effect of slight doping on the steady-state photogenerated free carrier densities can be understood by modeling the recombination in *a*-Si:H, assuming monomolecular recombination of the free carriers on the dangling bonds.[1] Doping dramatically affects the average charge condition of the dangling bonds.[4] As the latter act as the main recombination centers in *a*-Si:H under illumination, any modification of their average charge condition, to which is related an important change of the capture cross-section involved in the process of monomolecular recombination, will thus affect the steady-state transport properties of the films.[2] In the framework of this model, the study of slightly doped *a*-Si:H samples should allow one to understand better any possible relationship between the average charge condition of the dangling bonds and the degradation kinetics; such a relationship would then be an important further step toward the understanding of light-induced degradation in *a*-Si:H *p-i-n* solar cells.

In *a*-Si:H, the steady-state photocarrier grating (SSPG) experiment[5] is currently the best method available to evaluate the ambipolar diffusion length L_{amb}, and it has been used by the authors in this study. One of its advantages is that it can be performed on the same experimental configuration as the one used for the measurement of the photoconductivity σ_{ph} (coplanar contacts on the surface of the sample). From the measurement of σ_{ph} one can evaluate the value of the product of the majority free carrier density times the corresponding band mobility, whereas from the measurement of L_{amb} one can evaluate the product of the minority free carrier density times their band mobility.[2] Therefore, assuming both band mobilities to remain constant during the process of interest, the variations of the ratio of free carriers densities can be monitored by measuring simultaneously the variations of σ_{ph} and L_{amb}.

In this article, we will present experimental observations on the variation of both σ_{ph} and L_{amb} during exposure to an intensive light. This is done for a series of lightly doped *a*-Si:H samples.

II. EXPERIMENT

The samples have been deposited on a glass substrate at 220 °C with the VHF deposition technique (plasma frequency $f = 70$ MHz), described elsewhere.[6] All films studied have thicknesses ranging between 1.7 and 2.5 μm. The doping of *a*-Si:H was achieved by mixing dopant gases [diborane (B_2H_6) or phosphine (PH_3)] in hydrogen, this mixture being then used with pure silane for the film deposition. The gas phase doping level of the *p*-type films was varied between 0.2 and 10 ppm_{vol} of B_2H_6 in silane; for the *n*-type films, it was varied from 0.1 to 1 ppm_{vol} of PH_3 in silane. The effect of ppm doping on the activation energy (E_{act}) is shown in Fig. 1. E_{act} was evaluated from the measurement of the dark conductivity at room temperature and by using the conductivity prefactor

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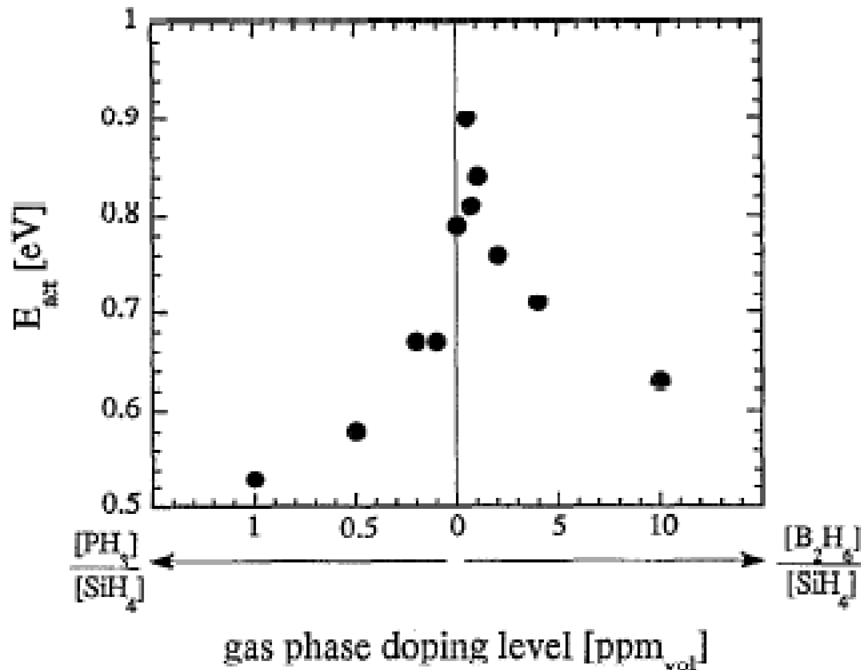

FIG. 1. Effect of ppm gas phase doping levels on the activation energy (E_{act}). Note the difference in scales for PH_3 doping and B_2H_6 doping. Above 0.5 ppm_{vol} of diborane doping, the material is p type; below it, it is n type. The undoped material is slightly n type.

150 $\Omega^{-1}\,cm^{-1}$. For n-type samples (the samples doped with PH_3 and the undoped sample), the value of E_{act} gives the position of the Fermi level relative to the conduction band ($E_c - E_F$). For the samples doped with more than 0.5 ppm_{vol} B_2H_6, (p-type samples), E_{act} gives the position of the Fermi level relative to the valence band ($E_F - E_v$). The value of $E_c - E_F$ for the series of samples was obtained from the value for E_{act} using $E_g = E_c - E_v = 1.8$ eV evaluated from measurement of the absorption spectra.[7] $E_c - E_F$ varied from around 1.2 eV (for the 10 ppm_{vol} B_2H_6 doped sample) to about 0.5 eV (for the 1 ppm_{vol} PH_3 doped sample).

Photothermal deflection spectroscopy (PDS) as well as constant photocurrent method (CPM) measurements have been performed on the annealed films (initial state). The effect of doping on the CPM measurement is such that the deep defect density (N_{DB}) cannot be properly evaluated.[8] The value for N_{DB} derived from the measurement of the absorption coefficient at a photon energy of 1.2 eV ($\alpha_{1.2}$) measured by PDS is 2×10^{16} cm^{-3}. This value showed no significant variation with the doping level.[8] Under the experimental conditions used to perform the PDS measurement (thickness of the samples around 2 μm) on the different samples, variation of bulk deep defect density within a factor of 2 are difficult to detect. In the worst case, our experimental observation of an almost constant value of $\alpha_{1.2}$ with doping level could correspond to a variation of N_{DB} within an order of magnitude. But as the ratio of free photogenerated carrier densities n_f/p_f has been observed to vary within seven orders of magnitude in this series,[2] we have to attribute the latter to an effect other than that of the variation of N_{DB}. In fact, it can be attributed to the variation of the average charge condition of the dangling bonds,[2,9] the latter being clearly dependent on the dopant concentration.

Degradation of the films has been performed with cw Kr laser light ($\lambda = 647$ nm), at an incident power density of 150–170 mW/cm^2. The samples were air cooled during the degradation, and degradation was interrupted in order to measure σ_{ph} at an incident power light intensity of 4 mW/cm^2. L_{amb} was evaluated using the SSPG technique under a bias light of 4 mW/cm^2, the same light intensity as the one used to measure σ_{ph}. All our measurements have been done at the same light intensity, i.e., approximately at the same generation rate (this approximation being due to samples having different thicknesses). For the steady-state conditions prevailing in both σ_{ph} and SSPG measurements, this means that our measurements have been performed under roughly constant recombination rate.

According to Refs. 2 and 10, a parameter b can be introduced; this parameter is defined in an electrically neutral material by the relationship:

$$b = \frac{\mu_n^0}{\mu_p^0}\frac{n_f}{p_f}, \tag{1}$$

where $\mu_{n,p}^0$ are the band mobilities and n_f and p_f are the free photogenerated carrier densities due to the bias light (corresponding here to the 4 mW/cm^2 light). By combining the values of σ_{ph} and L_{amb} we are able to evaluate b according to the formula given in Ref. 10. The parameter b has proven to be a key parameter for the interpretation of σ_{ph} and L_{amb}.[1,2,10] It is a good indicator of the offset of the two quasi-Fermi levels with respect to midgap at a given generation rate. It is more meaningful for the experimental conditions used here (and should be used for quantitative analysis) than the value of $E_c - E_F$, the latter being the relevant monitor for the variation of the free carrier densities in the dark, i.e., under thermal equilibrium.

III. DISCUSSION

We have plotted in Fig. 2 the observed variations of both L_{amb}^2 and σ_{ph} during exposure to the degradation beam for different doped samples. In all lightly doped samples with the exception of the 0.5 $ppm_{vol}B_2H_6$ doped sample, L_{amb}^2 can be observed (at least during the degradation time periods and illumination conditions as used in our experiments) to remain almost constant during this process.

It is indeed possible to understand why the ambipolar diffusion length L_{amb} does not decrease at all during the initial phase of degradation (the phase observed here) in all sufficiently doped samples by using the approach given in Ref. 10. Briefly, we shall relate σ_{ph} and L_{amb} with the material transport parameters. Assuming the standard transport model,[11] where conduction takes place by transport of free carriers above a mobility edge, σ_{ph} and L_{amb} can be written as:[10]

$$\sigma_{ph} = e(\tau_n^R\mu_n^0 + \tau_p^R\mu_p^0)G_0, \tag{2}$$

$$L_{amb}^2 = \frac{kT}{e}C\frac{\mu_n^0\mu_p^0}{\tau_n^R\mu_n^0 + \tau_p^R\mu_p^0}, \tag{3}$$

where e is the unit charge, kT the thermal energy, $\tau_{n,p}^R$ are defined as $\tau_n^R = n_f/G_0$ and $\tau_p^R = p_f/G_0$, G_0 is the generation

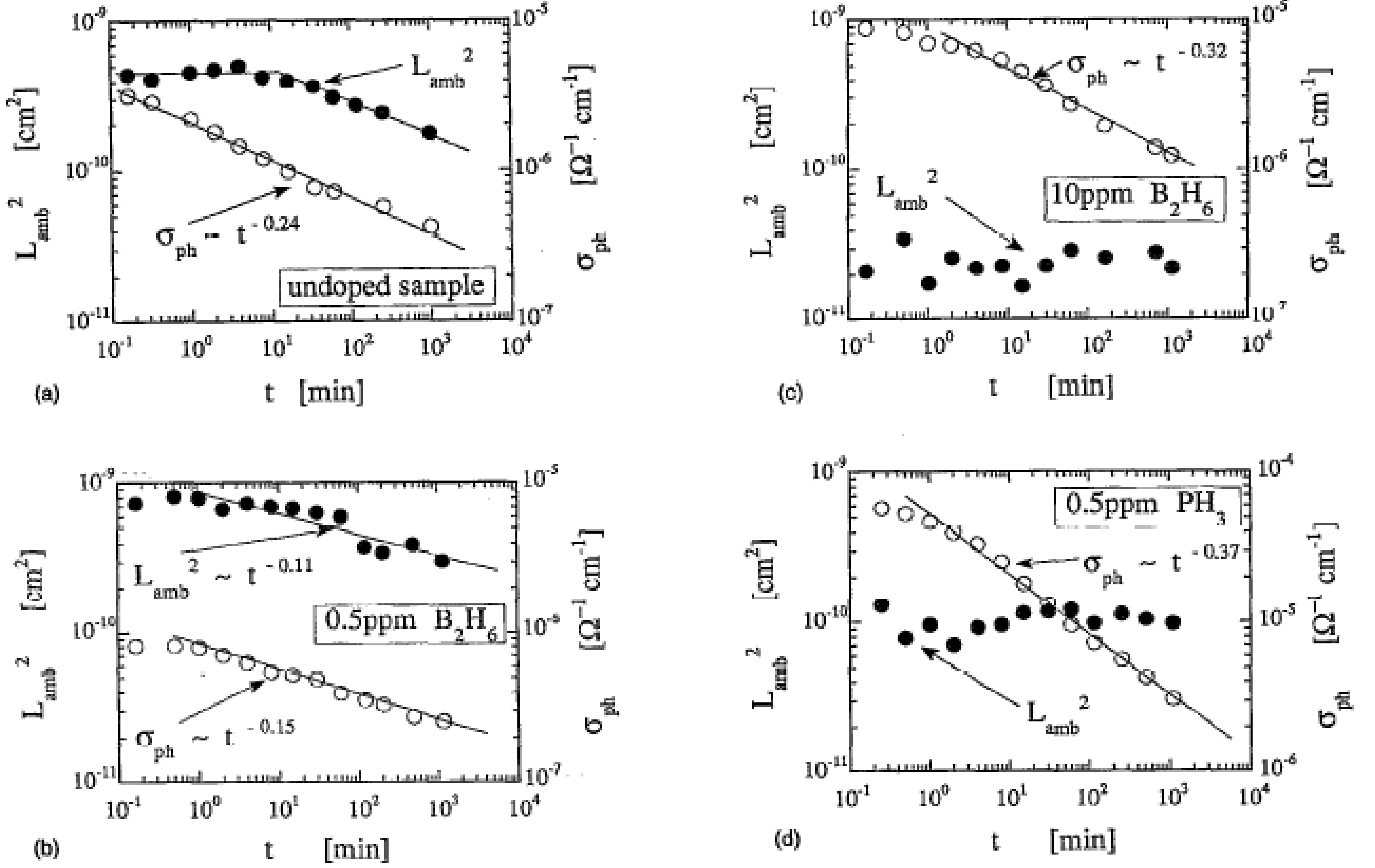

FIG. 2. Variation of σ_{ph} and L_{amb}^2 during exposition time to a cw Kr laser light beam ($\lambda = 647$ nm), $P_{deg} = 170$ mW cm^{-2}; (a) undoped sample, (b) 0.5 ppm$_{vol}$ B_2H_6 doped sample ("intrinsic" sample), (c) 10 ppm$_{vol}$ B_2H_6 doped sample, (d) 0.5 ppm$_{vol}$ PH_3 doped sample. A power law has been fitted to the variation of σ_{ph}. The value of its exponent allows one to characterize the "degradation rate" of $\sigma_{ph}(t)$.

rate, and $\mu_{n,p}^0$ are the band mobilities. The constant C appearing in the expression for L_{amb} is a correction factor experimentally evaluated[10] as being between 1 and 2. Now, in order to identify τ_n^R and τ_p^R one has to introduce a model for the recombination process. We will consider that recombination occurs by the successive capture of free carriers on the dangling bonds (monomolecular recombination). Using the results of the detailed treatment of recombination as given in Ref. 1 which was derived for the case of a single discrete level of recombination centers in the gap, which, however, have three different charge states (D^0, D^+, D^-), one obtains for the recombination times:[10]

$$(\tau_p^R)^{-1} = \frac{f^0}{\tau_p^0} + \frac{f^-}{\tau_p^-}, \tag{4}$$

$$(\tau_n^R)^{-1} = \frac{f^0}{\tau_n^0} + \frac{f^+}{\tau_n^+}, \tag{5}$$

where f^0, f^+, and f^- are the recombination center occupation functions, i.e., the probability that a recombination center is occupied by one electron (D^0), zero electrons (D^+), or two electrons (D^-). We will assume that *all* the dangling bonds act as recombination centers. Then τ_p^0, τ_p^-, τ_n^0, and τ_n^+ are defined as $\tau_n^{0,+} = (v_{th}\sigma_n^{0,+} N_{DB})^{-1}$ and $\tau_p^{0,-} = (v_{th}\sigma_p^{0,-} N_{DB})^{-1}$, where v_{th} is the thermal velocity, N_{DB} the total density of dangling bonds, and σ the capture cross section for free carriers.

Take, now, an n-type, i.e., phosphorus-doped sample. Here, we assume that $\mu_n^0 n_f \gg \mu_p^0 p_f$. Then, according to Eq. (3), $L_{amb}^2 = (kT/e) C \tau_p^R \mu_p^0$. Thus, the observation that L_{amb} does not decrease with exposure to the intense laser beam means that τ_p^R and thus the density of free minority carriers does not vary with degradation. At the onset of the degradation, there are mainly negative ionized dangling bonds (D^-), whose density N_{D^-} is approximately equal to that of the ionized dopants (P^+); free holes are mainly captured by D^- (which not only form the majority of recombination centers here, but also have a much larger capture cross section for holes than the neutral dangling bonds[9,10,12]), so that we have $f^0 \ll f^-$ and $\tau_p^0 \gg \tau_p^-$. Thus, $\tau_p^R = 1/(v_{th}\sigma_p^- N_{D^-})$, where N_{D^-} is the density of negatively charged dangling bonds. As degradation proceeds, N_{D^-} can be considered to remain constant (to assure charge neutrality) and the newly created dangling bonds will therefore have to be preponderantly neutral (D^0). (This means we are deliberately excluding here a simultaneous creation of two charge dangling bonds of opposite sign, D^+ and D^-.) Thus, τ_p^R will stay constant and L_{amb}, too. In this model, only if the density of neutral dangling bonds (N_{D^0}) increases so much that we have $\sigma_p^0 N_{D^0} < \sigma_p^- N_{D^-}$, will the situation change and will neutral dangling bonds become important for the capture of holes. But this would require a large increase in dangling bond density, because $\sigma_p^- \gg \sigma_p^0$. Such a transition point is not ob-

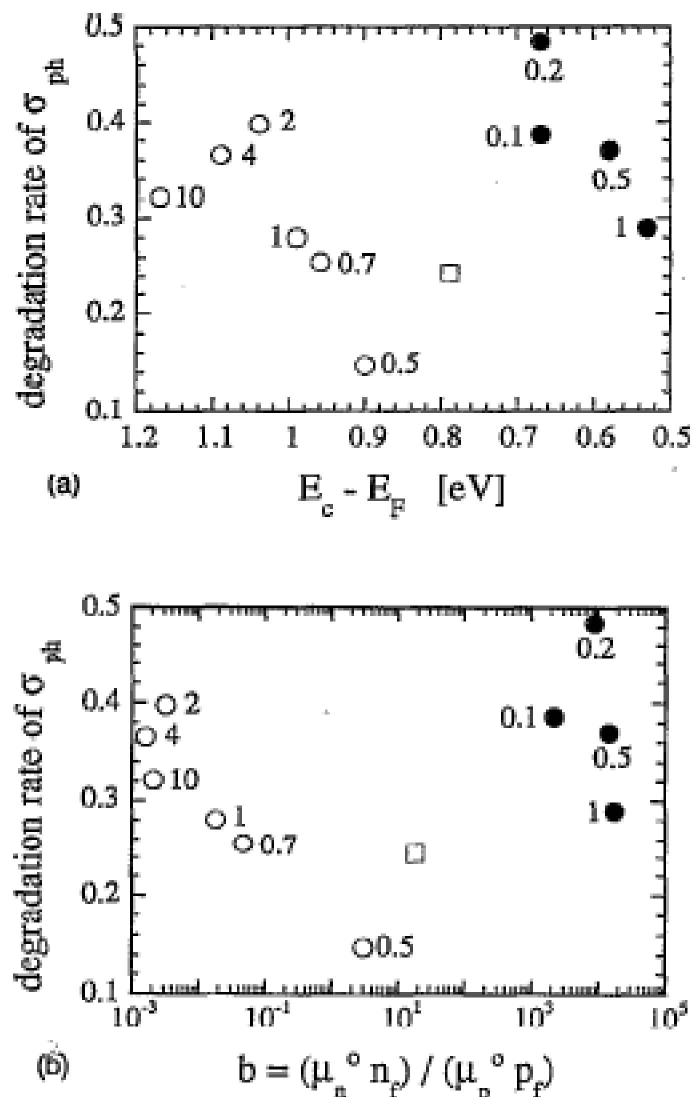

FIG. 3. Variation of the exponent of the observed power-law decrease in $\sigma_{ph}(t)$ (so-called "degradation rate"); (a) as a function of the initial value of E_c-E_F, (b) as a function of the initial value of b. The figure indicates the ppm_{vol} doping level of each particular sample. Filled circles are for n-doped samples, open circles for p-doped samples, and filled squares for the undoped sample.

served in our present data on doped samples. It is, however, observed for the undoped sample (Fig. 2). Similar reasoning is applicable for the p-type case, i.e., for sufficiently boron-doped samples. The case of the undoped sample has already been extensively treated by the authors (albeit in a more complicated way) in previous papers[13,14] and the case of the 0.5 ppm_{vol} B_2H_6 doped sample where L_{amb}^2 and σ_{ph} both decrease with approximately the same power-law dependence with time will be discussed later.

As for the photoconductivity σ_{ph}, we have observed that (under the experimental conditions used for the measurements) it decreases with exposure time (t). The decay of σ_{ph} can be fitted either by a power law[15] or by a stretched exponential.[16] In the limited range of exposure times used here, both fits give similarly good results, so that we have decided arbitrarily to fit power laws to the observed variations of σ_{ph} (Fig. 2). The "rate of degradation" of σ_{ph} has been characterized by the value of the exponent of the power law. The absolute value of the exponents thus obtained (they are always negative) are plotted in Fig. 3 as a function of the initial value of E_c-E_F and as a function of b measured in the initial state (annealed state). Figures 3(a) and 3(b) show that the "degradation rate" of σ_{ph} (i.e., the exponent of the power law) depends on the gas phase doping level.

We can qualitatively understand this behavior if we keep in mind that σ_{ph} is proportional to the $\mu\tau$ product of majority carriers [Eq. (2)]. These carriers have (in the doped case) the same polarity as the ionized dangling bonds (e.g., as D^- in the phosphorus-doped case). Such carriers therefore cannot be captured by the ionized dangling bonds, but only by the neutral dangling bonds D^0 of density N_{D^0}. Taking as an example, again, the n-type (phosphorus-doped) case, $\sigma_{ph}=e\tau_n^R\mu_n^0G_0$ with $\tau_n^R = 1/(v_{th}\sigma_n^0 N_{D^0})$. Now, as already explained above, during the degradation process, the newly created dangling bonds will have to be neutral for charge neutrality to be maintained. Thus, the relative increase in N_{D^0} will be larger, if their proportion is smaller at the onset of degradation, i.e., it will be larger if the parameter b is very different from unity and the sample is stronger doped. This can (at least partly) explain the variation in the exponent of $\sigma_{ph}(t)$ with the parameter b, as shown in Fig. 3(b). Although the proposed explanation is only qualitative, the models for transport and recombination used here have yielded quantitative information for the same series of samples.[9,10] Until now, the influence of the dangling bond occupation function on the value of L_{amb} and σ_{ph} had been omitted. The experimental observations presented here are another illustration of the importance of clearly distinguishing between the densities of neutral and charged dangling bonds when evaluating steady-state transport properties.

In *undoped*, so-called "device-quality" a-Si:H, the degradation rate of σ_{ph} is commonly found to be around 0.3. This particular value had in the past been considered[15] as an experimental quantity allowing to discriminate between different models proposed for the microscopic mechanism of the Steabler–Wronski effect; such a point of view has been subsequently contested.[16] Nevertheless, the pronounced variation of the value of this exponent observed here is experimental evidence proving that effects of the degradation process on the steady-state transport properties differ considerably depending on the doping level of the sample, i.e., on the Fermi-level position. Let us remark also here that in "undoped" a-Si:H prepared under nonconventional conditions, values for the degradation rate different from 0.3 have already been reported elsewhere.[17]

The lowest degradation rate of σ_{ph} was observed on the sample doped with 0.5 ppm_{vol} B_2H_6. This sample shows a "true intrinsic" behavior characteristic of a sample with the Fermi-level at (or near) midgap: E_{act} is the largest one reached in our series of samples, and the values of L_{amb} and σ_{ph} measured on this particular sample attained their maximum and minimum values, respectively.[2] In this case, one may assume that there are so few ionized dangling bonds (D^+ or D^-) that neutral dangling bonds act here as the main capture centers for both carriers. Thus, L_{amb} and σ_{ph} will both have to decrease in roughly the same manner with the increase of the total dangling bond density N_{DB} (and thus of N_{D^0}).

The observation of a very slow decrease of both σ_{ph} and L_{amb} in this particular sample can be compared with earlier observations made on compensated a-Si:H samples:[18] it had been found that in compensated samples

(samples doped with approximately the same amount of both doping species), the density of metastable dangling bonds that can be created by a fixed illumination procedure decreases with increasing doping level. With this observation in mind and according to the predictions of our model,[2] the observation of a very slow decrease of both σ_{ph} and L^2_{amb}, in this particular film, can be attributed to a very slow increase of N_{DB}. This assumption clearly requires an independent (and more direct) measurement of the variation of $N_{DB}(t)$ on this particular sample before concluding anything definitively.

IV. CONCLUSIONS

It has been observed on a series of lightly doped a-Si:H samples (gas phase doping levels of the order of the ppm_{vol}) that light-induced degradation causes the photogenerated majority free carrier density to decrease (i.e., σ_{ph} decreases) with exposure to light in a fashion that depends on the initial ratio of free photogenerated carrier densities, i.e., on the initial Fermi-level position. On the other hand, the density of photogenerated minority free carriers is in general not affected by light-induced degradation (i.e., L^2_{amb} keeps constant except for certain particular cases). The latter set of observations can be explained by postulating that all newly created dangling bonds are neutral (D^0).

At this moment, we are unable to decide whether the variation in the degradation kinetics of $\sigma_{ph}(t)$ with the parameter b is fully or only partly related to the charge condition of the dangling bonds as explained in detail above. However, we may already now conclude that one has to be very cautious when taking photoconductivity as a monitor for the degradation process; the variation of photoconductivity is not a monitor for the variation of the total density of dangling bonds, but, under usual conditions, only for the density of neutral dangling bonds. One may safely compare the decay rates of photoconductivity only for samples having the same proportion of neutral (D^0) and ionized (D^- or D^+) dangling bonds. It is therefore prudent to always look, at the same time, also at the ambipolar diffusion length when studying degradation and to evaluate the parameter b from σ_{ph} and L_{amb}.

Further degradation experiments, over longer time periods (extending into saturation, if the latter is really observed) and where the total density of dangling bonds, σ_{ph} and L_{amb}, are evaluated simultaneously on a multitude of lightly doped samples are now called for. This work is extremely time consuming, but it is needed as a basis for a proper evaluation of the light-induced degradation process.

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