Sensitization of the electron lifetime in *a*-Si:H: The story of oxygen

I. Balberg and R. Naidis
The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

L. F. Fonseca and S. Z. Weisz
Department of Physics, University of Puerto Rico, Rio Piedras 00931, Puerto Rico

J. P. Conde
Department of Material Engineering, Instituto Superior Technico, 1009-001 Lisbon, Portugal

P. Alpuim and V. Chu
Instituto de Engenharia de Sistemas e Computadores, R. Alves Redol 9, 1000 Lisbon, Portugal

(Received 10 July 2000; published 26 February 2001)

We have found, in hydrogenated-amorphous silicon (*a*-Si:H), values as low as 0 for the exponent γ_h that characterizes the light-intensity dependence of the minority-carrier concentration. The model simulation analyses of the temperature dependence of γ_h and the phototransport properties of the majority carriers show that these unprecedented low values in general, and in *a*-Si:H in particular, are associated with the presence of an acceptorlike center, the energy level of which lies 0.3–0.5 eV above the valence-band edge. Our results show then that the common analyses of the photoelectronic properties of *a*-Si:H only in terms of dangling bonds and band-tail states are not justified, and that the ''safe hole traps'' that were proposed to exist in *a*-Si:H can be identified now as oxygen-induced acceptorlike centers.

DOI: 10.1103/PhysRevB.63.113201 PACS number(s): 72.20.Jv, 71.23.−k, 73.50.Gr, 73.50.Pz

The most conspicuous feature of the phototransport in hydrogenated amorphous silicon (*a*-Si:H) is the thermal quenching (TQ) of the photoconductivity $\sigma_{\rm ph}$. This feature is the decrease of $\sigma_{\rm ph}$ with increasing temperature over a limited temperature range.[1–7] Following numerous model simulations,[6–10] it is now widely agreed that this TQ is due to the transfer of the dominant recombination channel from the valence-band-tail states to the dangling bonds. This is a very central conclusion for *a*-Si:H since it accounts for the phototransport properties in *a*-Si:H by the above two very fundamental ''intrinsic'' defects of disordered tetrahedrally bonded semiconductors. On the other hand, while it was shown[11] that impurities can somewhat modify the features of the TQ, in no study was it suggested that they can *dominate or control* these features or other phototransport properties in this material. The purpose of this paper is to show that in *a*-Si:H the TQ is usually associated with the transfer of the dominant recombination channel from impurity (rather than from band-tail) centers to the dangling bonds. We show that this impurity level is very likely to be a result of the well-known[11,12] unintentional doping by oxygen. The significance of this conclusion is that the phototransport in *a*-Si:H, which is so widely studied and which is so important for many photoelectronic applications, is more likely to be controlled by these impurity centers than by the band-tail states. In turn, we also argue that these centers are the ''safe hole traps'' that were suggested a decade ago to exist in *a*-Si:H.[13]

The tool we applied for the derivation of the above conclusions was the measurements of the temperature dependence of four phototransport quantities.[14–18] These are the mobility-lifetime product of the majority carriers $(\mu\tau)_e$, their corresponding light-intensity exponent γ_e, the mobility-lifetime product of the minority carriers $(\mu\tau)_h$, and the corresponding light-intensity exponent γ_h. In undoped *a*-Si:H the majority carrier is the electron and thus $(\mu\tau)_e$ is determined[14,15] from the measurement of the photoconductivity [$(\mu\tau)_e=\sigma_{\rm ph}/qG$, where q is the electronic charge and G is the carrier generation rate] and γ_e is determined from the well-known[14,15] power-law relation $\sigma_{\rm ph}\propto G^{\gamma_e}$. The mobility-lifetime product for the holes $(\mu\tau)_h$ is determined[16–18] here from the measurement of the ambipolar diffusion length L and its light-intensity exponent is determined[7,18] from the relation $L\propto G^{(\gamma_h-1)/2}$. These four quantities and their determination from experimental data[14–18] are well established. In particular, their significance for *a*-Si:H has been discussed in many papers.[4,7,9,19–22]

The nonmonotonic $\sigma_{\rm ph}(T)$ dependence associated with the TQ is usually accompanied by a ''superlinearity,''[14,15] i.e., with $\gamma_e>1$ values and with a peaked γ_e in the temperature range where the TQ takes place.[7–10] The general explanation of these coupled phenomena was given initially by Rose[14] to be due to the sensitization effect, i.e., the replacement of one recombination channel by another such that when some conditions are fulfilled, $(\mu\tau)_e$ increases. These coupled phenomena in *a*-Si:H have been explained[1–11] to be the result of the replacement of the dangling bonds, as the dominant centers for recombination, by the valence-band-tail states upon the decrease of temperature. In particular, the comprehensive model-simulation studies of Tran[9] and Bruggemann[10] left little doubt that with reasonable parameters of the *a*-Si:H system, this sensitization is the only explanation of the above phenomena. In fact there were no experimental data that suggested otherwise. The experimental finding reported in this Brief Report and its explanation by a model that accounts for it suggest that discrete-level acceptorlike recombination centers should be added to the

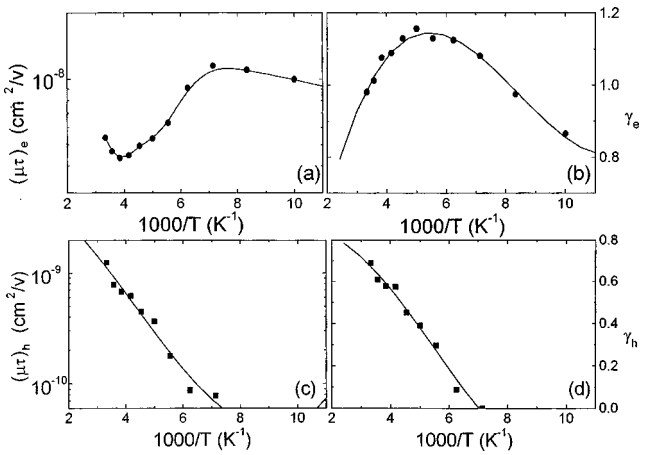

FIG. 1. The measured temperature dependence of the mobility-lifetime product and the light-intensity exponent of the electrons [(a) and (b)] and holes [(c) and (d)] in our *a*-Si:H samples. The curves are guides to the eye.

above mentioned models of *a*-Si:H. The approach of our present study is to use the above tool for the reexamination of the above intrinsic-defects model and to point out the conclusions that follow.

The samples used in this study were deposited by both the rf-glow discharge (GD) technique and the hot wire (HW) technique.[23] The depositions were carried out with relatively low hydrogen dilution of silane. Correspondingly, our Raman spectroscopy measurements[23] have revealed no microcrystalline phase in the films. The common substrate temperature for all the samples was 175 °C and their thicknesses were between 0.3 and 1 μm. We have determined the oxygen content in the samples by both secondary ion mass spectroscopy and the relative infrared absorption of the Si-O band at 1150 cm^{-1}. The oxygen concentrations found for all our films were of the order of $10^{18}\,cm^{-3}$, which is typical for device-quality samples.[24]

For the electrical measurements we evaporated coplanar silver contacts that were 0.4 mm apart.[7,16,22] The measured temperature dependence of the dark conductivity yielded[25] an estimated conduction band-edge to Fermi-level separation of 0.6–0.7 eV. Finally, our temperature-dependent phototransport measurements[7,18,22] were carried out using a He-Ne laser that yielded a carrier-pair generation rate G of about $10^{21}\,cm^{-3}\,sec^{-1}$. The values of γ_e and γ_h were derived then in the range of $10^{19} \leqslant G \leqslant 10^{21}\,cm^{-3}\,sec^{-1}$.

Turning to the results, we show in Fig. 1 the measured temperature dependence of the four phototransport quantities of a typical ''HW sample'' (50% hydrogen dilution). In Fig. 1(a) we show the temperature dependence of $(\mu\tau)_e$, which is very typical of, and very similar to, the numerous results[1–11] of the TQ in *a*-Si:H. This sensitization-associated behavior is emphasized by the temperature dependence of γ_e as seen in Fig. 1(b). Two features characterize this behavior; the superlinearity, i.e., $\gamma_e > 1$ values, and the peak of γ_e around 150 K. These results are very well understood for a sensitization process in general[14,15,18] and seem to be well understood for *a*-Si:H in particular.[7,9,10,22] Turning to the minority carriers, the temperature dependence of $(\mu\tau)_h$ is shown in Fig. 1(c). The behavior observed is to be expected since during the sensitization process the increase of $(\mu\tau)_e$ should yield[14,15] a decrease of $(\mu\tau)_h$. We note in passing that the present method[16–18] does not enable the determination of $(\mu\tau)_h$ values that are lower than the ones shown around 150 K.

The agreement found in Figs. 1(a)–1(c) with all the previous experimental results[1–11,22] and their simulations[7–10,22] does not hold when we turn to the less common measurement[7,22] of the temperature dependence of γ_h. In Fig. 1(d) we find a strong decrease of γ_h down to the unprecedented low value of $\gamma_h = 0$. We note that this value is found in the temperature region where $\gamma_e > 1$, i.e., in the sensitization regime. We have obtained qualitatively similar results for all our other HW and GD samples which, for brevity, are not displayed here.

The fact that the very many simulations of the sensitization by so many other workers[8–11] as well as by us[7,22] have not reproduced the behavior shown in Fig. 1(d), in particular the sub-1/2 values of γ_h, suggest that the intrinsic-defects models do not provide a proper description of the system under study. Following this conclusion we have conducted computer simulations in which we have added to our above-mentioned intrinsic-defects (or ''standard'') model[7,9,22] centers with a discrete energy level. Trying various kinds of centers we were able to reproduce semiquantitatively *all* the behaviors shown in Fig. 1, *only* by the introduction of an acceptor level that is located between 0.3 and 0.5 eV above the valence-band edge E_v. All other parameters of the system were as in our previous simulations[7,22] of the standard[9,10] model. The important features of the discrete acceptor centers that we introduced are that they have a hole-to-electron capture coefficient ratio of 100 and an electron capture coefficient that is smaller, by a factor of 3, than that of the neutral dangling bond. The concentration of the above ''extrinsic'' centers is $10^{18}\,cm^{-3}$ while that of the dangling bonds is $10^{16}\,cm^{-3}$. Hence, the necessary conditions[14,15] for the sensitization [i.e., for the increase of $(\mu\tau)_e$ with decreasing temperature] that should follow the transfer of the dominant recombination channel from the dangling bonds to the extrinsic centers are fulfilled. Indeed, our computer simulations show that this transfer takes place at the temperature where $\gamma_e(T)$ is peaked, and that it replaces the corresponding transfer (from the dangling bonds to the tail states[7,9,10]) in the standard model. In particular, the sensitization here with decreasing temperature follows the increase of the concentration of recombination-effective acceptors in comparison to that of recombination-effective dangling bonds (and here also to that of recombination-effective valence band-tail states). The corresponding capture coefficients, as given above, yield then an increase of the electron lifetime and a decrease of the hole lifetime. The simulation results obtained with the above given parameters are shown in Fig. 2. As these results reproduce the behavior shown in Fig. 1 it is clear that the properties of the extrinsic center in our *a*-Si:H material are similar to those used in the simulations. One notes, of course, that when one finds[7] that $\gamma_h > \frac{1}{2}$ throughout the entire temperature range, the standard model scenario[7,9,10] is applicable and the band-tail states are the dominant recombination centers at the lower temperatures.

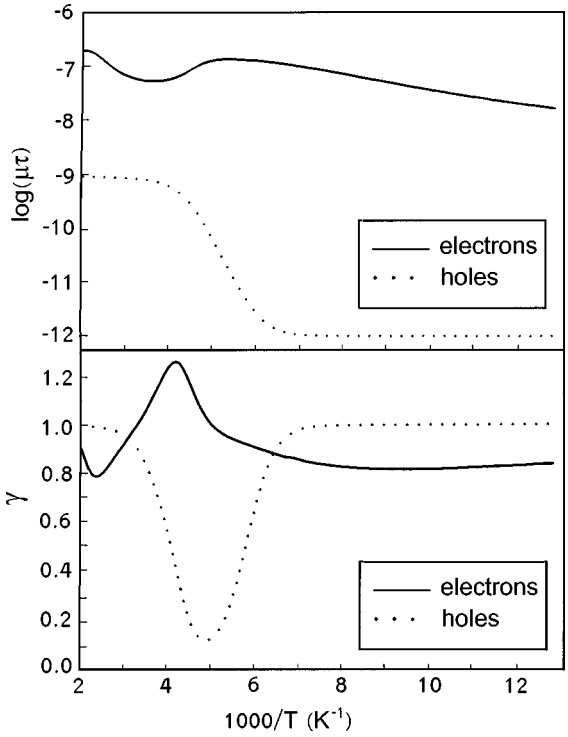

FIG. 2. The simulated temperature dependence of the phototransport quantities shown in Fig. 1 for a model that consists of a standard *a*-Si:H model with an addition of $10^{18}\,\mathrm{cm}^{-3}$ acceptorlike centers (with an energy level that is located 0.3 eV above the valence-band edge).

It is to be noted that we did not try to reproduce the results of Fig. 1 quantitatively (e.g., the magnitude and width of the TQ) as this requires changes in the other, previously used[7,22] generation rates, as well as intrinsic defect and/or mobility parameters. All this and the ''recombination-competition'' between the impurity-induced centers and the band-tail states will be discussed elsewhere.

Let us turn now to the identification of the extrinsic acceptorlike centers suggested by the above agreement of the experimental and the simulation results. The observation[3] of the TQ in the samples used by McMahon and Crandall[13] who found (by another technique) acceptorlike states (safe hole traps) that lie in the same energy range that we have in our simulations, strongly suggests that we encounter here the same type of centers. Also, we saw above that one would need more than $10^{18}\,\mathrm{cm}^{-3}$ discrete-level centers to get all the behaviors shown in Figs. 1 and 2. This, and the fact[24] that in undoped *a*-Si:H in general and in our samples in particular, the oxygen content is of the order of $10^{18}\,\mathrm{cm}^{-3}$ (while other impurities and the dangling bonds have significantly lower concentrations), suggest that the natural defect to be considered in our attempt to explain the above observations is an oxygen-induced acceptorlike defect. Let us examine then this possibility.

About 20 years ago Paesler *et al.* had pointed out the importance of the presence of oxygen in *a*-Si:H, attributing various properties to this ''story of O.'' [26] While some studies[12,24,26–28] were concerned with various oxygen-associated effects, and others have suggested that oxygen induces acceptor centers,[11,12,27] very few of them[11] considered the effect of this presence on the transport and steady-state phototransport properties. In particular, because usually only the behavior of the majority carriers has been considered, the *dominance* of the unintentional oxygen doping on these properties has never been suggested. Indeed we note that in the materials for which the oxygen-induced acceptors were suggested,[11,12] the TQ effect has been found.[1,11] Also, oxygen in *a*-Si:H has been found[28] to increase the response time of the photoconductivity, which is essentially the effect associated with the safe hole traps.[12] Following these considerations and since the above concentration of $10^{18}\,\mathrm{cm}^{-3}$ oxygen centers is so common in *a*-Si:H, it appears that the present scenario, of oxygen-induced acceptorlike centers that are responsible for the TQ, may be the rule rather than the exception in this material. The important conclusion of this finding is that in a wide temperature-illumination regime the phototransport in *a*-Si:H materials may be controlled by the oxygen-induced recombination centers rather than by intrinsic defects.

In conclusion, we suggest that the thermal quenching and the sensitization effect in *a*-Si:H can result from two scenarios. This is either from the band-tail states to the dangling-bonds recombination transfer scenario (as suggested so far) or from the oxygen-induced states to the dangling-bond transfer scenario (as appears now to be the more common case). These two possible scenarios and thus the types of defects that control the phototransport properties can now be distinguished by the measured (larger or smaller than 1/2) value of γ_h.

This work was supported in part by the Israel Science Foundation.

[1] P.E. Vanier, A.E. Delahoy, and R.W. Griffith, J. Appl. Phys. **52**, 5235 (1981).

[2] See also A. Arene and J. Baikeras, Phys. Rev. B **30**, 2106 (1984); F. Vaillant, D. Jousse, and J-C. Bruyere, Philos. Mag. B **57**, 649 (1989); H.-D. Mohring *et al.*, J. Non-Cryst. Solids **137&138**, 847 (1991).

[3] T.J. McMahon and R. Tsu, Appl. Phys. Lett. **51**, 412 (1987).

[4] P. Stradins, M.Q. Tran, and H. Fritzsche, J. Non-Cryst. Solids **164–166**, 175 (1993).

[5] N. Kopidakis *et al.*, J. Non-Cryst. Solids **227–230**, 175 (1993).

[6] T. Smail and T. Mohammed-Brahim, Philos. Mag. B **64**, 675 (1991).

[7] Y. Lubianiker, I. Balberg, and L. Fonseca, Phys. Rev. B **55**, R15987 (1992).

[8] See also B. Gu *et al.*, Philos. Mag. B **53**, 321 (1986); F. Vaillant, D. Jousse, and J-C. Bruyere, J. Non-Cryst. Solids **97&98**, 639 (1987); E. Morgado, *ibid.* **164–166**, 627 (1993).

[9] See for a detailed simulation study M.Q. Tran, Philos. Mag. B **72**, 35 (1995).
[10] For recent simulations and review see R. Bruggemann, in *Proceedings of the Ninth ISCMP on Future Directions in Thin Film Science and Technology*, edited by J. M. Marshall, J. J. Naud, N. Kirov, and A. Varek (World Scientific, Singapore, 1997), p. 80.
[11] M. Aoucher, T. Mohammed-Brahim, and B. Fortin, J. Appl. Phys. **79**, 7041 (1996).
[12] P.E. Vanier, A.E. Delahoy, and R.W. Griffith, in *Tetrahedrally Bonded Amorphous Semiconoductors*, edited by R.A. Street, D.K. Biegelsen, and J.C. Knights, AIP Conf. Proc. No. **73** (AIP, New York, 1981), p. 227.
[13] T.J. McMahon and R.J. Crandall, Phys. Rev. B **39**, 1766 (1989).
[14] A. Rose, *Concepts in Photoconductivity and Allied Problems* (Wiley Interscience, New York, 1963).
[15] R.H. Bube, *Photoelectronic Properties of Semiconductors* (Cambridge University Press, Cambridge, 1992).
[16] For reviews see J.W. Orton and P. Blood, *The Electrical Characteristics of Semiconductors: Measurements of Minority Carrier Properties* (Academic, London, 1990); I. Balberg, in *Amorphous Silicon Technology*, edited by M.J. Thompson, Y. Hamakawa, P.G. LeComber, A. Madan, and E.A. Schiff, MRS Symposia Proceedings No. **258** (Materials Research Society, Pittsburgh, 1992), p. 693.
[17] D. Ritter, E. Zeldov, and K. Weiser, J. Appl. Phys. **62**, 4563 (1987).
[18] I. Balberg, D. Albin, and R. Noufi, Appl. Phys. Lett. **54**, 1244 (1989); I. Balberg and R. Naidis, Phys. Rev. B **57**, R6783 (1998).
[19] I. Balberg, J. Appl. Phys. **75**, 914 (1994).
[20] F. Wang and R. Schwarz, Phys. Rev. B **52**, 14586 (1995).
[21] M. Hack, S. Guha, and M. Shur, Phys. Rev. B **30**, 6991 (1984).
[22] R. Rapaport *et al.*, Appl. Phys. Lett. **72**, 103 (1998).
[23] P. Alpuim, V. Chu, and J.P. Conde, J. Appl. Phys. **86**, 3812 (1999).
[24] See, for example, M. Nakata, S. Wagner, and T.M. Peterson, J. Non-Cryst. Solids **164–166**, 179 (1993); A. Morimoto *et al.*, Appl. Phys. Lett. **59**, 2180 (1990); U. Krol *et al.*, in *Amorphous Silicon Technology*, edited by M. Hack, E.A. Schiff, M. Powell, A. Matsuda, and A. Madan, MRS Symposia Proceedings No. **377** (Materials Research Society, Pittsburgh, 1995), p. 39.
[25] Y. Lubianiker and I. Balberg, Phys. Rev. Lett. **78**, 2433 (1997).
[26] N.A. Paesler *et al.*, Phys. Rev. Lett. **41**, 1492 (1978).
[27] See also, for example, C.E. Michelson and J.D. Cohen, Phys. Rev. B **41**, 1529 (1990); G. Lucovsky *et al.*, J. Non-Cryst. Solids **190**, 169 (1995); K. Winer, J. Vac. Sci. Technol. B **7**, 1226 (1989).
[28] C.I. Ukah *et al.*, J. Non-Cryst. Solids **107**, 301 (1989).