PHYSICAL REVIEW B VOLUME 44, NUMBER 3 15 JULY 1991-I

Transient photoconductivity of a-Si$_{1-x}$Ge$_x$:H alloys

M. Kunst and H. C. Neitzert
Hahn-Meitner Institut, Glienicker Strasse 100, D-1000 Berlin 39, Federal Republic of Germany

H. Ruebel
Phototronics Solartechnik G.m.b.H., D-8011 Putzbrunn, Federal Republic of Germany

(Received 14 November 1990)

Contactless measurements of the transient photoconductivity in a-Si:H and in a-Si$_{1-x}$Ge$_x$:H alloys are reported. A decrease of the effective electron mobility with increasing Ge content is observed. Because of a difference of dependence of the excitation density, two different processes are distinguished that lead to this decrease of the mobility. One is attributed to trapping and the other one leads to a decrease of the drift mobility. No increase of the recombination rate upon alloying of a-Si:H with Ge is observed as, on the contrary, the long-time decay in alloys is slower than in pure a-Si:H.

INTRODUCTION

For many applications, such as, for example, solar cells, the optical band gap of amorphous hydrogenated silicon (a-Si:H) is too large. So alloys of a-Si:H have been investigated in order to obtain lower band-gap material. In particular, amorphous silicon-germanium (a-Si$_{1-x}$Ge$_x$:H) alloys have been shown to be promising, because the optical gap can be varied between 1.2 and 1.7 eV.[1,2] Unfortunately, admixture of Ge to a-Si:H leads also to a deterioration of the electronic properties of the material.[1,2]

In this work, the optoelectronic properties of a-Si$_{1-x}$Ge$_x$:H alloys are investigated by contactless transient photoconductivity measurements. Experimental results of films with 12% and 23% Ge content are compared to those of pure a-Si:H films.

EXPERIMENT

In our work we use decompositions of SiH$_4$/GeH$_4$ or SiH$_4$/GeH$_4$/H$_2$ gas mixtures in a glow discharge apparatus with a load-lock system.

In Fig. 1 the specific data, dark-conductivity (σ_D) and photoconductivity (σ_{Ph}) at room temperature for our a-Si$_{1-x}$Ge$_x$:H films prepared under various conditions, are presented. If we compare with some results from the literature (see figure caption) we see that the photoelectric properties of our films exhibit international standard for $1.5 < E_{\text{opt}} < 1.75$ eV. The films we used for time-resolved microwave conductivity (TRMC) measurements were the phototronics (PST) films prepared with hydrogen dilution.

The TRMC measurements were performed in a Ka-band microwave system as described previously.[5] The TRMC method monitors the relative change of the microwave power reflected from a semiconductor ($\delta P/P$) upon pulsed illumination of this semiconductor. In a small perturbation approximation the TRMC signal in a-Si:H is proportional to the photoconductivity ($\delta\sigma$) induced by the illuminating laser pulse as it is shown before:[5,6]

$$\delta P(t)/P = A\,\delta\sigma(t)\ , \tag{1}$$

where A is the sensitivity constant.

In intrinsic a-Si:H and a-Si$_{1-x}$Ge$_x$:H films the transient photoconductivity $\delta\sigma(t)$ can be attributed solely to mobile electrons because the drift mobility of holes is much smaller than that of electrons.[7,8] This reduces Eq. (1) to

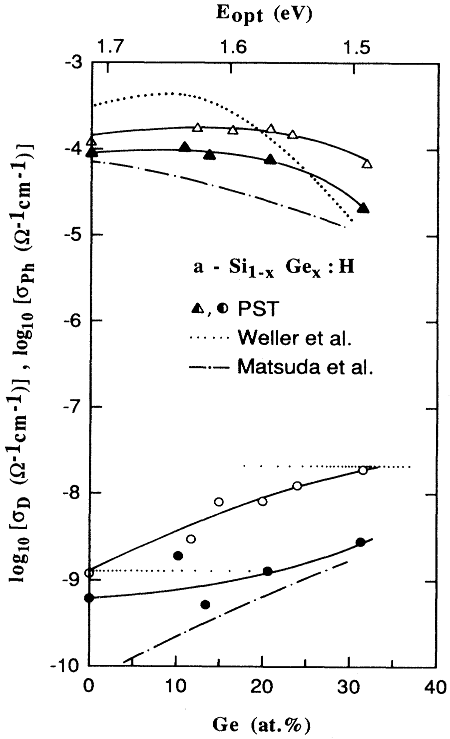

FIG. 1. σ_D and σ_{Ph} for a-SiGe:H films as a function of Ge content [or Tauc optical gap (E_{opt})]. The PST films (▲,●: without H dilution; △,○: with H dilution) are compared to data from Weller *et al.* (Ref. 3) (triode configuration and H dilution) and Matsuda *et al.* (Ref. 4) (diode configuration and H dilution).

$$\delta P(t)/P = A\,\delta n(t)\mu_n e \qquad (2)$$

with $\delta n(t)$ the density of mobile electrons and μ_n their mobility.

Although it is possible to perform absolute TRMC measurements and to determine the sensitivity constant A absolutely,[9,10] this is rather complicated and relatively inaccurate. Therefore it is preferred in this work, where TRMC signals of several films are compared, to do measurements in such a way that the value of A is not determined, but this value is essentially identical for all films. This is possible with an accuracy of about 10%.

Excess charge carriers were excited by 10-ns [full width at half maximum (FWHM)] pulses at 532 nm of a Nd:YAG (where YAG denotes yttrium aluminum garnet) laser with intensities between 2 $\mu J\,\mathrm{cm}^{-2}$ and 2 $\mathrm{mJ\,cm}^{-2}$.

In the present work investigations of the transient photoconductivity by the TRMC method in two a-$\mathrm{Si}_{1-x}\mathrm{Ge}_x$:H films, with Ge content $x=0.13$ and 0.23 will be reported. Also a film with $x=0.15$ was investigated but as the results were essentially the same as in the film with $x=0.13$, these results are not explicitly presented.

RESULTS AND DISCUSSION

In the nanosecond time range the TRMC signals in a-Si:H and a-$\mathrm{Si}_{1-x}\mathrm{Ge}_x$:H films are characterized by a rise determined by the width of the excitation pulse (i.e., 10 ns) followed by a fast decay giving way to a much slower decaying tail (Fig. 2). The maximum signal height (signal amplitude) depends linearly on the excitation density in the low excitation range changing to a sublinear behavior at higher excitation densities (Fig. 3). The height of the tail at 40 ns relative to the signal amplitude increases with decreasing excitation density (Fig. 2). The sublinear behavior at high excitation densities must be attributed to a higher-order recombination process already active during the excitation as previously proposed for pure a-Si:H films.[11,12] Also the decay between 10 and 40 ns must at least partially be due also to higher-order recombination. This is concluded from the increase of the decay rate in this time range with increasing excitation density. These general features are common to the samples investigated in this work.

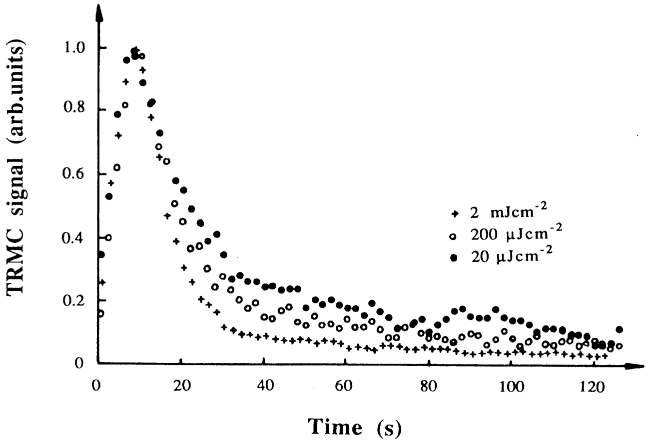

FIG. 2. The transient photoconductivity induced by 10-ns (FWHM) 532-nm pulses of 2 $\mathrm{mJ\,cm}^{-2}$ (+), 200 $\mu\mathrm{J\,cm}^{-2}$ (○), and 20 $\mu\mathrm{J\,cm}^{-2}$ (●) in intrinsic a-Si:H. The signal amplitude at the three excitation densities is normalized to the same value to facilitate comparison of the shape of the signals.

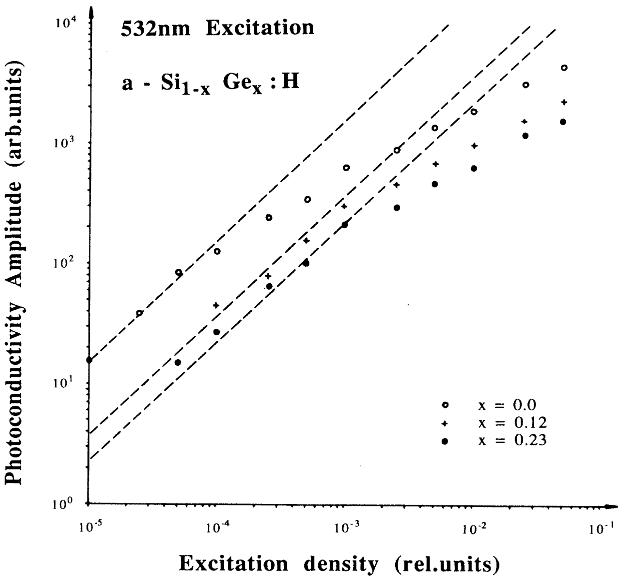

FIG. 3. The amplitude of the transient photoconductivity in pure a-Si:H (○), $\mathrm{Si}_{0.88}\mathrm{Ge}_{0.12}$:H (+), and a-$\mathrm{Si}_{0.77}\mathrm{Ge}_{0.23}$:H (●) as a function of the excitation density. The three lines are drawn as a fit to a linear dependence of the low excitation density data points. The excitation densities indicated refer to a reference value of 200 $\mathrm{mJ\,cm}^{-2}$.

The photoconductivity amplitude reflects the density of mobile excess electrons at the end of the optical excitation [$\delta n(t=10\ \mathrm{ns})$]. For the amplitude, Eq. (2) can be written

$$[\delta P(t)/P]_{t=10\ \mathrm{ns}} = A\,\delta n(t=10\ \mathrm{ns})\mu_n e\ . \qquad (3)$$

Consequently, if no decay processes occur during the excitation, the amplitude is proportional to the product of the excess electron density produced by the excitation pulse (δn_0) and their mobility. However, this is certainly not warranted for the presented investigations, where at high excitation densities a higher-order decay process decreases the induced mobile electron density already during the excitation pulse (Fig. 3). This suggests comparison of the amplitudes in the excitation density range where the amplitudes depend linearly on the excitation density if the mobilities of the different samples must be compared.

But, also in the low excitation range, there is already a multitude of trapping processes within the duration of the excitation pulse in a-Si:H. Even in the picosecond time range trapping processes of excess electrons in a-Si:H films are reported.[13,14] These and other observations have led to the standard model for electron conduction in a-Si:H at room temperature where electrons are mobile characterized by a band mobility μ_n at a mobility edge in strong interaction by multiple trapping with localized states under this mobility edge. The shape of the density of states under this mobility edge is generally assumed to be exponential[7] but other shapes are also proposed.[15] The interaction (i.e., multiple trapping) of mobile electrons with states under the mobility edge cannot be resolved by present-day experimental techniques as it starts already in the picosecond time range. At room temperature in pure a-Si:H the distribution of excess electrons over mobile states and localized states under the mobility edge (i.e., band tail states) is observed to be stationary in the time range of interest for this work (larger than 1 ns) (Refs. 7 and 15) leading to a time-independent drift mobility.

For the interpretation of the present measurements it is convenient to define an effective mobility μ_{eff} as the photoconductivity at 10 ns divided by the product of the excess electron density induced by the laser pulse (δn_0) and the unity charge. It is clear that μ_{eff} is equal to the product of the band mobility and the ratio between the density of mobile excess electrons [$\delta n(t=10$ ns)] and the excess electron density induced by the laser pulse:

$$[\delta P(t)/P]_{t=10\text{ ns}} = A\,\delta n_0 \mu_{\text{eff}} e = A\,[\mu_n \delta n(t=10\text{ ns})/\delta n_0]\delta n_0 e\ . \quad (4)$$

For the present measurements this yields the fact that the ratio between the amplitudes of two samples at the same excitation density is equal to the ratio between their effective mobilities.

In Fig. 3 the amplitude of the transient photoconductivity is plotted as a function of the excitation density for the three samples. It is observed that at all excitation densities the amplitude and so the effective mobility is maximal in pure a-Si:H and decreases with increasing Ge content. The transition from a linear dependence on the excitation density to a sublinear dependence can be distinguished for all three samples in Fig. 3, where three straight lines with slope +1 are drawn as an approximate fit of the low excitation density data points to a linear dependence. The experimental data in Fig. 3 suggest that the transition from a linear behavior to a sublinear behavior occurs in the alloys at a higher excitation density than in pure a-Si:H. This can be observed better in Fig. 4 where for both a-Si$_{1-x}$Ge$_x$:H films the amplitude divided by the amplitude in the pure a-Si:H film at the same excitation density (i.e. the effective mobility relative to that of the pure a-Si:H film) is plotted against the excitation density. In the high excitation range ($I > 100\ \mu$J cm^{-2}) the relative effective mobility is constant due to a similar excitation density dependence of the signal in the pure a-Si:H film and the alloys, where for a-Si$_{0.88}$Ge$_{0.12}$:H the relative effective mobility is 0.5 and for a-Si$_{0.77}$Ge$_{0.23}$:H a value of 0.35 is found. At lower excitation densities ($I < 100\ \mu$J cm^{-2}) the relative effective mobility decreases in both films (Fig. 4) indicating the onset of a linear dependence in a range where the amplitude of the pure a-Si:H film is still sublinearly dependent on the excitation density. Except for the absolute value no difference in behavior between the two a-Si$_{1-x}$Ge$_x$:H samples is observed within the accuracy of the measurements (Fig. 4).

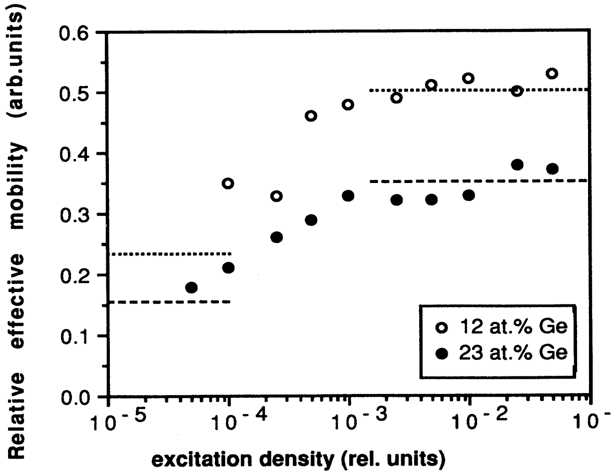

FIG. 4. The amplitude of the transient photoconductivity in a-Si$_{0.88}$Ge$_{0.12}$:H (○) and a-Si$_{0.77}$Ge$_{0.23}$:H (●) films divided by that of the pure a-Si:H film (relative effective mobility) as a function of the excitation density. The two lines drawn at the high excitation density side represent an average of the high excitation density data points. The two lines drawn in the low excitation density range are calculated from the fits in Fig. 4.

It seems sound to assume that the linear dependence of the amplitude on the excitation density in the alloys continues also at excitation densities lower than those employed in the present measurements. This assumption implies that the relative effective mobilities in Fig. 3 will attain at low excitation densities ($I < 5\ \mu$J cm^{-1}) a value independent of the excitation density. By linear extrapolation of the experimental results to this low excitation density range this yields for the relative effective mobility in a-Si$_{0.88}$Ge$_{0.12}$:H a value of 0.23 and for a-Si$_{0.77}$Ge$_{0.23}$:H a value of 0.15.

In the longer time range the decay behavior of the a-Si$_{1-x}$Ge$_x$:H films is different from that in the pure a-Si:H film. This can be observed in Fig. 5 where the transient photoconductivity is displayed on a double logarithmic scale. In the a-Si:H film the decay in the time range between 40 ns and 1 μs is characterized by a power-law decay (i.e., proportional to $t^{-\alpha}$) with $\alpha = 0.9$. In the same time range both a-Si$_{1-x}$Ge$_x$:H alloys also show a decay behavior characterized by a power law, however, with a slope $\alpha = 0.6$. Measurements in the same time range with an excitation density ten times smaller than that used for the data displayed in Fig. 5 show essentially the same decay behavior: within the accuracy of the measurements (about 10%) the values of α observed are the same.

A qualitative explanation of the long-time decay behavior in a-Si:H films with similar decay behavior has been given before:[12] The decay is due to a combination of deep electron trapping and electron-hole recombination controlled by hole emission from tail states. The slower decay in the a-Si$_{1-x}$Ge$_x$:H alloys can be explained if at least one of these two processes is reduced upon admixture of Ge. A possibility is the decrease of the electron

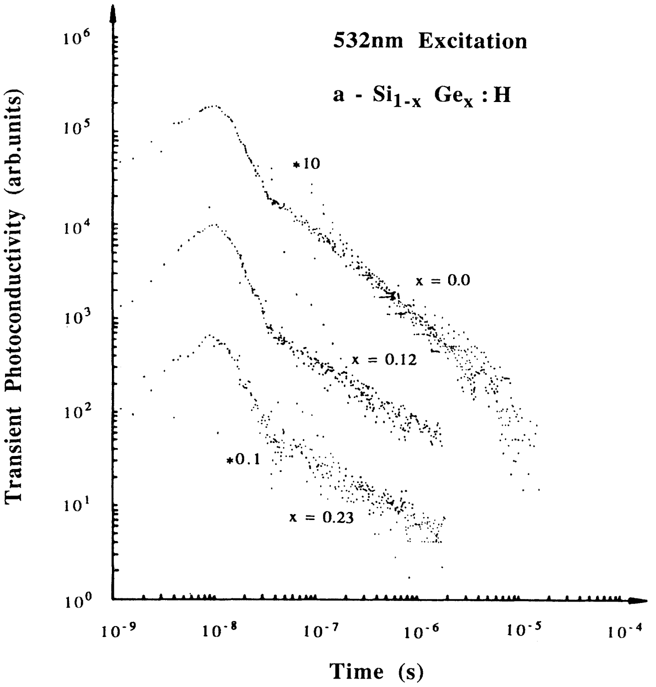

FIG. 5. The transient photoconductivity induced by 10-ns (FWHM) 532-nm laser pulses of 2 mJ cm^{-2} in pure *a*-Si:H, in *a*-Si$_{0.88}$Ge$_{0.12}$:H, and in *a*-Si$_{0.77}$Ge$_{0.23}$:H.

recombination rate due to a decrease of the number of holes available for recombination by an increase of deep hole trapping with Ge content. However, it cannot be excluded that part of the decay in the long-time range in *a*-Si$_{1-x}$Ge$_x$:H alloys is due to multiple trapping in the conduction band tail as it is generally observed that electron transport in *a*-Si$_{1-x}$Ge$_x$:H alloys is still dispersive at room temperature[1,16] in contrast to the behavior in pure *a*-Si:H.

The effective mobility as defined by Eq. (3) consists of two factors: in the first place the band mobility and in the second place the ratio between the mobile and the induced excess electron density. The relative effective mobility describes the change of these two factors upon alloying relative to pure *a*-Si:H. In this respect it is important to know how accurately the amplitude can be determined and which differences in amplitude between nominally pure *a*-Si:H films are observed. The accuracy is about 10% and in pure *a*-Si:H films produced under conditions considered as optimal the same dependence on the excitation density and the same absolute value of the amplitude within this accuracy were found, although the decay in the long-time range may be different.[12,17] This suggests that for state-of-the-art pure *a*-Si:H films in the excitation range covered (2 μJ cm^{-2}–2 mJ cm^{-2}) the band mobility and the ratio between the mobile and the induced excess electron density at 10 ns are equal. Especially the second point is important as it implies that the rate of all decay processes occurring within 10 ns is equal. For the higher-order recombination active at high excitation densities this is obvious because a relatively high defect density is necessary to affect it.[17,18] However, in the low excitation density range this is less evident because deep trapping processes may play a role, as may be concluded from observations where for pure *a*-Si:H films with equal photoconductivity amplitude, different sub-band-gap absorption was observed.[12] Obviously, the defects giving rise to this sub-band-gap absorption are not active within 10 ns after excitation. If the deep defect density is on the order of 10^{16} cm^{-3}, this implies that the rate parameter for electron decay via these defects must be much smaller than 10^{-9} cm^3 s^{-1}, which is acceptable.[19] In view of the considerations given above it can be assumed that in pure *a*-Si:H films at 300 K the amplitude in the low excitation range represents a drift mobility given by the product of the band mobility and the ratio between mobile and induced charge carriers determined by a stationary distribution of electrons between the mobility edge and localized states under this edge (band tail), comparable to the drift mobility from time-of-flight (TOF) measurements.

The preceding considerations imply a distinction between the interaction via multiple trapping of mobile electrons with states under the mobility edge in the band tail, determining the drift mobility, and other electron decay processes. This is convenient if the other decay process is of higher order and the distinction can be observed by a different excitation density dependence of both processes. However, in other cases (e.g., fast deep trapping) this distinction cannot be made so simply.

In the high excitation range the amplitudes of all samples show an identical sublinear dependence on the excitation density (Fig. 3) or in other words the relative effective mobility is independent of the excitation density (Fig. 4). This suggests that the higher-order recombination process is identical in the three samples and the value of the relative effective mobility in this range reflects the electron drift mobility relative to that of pure *a*-Si:H, 0.5 for *a*-Si$_{0.88}$Ge$_{0.12}$:H and 0.35 for *a*-Si$_{0.77}$Ge$_{0.23}$:H. The decrease of the relative effective mobility with decreasing excitation density (for $I < 10$ μJ cm^{-2}) is explained by an additional decay process, not active in pure *a*-Si:H films, gaining importance at excitation densities smaller than 100 μJ cm^{-2}. As mentioned above, it is plausible that at low excitation density ($I < 5$ μJ cm^{-2}) the relative effective mobilities are again independent of the excitation density, 0.23 in *a*-Si$_{0.88}$Ge$_{0.12}$:H and 0.15 in *a*-Si$_{0.77}$Ge$_{0.23}$:H, implying that the additional decay channel in the alloys has become first order. The most obvious candidate for this decay channel is electron trapping active within 10 ns where this decay channel becomes saturated in the excitation density range from 5 to 100 μJ cm^{-2}. This saturation would lead to a superlinear dependence of the amplitude on the excitation density. However, the onset of the higher-order decay process in this range leads to a sublinear dependence and then superposition of both processes leads to the approximately linear dependence observed between 5 and 100 μJ cm^{-2} (see, for a comparable case, Ref. 18).

It seems speculative to give values for the parameters of this trapping process from the saturation behavior and the relative effective mobility at low excitation density but some crude estimates can be given. The deep defect density in both alloys may lie in the range of 10^{18} cm^{-3} and the rate parameter somewhere in the 10^{-10} cm^{-3} s^{-1} range.

It is rather difficult to compare the results of this work to those of other experiments. The most obvious comparison is to TOF measurements but this is not so easy. In its simplest form it can be concluded from the present work that the electron drift mobility and the electron trapping time drop strongly on alloying of a-Si:H with Ge where obviously the largest drop occurs between 0 and 15% Ge content and up to 23% the drop is more gradual. This is also the conclusion from TOF experiments.[1,8,20] Unfortunately, a more quantitative comparison reveals differences between the results of both techniques, as in general from TOF measurements a much larger reduction of the drift mobility is observed, about a factor of 10.[1,20] However, it must be remarked that the definition of the relevant parameters is not the same for both techniques. The definition of the effective mobility in Eq. (4) may seem arbitrary but it seems the only one convenient under the experimental conditions of the present work. Besides, it is only used for comparative aims and seems appropriate in this respect. For TOF measurements in pure a-Si:H films at 300 K the identification of the transit time is unambiguous and the drift mobility can be determined, although different definitions can lead to differences of a factor of 2 in the drift mobility calculated.[15] Problems arise if during the transit an appreciable decay of the signal is observed and evaluation of the data is only possible if the temperature and voltage dependence of the signal are considered and extensive modeling of the density of states is done.[16,21] This is the case for TOF measurements in a-Si$_{1-x}$Ge$_x$:H alloys at 300 K. Besides, still more problematic is the strong increase of the integrated TOF signal (reflecting the collected charge) with increasing applied field due to electron trapping in deep traps where no emission occurs within the time scale of the experiment.[1,20,22] This makes determination of transit time and drift mobility rather delicate and determination of the mobility-deep-trapping lifetime product from collected charge measurements probably more trustworthy.[22] These considerations suggest that the drift mobility determined from the transit time in a-Si$_{1-x}$Ge$_x$:H alloys at room temperature is systematically lower than the drift mobility as defined in the present work. This would explain that the parameter drift mobility as defined in the present work is only reduced by a factor of 2 relative to pure a-Si:H in the investigated alloy films. A more meaningful comparison of the present experimental results is to the mobility-lifetime product obtained from TOF measurements. The mobility-lifetime product is observed to be reduced in a-SiGe:H alloys to about 5–10% of the value of pure a-Si:H in the range up to about 25% Ge.[1,20] This reduction reflects the relative decrease of the mobile excess carrier density in alloys on a time scale much longer than the reference time of 10 ns used in the present measurements. If part of the decay in the alloys in the long-time range (Fig. 5) is also due to trapping, this would decrease the mobility-lifetime product with a factor reflecting the ratio to trapping in pure a-Si:H. As the decay (Fig. 5) in pure a-Si:H is mainly due to recombination,[12] the decay due to trapping in a-Si$_{1-x}$Ge$_x$:H is probably faster. For comparison to the mobility-lifetime product in TOF measurements the relative effective mobility at low excitation density must be multiplied with this factor. This leads to values in the range between 5% and 10%, in the same order as obtained by TOF measurements.[1,20]

In summary the present measurements show a reduction of the effective electron mobility in a-Si$_{1-x}$Ge$_x$:H alloys relative to pure a-Si:H films. A part of this reduction can be attributed to trapping of electrons in states that can be saturated at high excitation densities. Another part of this reduction can be attributed to an effective electron mobility, decreasing with increasing Ge content. The decay in the long-time range (40 ns–10 μs) is slower in a-Si$_{1-x}$Ge$_x$:H alloys than in pure a-Si:H. This is tentatively ascribed to a decrease of the recombination rate in a-Si$_{1-x}$Ge$_x$:H.

---

[1] S. Aljishi, Z. E. Smith, and S. Wagner, in *Amorphous Silicon and Related Materials,* edited by H. Fritzsche (World Scientific, Singapore, 1988).

[2] W. Paul, in *Amorphous Silicon and Related Materials,* edited by H. Fritzsche (World Scientific, Singapore, 1988), p. 63.

[3] H. C. Weller, K. Kessler, E. Lotter, C. E. Nebel, S. M. Paasche, and G. H. Bauer, J. Non-Cryst. Solids **97 & 98**, 1071 (1987).

[4] A. Matsuda, M. Koyama, N. Ikuchi, Y. Imanishi, and K. Tanaka, Jpn. J. Appl. Phys. **25**, L54 (1986).

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

[6] M. Kunst and G. Beck, J. Appl. Phys. **60**, 3558 (1986).

[7] T. Tiedje, in *Semiconductors and Semimetals,* edited by J. I. Pankove (Academic, London, 1984), Vol. 21C, p. 207.

[8] G. H. Bauer, C. E. Nebel, M. B. Schubert, and G. Schumm, in *Amorphous Silicon Technology, 1989,* edited by A. Madan, M. J. Thompson, P. C. Taylor, Y. Hamakawa, and P. G. LeComber, MRS Symposia Proceedings No. 149 (Materials Research Society, Pittsburgh, 1989), p. 485.

[9] M. P. de Haas, Ph.D. thesis, Technical University, Delft, 1977.

[10] M. Kunst and G. Beck, J. Appl. Phys. **63**, 1093 (1988).

[11] A. Werner, M. Kunst, and R. Könenkamp, Phys. Rev. B **33**, 8878 (1986).

[12] P. Grunow, D. Herm, R. Könenkamp, H. Küppers, M. Kunst, H. C. Neitzert, and A. Werner, in *Amorphous Silicon Technology, 1989,* Ref. 8, p. 363.

[13] D. H. Auston, A. M. Johnson, R. R. Smith, and J. C. Bean, Appl. Phys. Lett. **37**, 371 (1980).

[14] A. M. Johnson, in *Semiconductors Probed by Ultrafast Laser Spectroscopy,* edited by R. R. Alfano, (Academic, London, 1984), Vol. II, p. 3.

[15] W. E. Spear, in *Amorphous Silicon and Related Materials,* Ref. 2, p. 721.

[16] C. Longeaud and R. Vanderhaghen, Philos. Mag. B **61**, 277 (1990).

[17] H. C. Neitzert, D. Herm, and M. Kunst (unpublished).

[18] D. Herm, H. Wetzel, and M. Kunst, in *Amorphous Silicon Technology, 1990,* edited by A. Madan, M. J. Thompson, P. C. Taylor, Y. Hamakawa, and P. G. LeComber, MRS Symposia Proceedings No. 192 (Materials Research Society, Pittsburgh, 1990), p. 651.

[19] R. A. Street, Philos. Mag. B **49**, L15 (1984).

[20] G. H. Bauer and C. E. Nebel, in *Physics and Applications of Amorphous Semiconductors,* edited by F. Demichelis (World Scientific, Singapore, 1980), p. 359.

[21] J. M. Marshall, in *Amorphous Silicon and Related Materials,* Ref. 2, p. 789.

[22] S. Wagner, V. Chu, J. P. Conde, and J. L. Liu, J. Non-Cryst. Solids **114**, 453 (1990).