Transient photoconductivity in amorphous silicon

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Transient photoconductivity measurements in a coplanar electrode configuration in undoped *a*-Si:H are explained by two decay channels. The first one, operative at excess charge carrier concentrations smaller than 10^{16} cm^{-3}, is ascribed to deep trapping, presumably in neutral dangling bonds. The second one, operative at higher excess charge carrier concentrations, is ascribed to electron-hole recombination where the availability of free holes controls the decay process. The transport parameters deduced from these measurements agree satisfactorily with those deduced from time-of-flight measurements. The, at first sight, paradoxical increase of transient lifetimes in material with larger densities of dangling bonds can be explained within the model presented here by an additional decay channel for free holes.

I. INTRODUCTION

Charge carrier kinetics in hydrogenated amorphous silicon (*a*-Si:H) have been extensively investigated by time-resolved techniques. In particular, transient photoconductivity measurements in a sandwich electrode configuration [time-of-flight (TOF) measurements] have been applied successfully to *a*-Si:H and there exists general agreement on their interpretation.[1] TOF experiments yield information on the interaction between charge carriers and states in the band gap. Information on recombination kinetics can be extracted from transient photoconductivity experiments in a coplanar electrode configuration (PC).[2–6] However, the interpretation of PC experiments is not generally accepted. One of the controversial points is the influence of the contacts on the measured signal.[7]

In this work PC measurements of undoped *a*-Si:H obtained by excitation with sub-band-gap and band-gap light over a large excitation density range will be presented. The influence of the electrodes on the PC signal is investigated by comparison of PC signals with transients obtained with the contactless time-resolved microwave conductivity (TRMC) (Ref. 4) technique. An attempt is made to interpret PC signals with a model that agrees with findings from TOF measurements.

The interpretation of the data presented in this work is based on a model mainly deduced from TOF experiments.[1,8] It is assumed that there are sharp mobility edges in undoped *a*-Si:H from where the density of states decays exponentially with energy into the band gap. The electron drift mobility μ_e in undoped *a*-Si:H is, at room temperature, about 1 cm^2 V^{-1} s^{-1} and thermally activated. The hole drift mobility μ_h is much smaller and consequently the PC signal can be attributed to electrons. The influence of the tail states on mobile charge carriers is described by energy-independent capture rates b_e and b_h, for electrons and holes, respectively. The influence of the conduction-band tail states on electron kinetics at room temperature can be described by Boltzmann distribution of the electrons over the tail states, because the width of the tail state distribution, characterized by kT_e, is approximately equal to the thermal energy kT at room temperature. The width of the valence-band tail kT_h is much larger, and in the intuitive thermalization model[8] adopted here it is assumed that excess holes are mainly localized above the hole demarcation energy E_d defined by $E_d = kT \ln(\nu_0 t)$, where ν_0 is an attempt-to-escape frequency.

II. EXPERIMENTAL PROCEDURE

High-quality undoped *a*-Si:H samples, prepared by glow-discharge decomposition of silane, were supplied from different sources to account for specimen-dependent differences. A typical film investigated in this study has a thickness of 1 μm, an activation energy of 0.72 eV, a dark conductivity of 4×10^{-9} Ω^{-1} cm^{-1}, and a photoconductivity of 4×10^{-5} Ω^{-1} cm^{-1} (illumination: Ar laser, 514 nm, 0.1 mW/cm^2).

Excess charge carriers were induced by 532- and 1064-nm light pulses from two Nd:YAG lasers (where YAG represents yttrium aluminum garnet). One has a pulse width of 12 ns [full width at half maximum (FWHM)] which determines the time resolution of the experiments, the other has a pulse width of 70 ps; in the latter case the time resolution (0.7 ns) is limited by the bandwidth of the digitizer. The light intensity is varied by optical density filters between 1 mJ/cm^2 and 25 nJ/cm^2, corresponding to an initial excess charge carrier concentration of about 2×10^{19}–5×10^{14} cm^{-3} for 532-nm excitation, referring to the total thickness of the sample.

PC and TRMC signals are identical under conditions where both techniques can be applied, as can be seen in Fig. 1. This proves that contacts do not have an appreciable influence on PC transients.[4] Consequently no more assumptions are involved in the interpretation of PC signals in terms of excess bulk charge carrier kinetics than for transient photoinduced absorption (PA) experiments.[9]

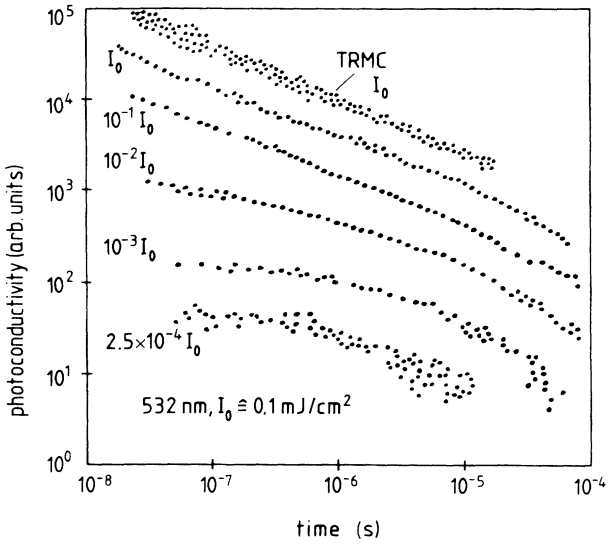

FIG. 1. Photoconductivity transients induced by a 532-nm laser pulse (12 ns FWHM) with different intensities. The upper curve is obtained by the TRMC technique, which is shifted arbitrarily towards the PC signals below.

III. RESULTS AND DISCUSSIONS

It has been reported before[10] that the transient photoconductivity decays initially with the laser pulse at higher excitation intensities ($I > 1$ μJ/cm^2) followed by a slower decay, which is displayed in Fig. 1. The signal amplitude is sublinearly dependent on the excitation density. At lower excitation densities ($I < 1$ μJ/cm^2) this initial decay disappears and the signal amplitude becomes linearly dependent on the excitation density. This points to an excitation-density-dependent decay process on a time scale smaller than the characteristic time of the measurements.

At the lowest two excitation densities in Fig. 1 ($I = 100$ and 25 nJ/cm^2) the decay behavior is similar over the first two μs, where the decay after excitation with 25 nJ/cm^2 is somewhat faster at longer times. The drift mobility μ_e estimated from these low-excitation-intensity data is about 0.2 cm^2 V^{-1} s^{-1}. Initially (over the first 100 ns) there is no appreciable decay, in agreement with the findings from TOF experiments, because the electron dispersion parameter $\alpha_e = T/T_e$ is about unity at room temperature.[1] It seems plausible to ascribe the decay to the trapping of mobile electrons. The decay is not exponential but the decay over the first microseconds after the excitation can be characterized by a decay time of about 2 μs.

The slower decay of the transient in the microsecond time range at higher excitation intensity ($I = 1$ μJ/cm^2) must be due to a saturation of this deep trapping decay channel. This leads to an estimate of about 5×10^{15} cm^{-3} for the deep trap density. As this density lies in the order of magnitude of neutral dangling bonds concentration D^0 in high-quality material it is suggested that this deep trapping is due to neutral dangling bonds. The reaction rate $1/\tau = 5\times10^5$ s^{-1} determined here can be compared to the rates obtained by other techniques. The value of this rate parameter deduced from rate-limited TOF experiments[11] is higher, but the value found by the transient-delayed-field technique[12] of about 10^6 s^{-1} lies in the same order of magnitude. This agreement seems satisfactory in view of the nonexponential decay found for this deep trapping.

Above excitation densities of about 1 μJ/cm^2 a new electron decay channel becomes active (Fig. 1). The underlying decay process must involve excess holes because of its activation at higher excitation densities. It is not a bimolecular recombination of excess electrons with trapped holes as described in the literature[8] because both transients ($I = 10$ and 100 μJ/cm^2) are characterized by power-law decay via $t^{-0.6}$ and not by a power-law decay t^{-1} as is derived for this model.[8] The most plausible model for this decay channel is the recombination of excess electrons with excess holes around the hole mobility edge. In this case the supply of these holes is the rate controlling step, and the density of excess electrons δn is equal to the density of trapped holes δp_t if the mobile hole density and the excess electron density in deep traps can be neglected. In that case and with the intuitive thermalization model[8] one obtains

$$\delta n = \delta p_t = F \int_{E_d}^{\infty} g(E)dE = FN_v(\nu_0 t)^{-\alpha_h} , \quad (1)$$

where α_h is the hole dispersion parameter $\alpha_h = T/T_h$, N_v is the total density of states in the exponential valence-band tail, $g(E)$ is the density of states, and F is the occupancy factor of valence-band tail states above the demarcation level. F is independent of the energy of the tail states[8] and is independent of time if all excess holes emitted from tail states recombine with excess electrons and are not retrapped in valence-band tail states above the demarcation level leading to a $t^{-\alpha_h}$ decay of the photoconductivity. From the transients induced with the excitation intensity $I = 100$ and 10 μJ/cm^2 a value of the hole dispersion parameter of 0.6 is deduced for both transients. This agrees very well with the value obtained with TOF experiments.[1]

The conditions for a $t^{-\alpha_h}$ decay of the transient photoconductivity can be deduced from consideration of the reaction kinetics. The electron-hole recombination responsible for the excess electron decay at high charge carrier densities ($\delta n > 10^{16}$ cm^{-3}) and the competitive process of retrapping of excess free holes are described by the following rate equations:

$$d\delta p/dt = -b_r \delta n \, \delta p , \quad (2)$$

$$d\delta p/dt = -b_h(1-F)N_V(\nu_0 t)^{-\alpha_h}\delta p . \quad (3)$$

According to the intuitive thermalization model[8] δp in Eq. (3) represents the density of excess mobile holes. For the electron-hole recombination expressed in Eq. (2) it is possible that δp also involves shallowly trapped excess holes with an energy of about a few kT above the mobility edge. This yields only a factor in Eq. (2) so it can be included in the rate parameter b_r. It is also assumed that in Eq. (2) δp represents the density of excess mobile holes, where b_r is an effective rate parameter. In the case of a negligible density of deep trapped excess

electrons and of excess free holes, the condition for a $t^{-\alpha_h}$ decay of the photoconductivity can be estimated by comparison of Eqs. (2) and (3):

$$b_r/b_h > (1-F)/F \ . \tag{4}$$

A minimum value for b_r can be estimated from the transient induced by an intensity $I=10$ μJ/cm^2 if it is assumed that at 10 ns the inequality (4) is satisfied. A maximum value for b_r can be estimated from the transient photoconductivity induced with $I=1$ μJ/cm^2, which reflects a transition range where at short times an appreciable number of excess holes will still be retrapped in tail states above the demarcation energy leading to an increase of F with time. Consequently the excess electron density will decay slower than with $t^{-\alpha_h}$, as can be derived from Eq. (1). If N_v is estimated to be 10^{20} cm^{-3} and $\nu_0=10^{12}$ s^{-1}, this leads to $10b_h > b_r > 2b_h$. If it is assumed that b_h lies between 10^{-10} and 10^{-8} cm^{3}s^{-1} (Refs. 1 and 8) this yields a value of b_r of approximately 10^{-8} cm^{3}s^{-1}.

A physically reasonable model for a process characterized by such a large rate parameter is a diffusion-controlled reaction with the Onsager radius as reaction radius. This model has proven its utility in systems with drift mobilities in the same order of magnitude as in the present case.[13] If the hole drift mobility is neglected relative to the electron mobility, this model yields, for the recombination rate parameter b_r,

$$b_r=\mu_e e/\epsilon_0\epsilon_r=4\times10^{-8}\ \text{cm}^{-3}\text{s}^{-1}\ , \tag{5}$$

where the drift mobility μ_e is deduced from the present measurements and $\epsilon_r=12$ is inserted.

It can be noted that the model for excess charge carrier kinetics in a-Si:H proposed in this work is perfectly described by the model of bimolecular recombination of Orenstein *et al.*[8] if the roles of electrons and holes are exchanged. In both works the decay channel involves the reaction between a not explicitly dispersive species (here mobile electrons and in the work of Orenstein *et al.*[8] trapped holes) and a species which is subject to dispersive transport.

At longer times the electron-hole recombination with a monotonously decreasing decay rate will give way to relatively slow decay channels with a time-independent decay rate. This has been observed[6] with PC experiments over a larger time range than covered here. An initial decrease of the photoconductivity of good quality undoped a-Si:H by $t^{-\alpha}$ with α about 0.6 is found in the literature,[6] agreeing with the present measurements in the same excitation intensity and time range, but at longer times a faster decay is observed. A possibility for this decay channel is the recombination traffic via dangling bonds, if the transition of hole to negatively charged dangling bond D^- takes place in this longer time range.

The model for the electron decay channel at high charge carrier concentrations can be tested by investigation of this decay as a function of the temperature (Fig. 2). The excitation intensity for the transients in Fig. 2 is ten times larger than the highest intensity in Fig. 1. In agreement with the model given before it can be seen

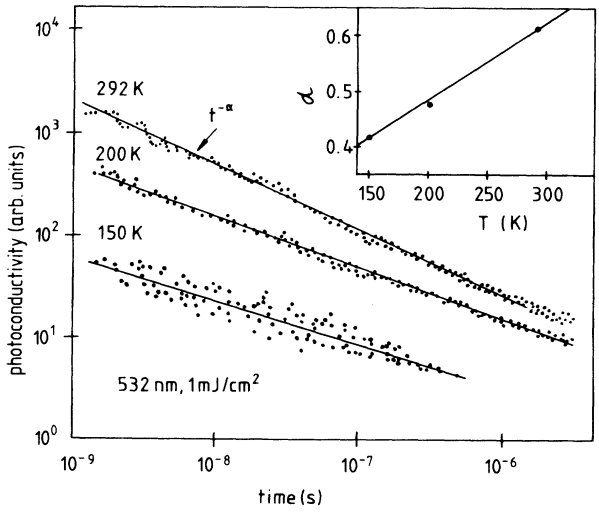

FIG. 2. PC signals after 532-nm excitation (70 ps FWHM) for three different temperatures. The inset shows the dependence of the slope parameter α on the temperature T.

that also at this excitation intensity the transient photoconductivity at room temperature decays via $t^{-0.6}$. At lower temperature the decay on a double logarithmic scale is still linear but the decay rate decreases with decreasing temperature. This confirms the identification of the slope with the hole dispersion parameter $\alpha_h=T/T_h$. Also, the numerical values of the slopes at the different temperatures are in reasonable agreement with the hole dispersion coefficient obtained from TOF measurements,[1] suggesting that both parameters are identical. It must be remarked that at lower temperatures the electron dispersion should also play a role. However, the broader valence-band tail mainly determines the electron decay rate in the temperature range covered here at this high excess charge carrier concentration. The accuracy of the present data does not warrant a detailed interpretation of the temperature dependence of the slopes. Possible deviations of the temperature dependence of the hole dispersion coefficient from predictions of the multiple trapping model can be better investigated by TOF measurements.

A way to modify the importance of the electron-hole recombination observed after 532-nm excitation is to induce excess charge carriers by sub-band-gap light. In high-quality a-Si:H, excitation by 1064-nm light induces mainly mobile electrons and trapped holes.[14] Also, after 1064-nm excitation there is no observable influence of the contacts in PC experiments, as can be seen in Fig. 3. The transient at the lowest excess charge carrier concentration (Fig. 3) is identical to the transient induced by 532-nm light at the lowest excitation densities. This confirms the attribution of the decay of these transients to trapping of electrons characterized by an electron dispersion parameter α_e of about unity. Additionally, the identical decay behavior after 532- and 1064-nm excitation at low excitation intensities shows that the surface has only a minor influence on the decay of the 532-nm signal. The slowing down of the decay at higher ex-

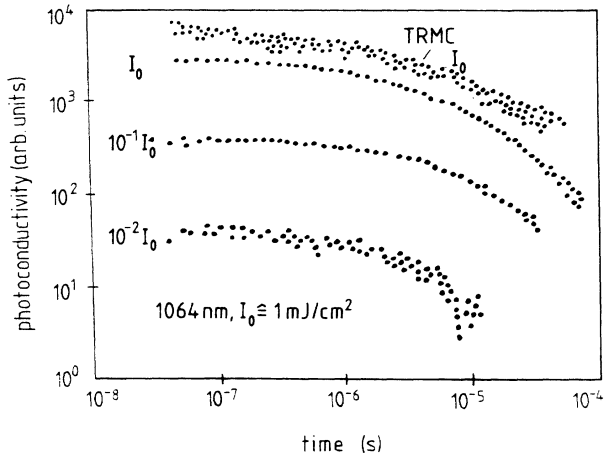

FIG. 3. Photoconductivity transients induced by sub-band-gap light at 1064 nm (12 ns FWHM) for different excitation intensities. The upper curve displays the decay obtained by the TRMC technique, which is shifted arbitrarily to the PC signals below.

citation densities in Fig. 3 must be due to saturation of this electron decay channel. At higher excitation densities, the decay after 1064-nm excitation is much slower than after 532-nm excitation. This points also to the involvement of mobile holes in the electron decay after 532-nm excitation.

We tentatively identify the observed electron-hole recombination process with the higher-order decay process that gives rise to the fast initial decay channel during the excitation pulse as it is observed at high charge carrier concentrations.[10] Although the initial nonuniform excess charge carrier distribution has to be taken into account, a qualitative picture of the decay behavior at short times can be given without an explicit consideration of this complication. Initially, at high excitation densities, the density of mobile holes cannot be neglected. This leads to an initial faster decay rate at higher excitation densities. Consequently the initial height $\delta\sigma_0$ of the transient photoconductivity for $I > 10$ μJ/cm^2 increases sublinearly with the excitation density (Fig. 1). Because $\delta\sigma_0$ represents a state where the mobile hole density can be neglected, this fast process is only observed in our experiments as a relative decrease of $\delta\sigma_0$. Formulated in another way, this fast process determines the stationary value of F, which is reflected in the amplitude of the transient photoconductivity.

The simple model for excess charge carrier kinetics in high-quality undoped a-Si:H proposed in the present work reflects a relatively low density of states in the mobility gap, as in the electron kinetics only a small density of deep states and a larger density of shallow valence-band tail states play a role. Electron decay kinetics are not only sensitive to deep electron traps which lead simply to an increase of the decay rate with a increase of the deep state density, but are also sensitive to hole traps. Hole traps will lead on the contrary to a slowing down of the electron decay. This effect has been observed in a-Si:H upon light n doping which leads to a decrease of the importance of the fast higher-order process and slows down the decay at longer times.[10] The conclusion must be that n doping introduces hole traps. This phenomenon does not seem to be restricted to n doping. Also, for lower-quality a-Si:H material without intentional doping a slower photoconductivity decay than observed here for high-quality material has been reported.[4] Although the density of deep electron traps is presumably larger in lower-quality films, their effect can be suppressed by the presence of a large density of hole traps in this material.

The model proposed for the decay channel at higher densities ($I > 10$ μJ/cm^2) leads to the same decay behavior for mobile electrons and trapped holes. Consequently, if the transient photoinduced absorption (PA) reflects trapped holes, PA transients should also reflect the shape of the valence-band tail at higher excess charge carrier concentrations and PC and PA should show similar decay characteristics. This does not agree with PA data for the microsecond range where it is claimed that PA decay reflects the conduction-band tail.[15] However, PA transients in the nanosecond range induced by approximately the same excitation density are reported to reflect the shape of the valence band.[16] The observation of the slower PA decay in low-quality a-Si:H can again be ascribed to a higher density of hole traps in this kind of material,[16,17] if holes in these traps are PA active.

PC experiments at room temperature on high-quality samples from other sources lead qualitatively to the same results as displayed in Fig. 1. As expected from the theory developed in this paper, it was observed that samples with higher initial decay rate than 5×10^5 cm^{-3}s^{-1} after excitation with 25 nJ/cm^2 did not show saturation of deep trapping until a higher excitation intensity than displayed in Fig. 2. The slopes of the transients induced with excitation densities higher than 10 μJ/cm^2 were found to vary between 0.5 and 0.6.

IV. CONCLUSIONS

In this work it has been shown that transient photoconductivity experiments in a-Si:H yield valuable and reliable information on charge carrier kinetics. It is probable that the wide range of PC decay characteristics reported in the literature are not due to contact phenomena but are due to different sample qualities and to different induced excess charge carrier densities.

Electron decay in high-quality a-Si:H proceeds at excess charge carrier concentrations smaller than 10^{16} cm^{-3} by trapping in deep states. For excess charge carrier concentrations higher than the deep trap density, electrons recombine with free holes, a process which is controlled by the emission of trapped holes from the valence-band tail.

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