PHYSICAL REVIEW B VOLUME 24, NUMBER 8 15 OCTOBER 1981

Rapid Communications

The Rapid Communications section is intended for the accelerated publication of important new results. Manuscripts submitted to this section are given priority in handling in the editorial office and in production. A Rapid Communication may be no longer than 3½ printed pages and must be accompanied by an abstract. Page proofs are sent to authors, but, because of the rapid publication schedule, publication is not delayed for receipt of corrections unless requested by the author.

Dispersive transport and electronic structure of amorphous silicon alloys

Marvin Silver
Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514

Leon Cohen
Department of Physics and Astronomy, Hunter College, New York, New York 10021

David Adler
Department of Electrical Engineering and Computer Science and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 20 April 1981; revised manuscript received 10 August 1981)

Recent experimental data on the dispersive transport and recombination lifetime in *a*-Si:H as functions of both phosphorus doping and temperature are analyzed using the results of a computer simulation. We conclude that undoped *a*-Si:H contains a distribution of deep charged intrinsic electron traps and a Gaussian band tail. The introduction of phosphorous leads to the formation of relatively shallow traps, which are also distributed in energy. The observed increase in recombination lifetime with phosphorus doping can be attributed entirely to the existence of these shallow traps, rather than to a change in the nature of the recombination centers.

The electronic structure of amorphous silicon (*a*-Si) alloys has been a matter of controversy for several years,[1] with few experimental results directly discriminating between the many models. Some of the presently unresolved issues[2] are the nature of the predominant intrinsic defects, the extent of the band tails, the sign of the effective correlation energy of the dangling-bond defect, the origin of the unpaired-spin density, the origin of the traps and recombination centers, and the effects of phosphorus and boron doping. Although successful semiconductor devices have been fabricated with *a*-Si alloys, a wide dispersion in the physical properties of deposited films has led to reproducibility problems. Any insights gained towards resolving some of the mysteries alluded to above could well help in understanding the origin of the large variations in film quality. It is the purpose of this Communication to show how the results of recent dispersive-transport experiments elucidate the nature of the traps and the band tails in *a*-Si:H.

Recently, Hvam and Brodsky[3] (HB) carried out transient photoconductivity experiments in *a*-Si:H as functions of both phosphorus doping and temperature. They used a coplanar geometry and excited the films with 2.1-eV photons for 3 ns. Their results are shown in Fig. 1. The major features are (1) at very short times ($t < 20$ ns), the transport appears to be nondispersive; (2) the initial photocurrent increases with both increasing temperature and increasing phosphorus doping concentration; (3) the rate of photocurrent decay at intermediate times ($20 < t < 50$ ns) is essentially independent of temperature, but decreases with increasing phosphorus concentration; (4) the rate of decay of the photocurrent at still longer times (50 ns $< t < 100$ μs) decreases with both increasing temperature and phosphorus doping. It was concluded by HB that (1) the drift mobility is controlled by trapping in intrinsic band-tail states; (2) the initial decay may arise from a parallel recombination channel such as near an interface; (3) the Fermi-energy shift due to the doping increases the carrier lifetime by changing the nature of the recombination centers. In this paper, we describe the results of computer simulations which indicate that the observed increase in carrier lifetime with phosphorus doping cannot be explained simply by a change in the nature of the recombination centers, but rather is predominantly due to the introduction of shallow

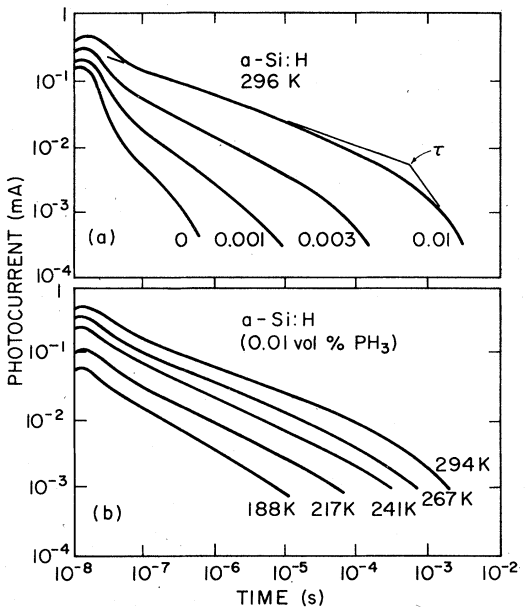

FIG. 1. Photocurrent decays in *a*-Si:H after short pulse excitation: (a) at 296 K and different doping concentrations, indicated by the volume percent PH_3 in the premix; (b) for 0.01 vol% PH_3 and different temperatures. Data from Hvam and Brodsky, Ref. 3.

traps by the phosphorus, as might be expected by analogy with *c*-Si:P. In addition, the temperature dependence of the initial photocurrent suggests that the shape of the band tail is not exponential, as assumed by HB; rather, the data are better understood by the assumption of a Gaussian distribution, as has been predicted from purely theoretical considerations.[4] We further conclude that the phosphorus-induced traps are separated from the major part of the band tail by about 0.1 eV. Finally, we suggest that an exponential distribution of intrinsic electronic traps exist below the shallow traps introduced by the phosphorus.

The technique of computer simulation of the transient photocurrent decay has been described previously,[5] and will be only outlined here. Given the density of localized states in the gap, we can vary both the temperature and the change in density of recombination centers as the Fermi energy is increased in order to determine if such a model can reproduce the experimental data. We first considered the case of an exponential distribution of traps characterized by a decay energy of kT_0 and beginning at an energy E_0 below the conduction-band mobility edge; i.e., if the conduction-band mobility edge is taken to be the zero of energy, then

$$N_t(E) = N_0 \exp[(E + E_0)/kT_0] \quad . \tag{1}$$

The trapping rate, ν_t, was taken to be 10^9 s^{-1}. The release rate, ν_r, is then proportional to $\alpha\nu_t \times \exp(E/kT)$, where $\alpha = T/T_0$.[6,7] In order to compare our results with the data of HB, we assumed that no free-carrier collection takes place at the electrodes. We analyzed the problem with two different values for the recombination frequency, 10^8 and 10^6 s^{-1}.

The calculation then proceeds using a Monte Carlo technique.[5] In order to obtain statistically meaningful results, we followed more than 10^4 photoexcited electrons until they recombined. At any time t, the photocurrent is proportional to the number of electrons which are at the conduction-band mobility edge. We also calculated the transient photocurrent under the assumption of bimolecular recombination kinetics. No difference was found in the short-time behavior between the two recombination modes. (There is a difference in long-time response, but this is not a concern here.)

First, we consider trapping by localized states in the conduction-band tail, $E_0 = 0$. For the choice $\nu_t/\nu_r = 10^3$ and two different temperatures, given by $\alpha = 0.5$ and 0.7, we found the results shown in Fig. 2. A major feature of these results is the independence of the initial peak current on the temperature. However, after the initial decay, the photocurrent does not obey the expected behavior for dispersive transport. It is clear from a comparison of Figs. 1 and 2 that this model is *not* in agreement with the data.

We next considered the effects of an increase in the density of recombination centers. We simulated such an increase by reducing the ratio ν_t/ν_r from 10^3 to 10. The corresponding results are sketched in Fig.

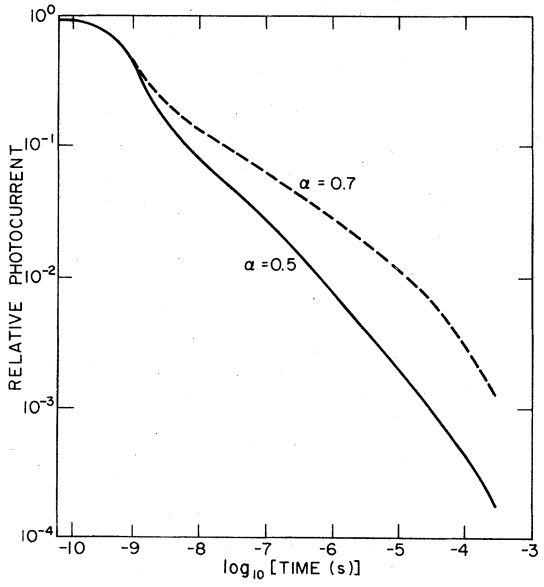

FIG. 2. Computer simulation of the photocurrent decay for $E_0 = 0$, $\nu_t/\nu_r = 10^3$, and two different values of α.

3 for the temperature $\alpha=0.7$. Clearly, both the $t=0$ photocurrent and the initial decay are independent of the density of recombination centers, again in disagreement with the experimental results.[8] We can conclude that the introduction of phosphorus into *a*-Si:H must have an effect beyond just the increase of the Fermi energy.

Finally, we tested the suggestion of HB that the traps must be located beyond a minimum energy, ϵ_t, below the conduction-band mobility edge in order to be effective. HB assumed

$$N_t(\epsilon)=\begin{cases}0 & (E>-\epsilon_t)\\ (N_t/kT_0)\exp[(E+\epsilon_t)/kT_0] & (E<-\epsilon_t)\end{cases}, \tag{2}$$

where $\epsilon_t\simeq 0.1$ eV and $kT_0\simeq 40$ meV. This is essentially equivalent to Eq. (1) with $E_0=\epsilon_t$. Choosing $E_0=0.1$ eV, $\alpha=0.7$, and $\nu_t/\nu_r=10^3$, we find the behavior indicated in Fig. 3. It is evident that again the $t=0$ photocurrent is independent of E_0; however, the initial decay is much greater when the traps begin 0.1 eV below the mobility edge. Note that the recombination time is increased when the traps begin 0.1 eV below the mobility edge. This happens because the electrons spend more time in traps for larger values of E_0.

We can conclude that with the exception of the power-law decay of the photocurrent that characterizes dispersive transport, all of the simulation results presented in Figs. 2 and 3 disagree with the experimental data. In order to account for the observations, a different model is essential. We first note that a distribution of intrinsic traps is necessary to understand the behavior when no phosphorus is present. It is generally accepted that the most abundant intrinsic defect in *a*-Si alloys is the dangling bond (T_3). Adler[9] has recently proposed a model in which the isolated T_3 defect has a positive effective correlation energy, but closely spaced T_3^+-T_3^- pairs are stabilized by the mutual Coulomb attraction. If this is the case, we should expect exponential distributions of charged electron and hole traps beginning somewhat below the conduction-band mobility edge and above the valence-band mobility edge, respectively. These distributions then account for the dispersive transport observed in undoped samples.

The apparent nondispersive transport observed at very short times can be understood simply by the existence of a Gaussian conduction-band tail. Such a tail is consistent with theoretical considerations as is known to yield a nondispersive temperature-dependent drift mobility. It is clear from Fig. 1 that the initial photocurrent is indeed temperature dependent, directly reflecting the effects of trapping in the band tail.

As phosphorus is introduced into *a*-Si alloys, several different effects are possible. The fact that doping does occur suggests that a major consequence is the formation of a significant concentration of

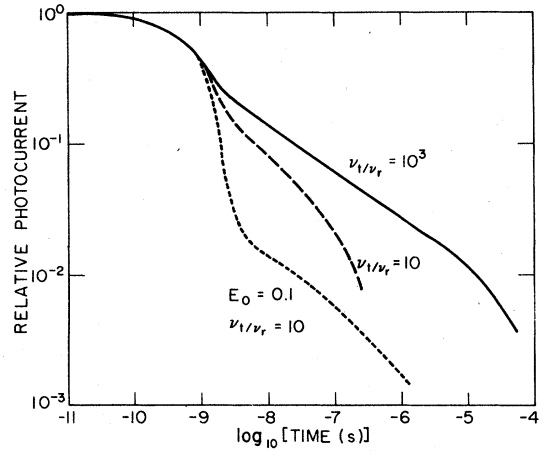

FIG. 3. Computer simulation of the photocurrent decay for $E_0=0$, $\alpha=0.7$, and two different values of ν_t/ν_r. Also shown is the case of $E_0=0.1$ eV, $\alpha=0.7$, and $\nu_t/\nu_r=10$.

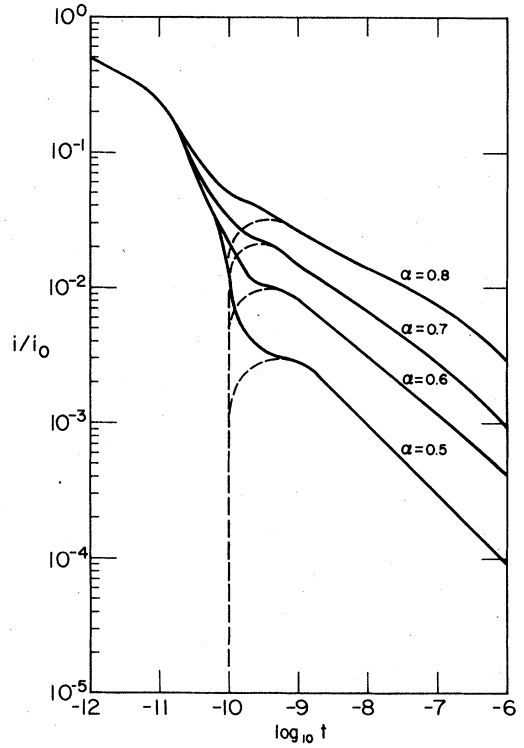

FIG. 4. Computer simulation of the photocurrent decay for $E_0=0.05$ eV, $T_0=600$ K, and a Gaussian band tail with a half-width $E_B=0.025$ eV for several different temperatures. The solid lines represents the photocurrent under the assumption of instantaneous excitation and response; the dotted lines represent sketches of the realistic situation of finite excitation and response times.

tetrahedrally bonded phosphorus. In accordance with this type of a situation in *c*-Si, we would expect such an environment (P_4) to yield states somewhat below the conduction-band mobility edge. The excess electron on the phosphorus atoms is then responsible for the observed increase of the Fermi energy since unoccupied lower-energy states exist due to the intrinsic defects. Thus, the phosphorus centers ionize, yielding positively charged electron traps (P_4^+). An exponential distribution of such traps has the major effect of increasing the time necessary for electrons to decay down to the intrinsic deeper traps, thus increasing the effective recombination time.

In order to demonstrate that this model can account for the observations of HB, we carried out a computer simulation for the case in which an exponential distribution of traps characterized by $T_0 = 600$ K exists beginning an energy $E_0 = 0.05$ eV below the conduction-band mobility edge and a Gaussian band tail characterized by a half-width of 0.025 eV is also present. The results are shown in Fig. 4. It is clear that this simulation accounts for the temperature dependence observed by HB in a quantitative manner.

Finally, we note that if U_{eff} is indeed negative for T_3 defects, the introduction of P_4^+ centers concomitantly reduces the concentration of T_3^+ traps (with pairs of excess electrons from the P_4 centers converting them to T_3^- centers). This has the effect of reducing the initial rate of decay of the photocurrent with increasing phosphorus doping, consistent with the data of Fig. 1.

To summarize, our computer simulations suggest that the data of HB cannot be understood simply by the assumption of a change in the nature of the recombination centers with phosphorus doping, whether or not the predominant electron traps are band-tail states or defect centers. Instead, we propose an alternative model in which (1) a Gaussian band tail exists and is responsible for both the nondispersive transport observed at very small times and the temperature dependence of the initial photocurrent; (2) an exponential distribution of intrinsic, positively charged traps (T_3^+) is responsible for the dispersive transport of later times; (3) as phosphorus is introduced, shallow positively charged electron traps (P_4^+) appear, leading to an increase in the effective recombination time; (4) concomitant with the appearance of these P_4^+ centers, there is a decrease in the density of T_3^+ traps, thus reducing the initial rate of decay of the photocurrent.

We should like to thank Marc Brodsky and Marc Kastner for useful discussions. This research was supported in part by the National Science Foundation under Grants No. DMR 79-20023 and No. DMR 78-24185.

[1]D. Adler, Solar Cells 2, 199 (1980).
[2]D. Adler and R. C. Frye, in *Tetrahedrally Bonded Amorphous Semiconductors,* AIP Conf. Proc. No. 73 (AIP, New York, 1981), p. 146.
[3]J. M. Hvam and M. H. Brodsky, Phys. Rev. Lett. 46, 371 (1981).
[4]T. P. Eggarter and M. H. Cohen, Phys. Rev. Lett. 25, 807 (1970).
[5]M. Silver and L. Cohen, Phys. Rev. B 15, 3276 (1977).
[6]J. Orenstein and M. Kastner, Phys. Rev. Lett. 46, 1421 (1981).
[7]T. Tiedje and A. Rose, Solid State Commun. 37, 49 (1981).
[8]Although the response time of the system used by HB (20 ns) should yield some differences in the measured initial photocurrent due to circuit effects, this cannot explain the full range of values indicated in Fig. 1. This is clear from the fact that the variations found for different phosphorus levels at a constant temperature is less than a factor of 3 despite large changes in the rate of decay, whereas the variations for different temperatures at a constant phosphorus concentration is about an order of magnitude for smaller changes in the rate of decay. Thus, we feel that the observed differences initial photoresponse are real.
[9]D. Adler, J. Phys. (Paris) (in press).