RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 33, NUMBER 12 15 JUNE 1986

Influence of doping on transport and recombination of excess charge carriers in *a*-Si:H

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(Received 7 April 1986)

Contactless transient photoconductivity measurements with a time resolution of 0.7 ns have been performed in *a*-Si:H films with different *p* and *n* doping levels. An initial fast biomolecular recombination followed by a slow recombination process can be distinguished. Both processes and their relative contribution to the total decay are strongly influenced by the doping level and excitation intensity. A recombination model is proposed which attributes the fast decay to a direct electron-hole recombination and explains the slow-decay regime by a recombination of charge carriers via charged and neutral recombination centers.

Transient photoconductivity measurements allow the observation of transport and recombination processes of excess charge carriers. In principle, if the time resolution is faster than the fastest decay process, it is possible to distinguish between the mobility and effective lifetime of excess charge carriers which appear only as a product in steady-state photoconductivity experiments.

Different varieties of transient photoconductivity methods, in particular the time-of-flight (TOF) technique,[1] have been successfully applied to *a*-Si:H. As the TOF method monitors the drift of excess charge carriers of one polarity while carriers of the other polarity are pulled off rapidly, TOF signals reflect interactions of excess charge carriers with states in the band gap.

The generally accepted interpretation of the huge wealth of TOF data on *a*-Si:H leads to a model of the density of states in the band gap characterized by an exponential energy dependence near the band edges[1] and a distribution of multivalent deep traps[2] in the middle of the gap with large carrier cross sections, which have been identified with dangling bonds.[2]

Transient photoconductivity (PC) measurements in a coplanar electrode geometry[3] should reflect principally the same interaction of excess charge carriers with states in the band gap. However, in addition, the mutual interaction of carriers of both polarities must be taken into account.

In the present work, the time-resolved microwave conductivity (TRMC) technique[4] has been applied to study charge-carrier dynamics in the nanosecond time scale of doped and undoped *a*-Si:H films at room temperature. In principle, the TRMC technique yields information identical to the PC method,[4] but at the same time the TRMC technique is not subject to the restrictions imposed by contact phenomena.[5]

Due to the high excitation densities used in this work and the low density of defect states of the *a*-Si:H films studied, interactions between excess holes and electrons could be analyzed in some detail.

Excess charge carriers have been induced by a 100-ps pulse (full width at half maximum) at 532 nm from a Nd:YAG laser (where YAG is yttrium alluminum garnet). The total time resolution, including electronic delays, amounts to 0.7 ns, as determined from the 10%–90% signal risetime. The *a*-Si:H films (0.5-μm thick) were deposited in a glow-discharge system where PH_3 and B_2H_6 were added to SiH_4 to achieve *n* doping and *p* doping, respectively. The films were characterized by dark conductivity and steady-state photoconductivity measurements (Table I). The steady-state measurements were performed in a coplanar electrode configuration.

Figure 1 shows photoconductivity transients in differently doped *a*-Si:H films. It is assumed that these signals reflect the dynamics of electrons at the doping levels used because the electron mobility in *a*-Si:H is much larger than the hole mobility.[6] This is definitely true in undoped and *n*-doped samples.[7] The decreasing decay time with increasing *p* doping level (Fig. 1) shows that this assumption also holds for *p*-type samples.

At least two decay channels can be distinguished. One decay channel is strongly dependent on the excitation intensity and operative at high excitation density, particularly in *p*-doped films. The other is active on a longer time scale and is responsible for the tail of the signals in Fig. 1, where its importance rises with higher *n* doping level.

As it is inferred from Fig. 1, that the initial decay can be faster than the time resolution of the measurements, the dependence of the signal maximum on the excitation intensity for the different films has been compared (Fig. 2), where at the lowest excitation density the signal in the *p*-doped samples lies outside the detection limit. At the highest excitation intensity the signal is higher in *n*-doped films, but this changes rapidly if the excitation density is decreased. It is deduced from Fig. 2 that the dependence of the signal maximum on the excitation density changes from a square-root dependence in the undoped film to a linear

TABLE I. Dark (σ_D) and steady-state photoconductivity ($\Delta\sigma_{ph}$) of *a*-Si:H films with different doping levels at room temperature. $\Delta\sigma_{ph}$ was determined using a Kr laser at 514 nm and 100 mW/cm^2 intensity. The activation energy E_A has been determined by an Arrhenius plot in the temperature region 100–400 K.

Doping level relative to SiH_4 mol	E_A (eV)	σ_D (Ω^{-1} cm^{-1})	$\Delta\sigma_{ph}$ (Ω^{-1} cm^{-1})
10^{-3} PH_3 mol	0.18	3.0×10^{-3}	1.6×10^{-4}
10^{-4} PH_3 mol	0.25	3.5×10^{-4}	6.3×10^{-4}
10^{-5} PH_3 mol	0.41	1.2×10^{-4}	9.7×10^{-4}
Undoped	0.72	4.1×10^{-9}	4.3×10^{-5}
10^{-5} B_2H_6 mol	0.76	2.3×10^{-9}	6.3×10^{-6}
10^{-4} B_2H_6 mol	0.60	4.6×10^{-9}	4.3×10^{-6}

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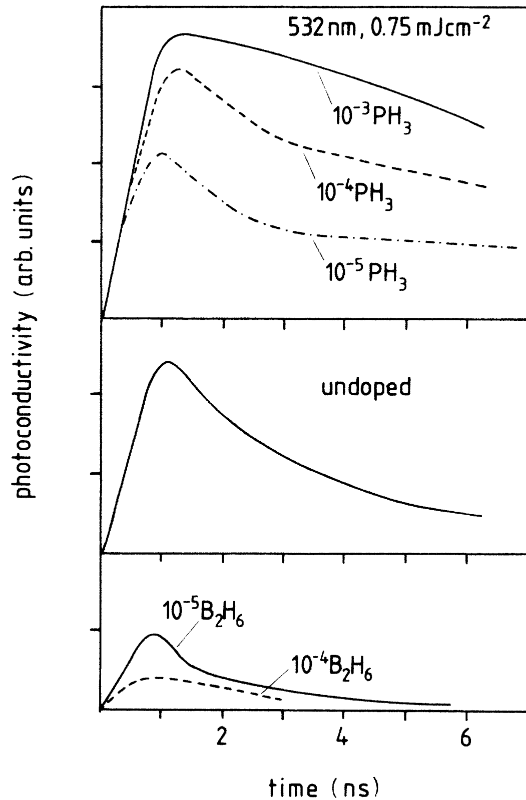

FIG. 1. Photoconductivity transients in different doped and undoped a-Si:H films at room temperature.

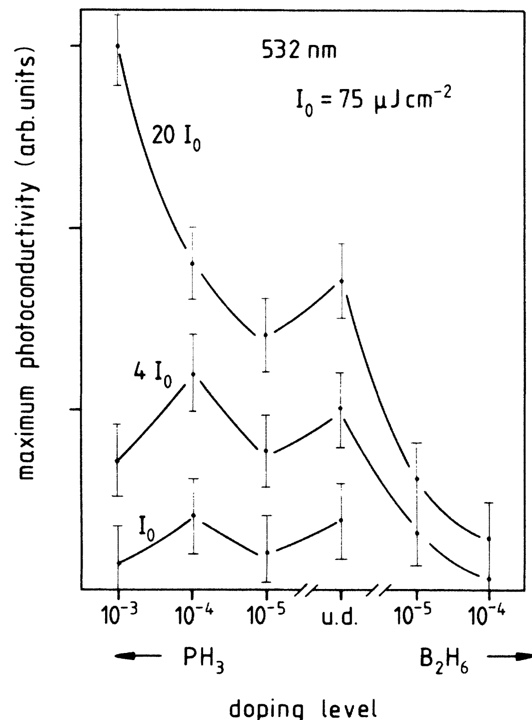

FIG. 2. Dependence of the maximum photoconductivity on the doping level and excitation intensity.

one in the highly n-doped film. This fact, in combination with the shape of the transients, shows that the sublinear dependence of the signal maximum and the initial fast decay in undoped and lightly n-doped films are due to the same decay channel. The second-order character of the fast-decay channel and the short-time scale where it is active point to the recombination of electrons and holes trapped in band tails as the underlying decay process. The decreaseing contribution of this process to the total decay with increasing n doping level can be explained by the rapid capture of holes in n-doped material. The high importance of the fast-decay channel in p-doped films can be attributed to the presence of a larger number of free holes in p-type material, but an increased electron decay due to an increase of positively charged recombination centers in the band gap can also contribute. Both p doping effects cause the dependence of the signal maximum on the excitation to change from square root to linear upon increasing the p doping level as it can be inferred from Fig. 2.

At low excitation densities, where the initial fast second-order decay does not play any role, the photoconductivity maximum reflects the mobility of electrons. It seems, within the experimental uncertainty, that the electron mobility is independent of the n doping level (Fig. 2). Undoped films should have the highest electron mobility, taking into account the second-order decay that is still present even at the lowest excitation intensity shown in Fig. 2. The electron mobility in p-doped films cannot be estimated due to the rapid electron decay, which is faster than the time resolution of these measurements.

Figure 3 shows the decay behavior of n-doped and undoped samples on a longer time scale in a double logaritmic plot. The transients of p-doped films decay so fast that display in the same figure is not convenient. Qualitatively, these results can be explained by recombination via a multivalent recombination center. These recombination centers will be identified with dangling bonds, as is generally accepted.

The undoped film shows a fast decay (Fig. 3), whereas light n doping increases the effective electron lifetime. In heavily n-doped material (10^{-3} mol PH_3/mol SiH_4), however, the lifetime is reduced. Two opposing effects of doping must be taken into account to explain this behavior. The first effect is active at low n doping levels and decreases

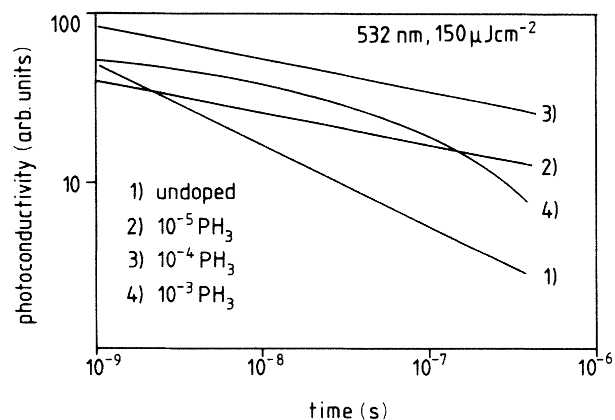

FIG. 3. Photoconductivity transients on a double logarithmic scale.

the electron decay rate. This can easily be explained if electron decay in undoped material takes place via capture by neutral dangling-bond (D^0) centers. Light n doping shifts the Fermi level to the conduction band and gradually neutral dangling bonds are transformed to doubly occupied dangling bonds (D^-).

Electrons can only be captured by the remaining dangling bond in the D^0 state and the D^0 states generated by capture of an excess hole in a D^- state. The latter process slows down the electron decay. The second effect can be ascribed to the increase of the dangling bond density in the D^- state by n doping. This increases the hole-D^- reaction rate leading to a faster D^0 generation which in turn accelerates the electron capture.

Although no quantitative evaluation of the transients will be tried, some additional remarks concerning capture rates have to be made. It is deduced from TOF experiments that hole capture is very fast in n-type material[2] and consequently does not appreciably slow down the electron capture.[8] It is possible that the generated hole-defect state $[h+D^- \rightarrow (D^0)^*]$ does not immediately become an efficient deep electron trap (D^0), since time-consuming lattice relaxation is required. Also, in transient luminescence data an increase of the effective electron lifetime in n-doped samples has been observed, although this has been explained in another way.[8]

Within the interpretation given here, the particular shape of the transient photoconductivity (Fig. 3) refers mainly to the interaction of holes with states in the band gap. In this view the decay curves are determined either by hole dispersion[6] or by recombination already active in the nanosecond time scale.

In summary, the TRMC data from 100-ppm p doping up to 1000-ppm n doping levels are explained by two decay channels. The first one is second-order recombination between electrons and holes in band tail states. It is active at higher excitation densities and if the hole lifetime is sufficiently large. A recombination via surface states should only have a minor influence because this process is not appreciably influenced by the film thickness as *in situ* measurements have indicated.[9]

The second one is recombination via dangling bonds. The majority charge carriers can only recombine if minority charge carriers are previously captured by the charged dangling bonds. In p-type a-Si:H films, photoconductivity transients reflect the capture of the minority charge carriers, and the fast decay of these transients is explained by the fast capture of these minority charge carriers by the recombination centers. In n-type a-Si:H, photoconductivity transients reflect the capture of majority charge carriers where this process is controlled by the minority charge carriers.

This model can be applied to steady-state excess charge carrier kinetics as deduced from the stationary photoconductivity (Table I) measurements. This can be done only qualitatively as the relative contribution of the direct recombination process is probably very different due to its strong dependence on the intensity and due to a possible saturation of the recombination centers in the steady-state case. However, the small photoconductivity of the p-type samples and the increase of the photoconductivity with increasing n doping level up to 10^{-5} mol PH_3/mol SiH_4 are analoguous to the behavior of the TRMC decay time upon doping. Higher n doping levels lead to a reduced TRMC decay time (Fig. 3) and correspondingly to a lower steady-state photoconductivity (Table I).

The transients of undoped material (Fig. 3) differ from those published before.[4] The present data have been obtained on films supplied by two different laboratories, and the results on films of both sources are equivalent. The undoped material investigated previously[4] probably has a somewhat different quality, and it can be deduced from the present data that in the previous material a larger number of hole traps were present, e.g., by unintentional light n doping.

A more quantitative evaluation of these data and the investigation of the light intensity dependence of the long-time decay will be the subject of further research.

We acknowledge the provision of some of the investigated samples by Dr. G. Müller, the Messerschmitt-Bölkow-Blohm Co., Munich and Dr. H. Mell, University of Marburg. The stimulating help of Dr. G. Beck is also gratefully acknowledged. This work has been supported by the Stiftung Volkswagenwerk.

[1]T. Tiedje, in *Hydrogenated Amorphous Silicon, Part B: Optical Properties,* Semiconductors and Semimetals, Vol. XXI, edited by J. I. Pankove (Academic, London, 1984), p. 207.

[2]R. A. Street, J. Zesch, and M. J. Thompson, Appl. Phys. Lett. **43**, 672 (1983).

[3]J. M. Hvam and M. H. Brodsky, Phys. Rev. Lett. **46**, 371 (1981).

[4]M. Kunst and A. Werner, J. Appl. Phys. **58**, 2236 (1985).

[5]R. A. Street, Phys. Rev. B **32**, 3910 (1985).

[6]T. Tiedje, J. M. Cebulka, D. L. Morel, and B. Abeles, Phys. Rev. Lett. **46**, 1425 (1981).

[7]H. Oheda, Philos. Mag. B **52**, 857 (1985).

[8]R. A. Street, D. K. Biegelsen, and R. L. Weisfield, Phys. Rev. B **30**, 5861 (1984).

[9]A. Werner, M. Kunst, G. Beck, J. Lilie, and H. Tributsch, Solid State Commun. **56**, 127 (1985).