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Spin-dependent conductivity in amorphous hydrogenated silicon

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Additional results concerning spin-dependent transport (photoconductivity and dark conductivity) in undoped, doped, and compensated amorphous hydrogenated silicon are reported. Undoped samples show in addition to the known dangling-bond and tail-state resonances a broad line, which is attributed to excitonic states and is demonstrated to be involved in light-induced degradation. In *n*-type and compensated samples, trapping and hopping in donor states is directly identified in spin-dependent conductivity. Implications of these results for recombination models are discussed.

Spin-dependent conductivity (SDC) measurements have been used to elucidate transport processes in a variety of semiconductors. Results for both recombination at surfaces[1] and dislocations[2] in crystalline silicon as well as at the Si/SiO_2 interface[3] have been published. Applied to amorphous hydrogenated silicon (*a*-Si:H) spin-dependent photoconductivity (SDPC) has led to the identification of different processes involved in recombination.[4–7] We report here the observation of additional transport and recombination channels in undoped, phosphorus-doped, and compensated *a*-Si:H, which were overlooked in earlier work on SDC, but which have significant implications on the overall model of charge trapping and recombination in this material.

If the two initial states of a transport process are paramagnetic, this process will generally be spin dependent. An elementary example is the transition of an electron in the conduction-band tail (*e*) to a neutral dangling bond (DB), yielding a negatively charged dangling bond. This final state is a singlet (antiparallel spins, $S=0$). Provided that interactions such as spin-orbit coupling, which mix different spin states, are small, the transition will only take place if the two initial states, each with $S=\frac{1}{2}$, form a singlet. Transition from a triplet ($S=1$) is forbidden. Therefore, singlets will have a shorter lifetime and the singlet:triplet distribution is shifted from its normal value (1:3) to the triplet side ($1-\epsilon$:$3+\epsilon$). Saturation of the electron-spin resonance (ESR) of either initial state will restore the normal distribution,[8] thus resulting in a net transfer of triplets to singlets and in an enhancement of the *e*-DB transition. Since this transition is part of the nonradiative recombination in *a*-Si:H, it is observed as a decrease in photoconductivity at both the *e* and DB resonances. Similarly, saturating ESR will also enhance processes where the final state is a triplet, e.g., hopping in the conduction-band tail.

The *a*-Si:H samples used in our study were prepared by conventional rf-glow discharge. Coplanar aluminum electrodes (0.5-mm gap) were evaporated. The samples were mounted on holders made of quartz tubes, with wires inside the tubes to minimize loading effects on the microwave cavity. Illumination was done with a tungsten lamp (30 mW/cm^2), the infrared part of the spectrum was filtered out. In most cases, a saturating microwave power of 400 mW was coupled into the *X*-band ESR cavity. As in conventional ESR, magnetic-field modulation was used.

Figure 1(a) shows the spin-dependent photoconductivity spectrum of low-defect-density undoped *a*-Si:H ($N_s \sim 10^{16}$ cm^{-3} as determined by photothermal deflection spectroscopy). The spectrum was recorded over an unusually broad magnetic-field range of 1000 G. The slowly increasing background is due to nonresonant magnetophotoconductivity, which is picked up because of the magnetic-

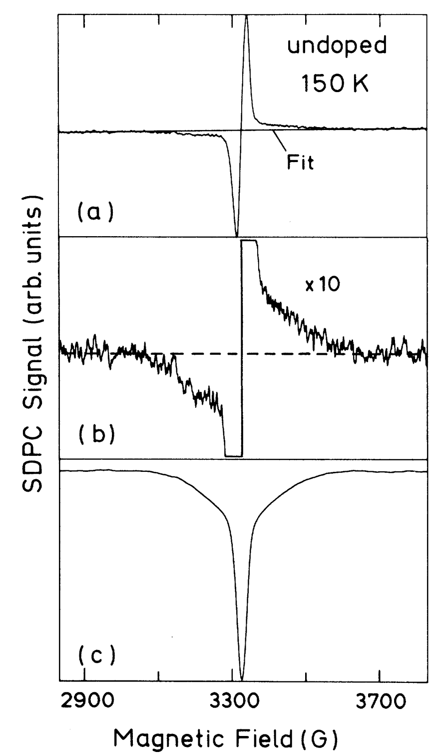

FIG. 1. Spin-dependent photoconductivity spectrum of low-defect-density undoped *a*-Si:H at 150 K. (a) Spectrum as measured with magnetic-field modulation. The additional line shows the fit to nonresonant magnetophotoconductivity. (b) The same spectrum after subtraction of magnetophotoconductivity. Note the change in scale. (c) Integrated spectrum. Again, the magnetophotoconductivity is taken out.

field modulation employed. It can be well accounted for by theory,[9] and was numerically subtracted from the spectra in the following figures. The central line in Fig. 1(a), corresponding to a decrease of photoconductivity at resonance, has already been analyzed in detail by Dersch, Schweitzer, and Stuke[7] as a combination of the well-known dangling-bond, conduction-band-tail, and valence-band-tail signals ($g=2.0055$, 2.0044, and 2.011, respectively). However, in addition to the central feature, we observe a very broad resonance line at $g\approx 2$, which is shown in more detail in Fig. 1(b). In Fig. 1(c) the integrated spectrum is seen, in which the broad line appears even more prominently with a full width at half maximum $\Delta H_{1/2}\sim 200$ G. The intensity of this resonance exhibits a strong temperature dependence [Fig. 2(a)]: While it reaches a maximum at 150 K, it decreases both at lower and higher temperatures and is hardly observable at 100 and 300 K. (Broadening of resonance lines due to high microwave fields as suggested by Street[10] cannot account for this temperature dependence.)

A resonance similar to the one discussed here has been observed in undoped *a*-Si:H with optically detected magnetic resonance (ODMR) at low temperatures (<20 K).[11] It is attributed to $\Delta m=\pm 1$ transitions of a triplet exciton. Such an exciton can either be formed (i) by bimolecular recombination of free carriers or (ii) during the thermalization of a geminate pair. Spin resonance then leads to an increased probability for the recombination of excitons. In case (i), where the exciton is formed by capture of previously free carriers, the spin-dependent enhancement of exciton recombination also decreases the free-carrier lifetime. In case (ii), on the other hand, the enhancement of exciton recombination decreases the lifetime of geminate pairs. To the extent that free carriers are formed by thermal breakup of geminate pairs, this latter process amounts to a spin-dependent generation rate. In both cases, one observes a quenching of photoconductivity at the exciton spin resonance.

The nonmonotonic temperature dependence of the exciton-signal strength in SDPC [see Fig. 2(a)] is due to the fact that at very low temperatures (<100 K) exciton recombination is much more probable than thermal dissociation, so that the exciton spin resonance is only observable in ODMR, whereas at higher temperatures thermal breakup is much faster than recombination, so that the exciton signal disappears both from ODMR and SDPC spectra. Only at intermediate temperatures (≈ 150 K) recombination and dissociation rates for the excitons are sufficiently balanced to allow their observation in SDPC.

An interesting question related to excitonic states in undoped *a*-Si:H is their role in the light-induced degradation of this material. It has been suggested that this degradation is due to nonradiative recombination of electron-hole pairs trapped at weak Si—Si bonds, i.e., by the decay of excitons bound to shallow-tail states.[12] If the broad resonance observed in SDPC is indeed due to such excitons, one should expect a drastic decrease of this line upon light soaking. This is in fact the case: After light soaking the low-defect-density sample of *a*-Si:H (state *A*) for two days, which increases the spin density due to dangling bonds to about 10^{17} cm^{-3} (state *B*), the broad signal is hardly observable anymore for temperatures in the range from 100 to 300 K [Fig. 2(b)]. A more detailed investigation of the relation between the broad 200-G exciton resonance and the light-induced degradation of undoped *a*-Si:H will be the subject of a separate publication.

Here we turn to a different topic, namely SDPC in *n*-type and compensated *a*-Si:H. Apart from a brief report[4] on a *g*-factor shift with doping, no study on spin-dependent transport in *n*-type and compensated *a*-Si:H is available as yet. Figure 3(a) shows the central SDPC line observed for phosphorus-doped *a*-Si:H. As in SDPC of the undoped counterpart, we find a decrease in photoconductivity at resonance. Applying a method introduced by Dersch, Schweitzer, and Stuke,[7] which analyzes the signal with respect to the phase shifts between the magnetic-field modulation and the constituent resonance lines, this central line can be decomposed into (i) a line at $g=2.0044$, corresponding to an electron in the conduction-band tail (*e*) and (ii) a line at $g=2.0075$, the mean value of $g=2.0044$ and 2.011, the latter corresponding to a hole in the valence-band tail (*h*). On a larger magnetic-field scale, hyperfine-split lines (hyperfine splitting 250 G) due to electrons in neutral, fourfold-coordinated (P_4^0) phosphorus states[13] can be seen [Fig. 3(b)]. This observation provides direct experimental evidence for the fact that this donor state actually contributes to recombination in doped *a*-Si:H. Phosphorus hyperfine lines have already been reported for SDPC in crystalline silicon[14] at 4 K. However, to our knowledge, there have been no similar reports based on ODMR or SDPC measurements for *a*-Si:H.

To understand further the underlying transport processes, we measured the spin-dependent conductivity of this sample in the dark [spin-dependent dark conductivity (SDC)]. In SDC, only the *e* line and the hyperfine line are observed, both as an increase in conductivity (Fig. 4).

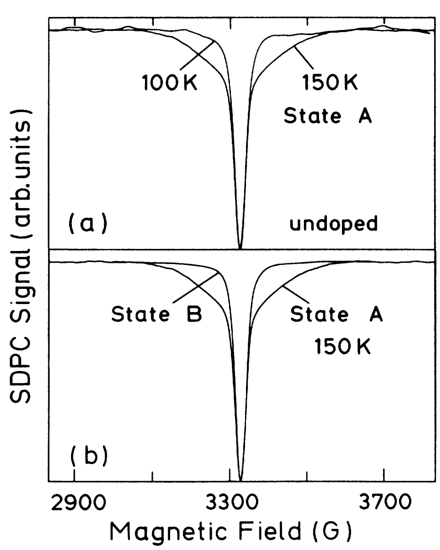

FIG. 2. (a) Integrated SDPC spectra of low-defect-density (state *A*) undoped *a*-Si:H, measured at 150 and 100 K. (b) Integrated SDPC spectra of low-defect density, annealed (state *A*) and high-defect density, light-soaked (state *B*) undoped *a*-Si:H, both measured at 150 K.

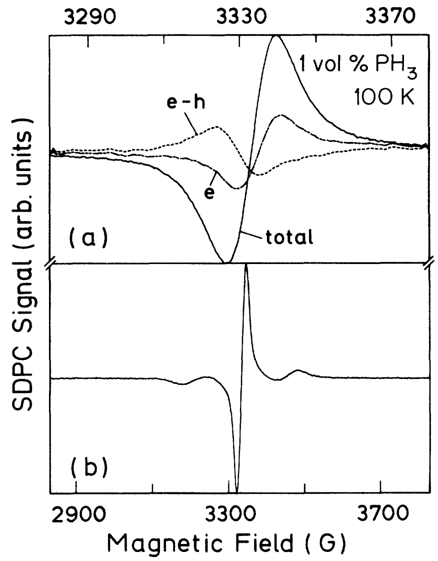

FIG. 3. (a) SDPC spectrum of the central line observed for n-type a-Si:H (1 vol% PH_3 in the gas phase). Shown as well are the results of the decomposition of this line by phase-shift analysis. The constituent lines, e-h and e, are detected in quadrature for different phase settings and do not add up to the in-phase total resonance (Ref. 7). (b) SDPC spectrum of the same sample, showing the hyperfine-split lines of the donor levels.

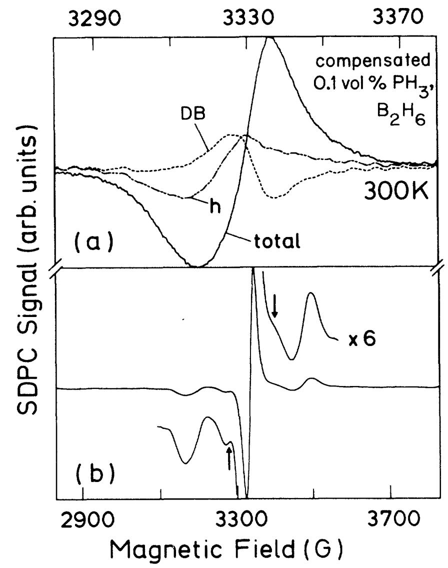

FIG. 5. (a) SDPC spectrum of the central line for compensated a-Si:H (0.1 vol% PH_3 and B_2H_6 in the gas phase) and the results of the decomposition by phase-shift analysis. DB and h denote dangling-bond and valence-band contributions, respectively. (b) SDPC spectrum of the same sample, showing both the hyperfine-split signals due to donors and to donor-bound-electron–hole pairs, the latter indicated by the arrows.

As pointed out in the introduction, saturating ESR enhances the spin-dependent transport processes, which in this case is hopping at the Fermi level involving the conduction-band tail as well as the donor states. Enhancing effects in SDC have already been published for boron-doped a-Si:H (Ref. 15) and for undoped a-Si,[16] but

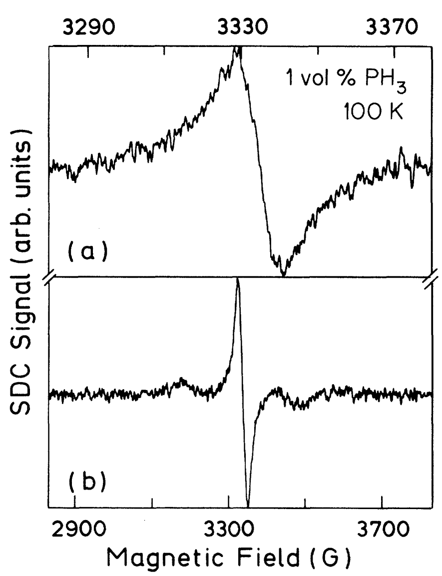

FIG. 4. Spin-dependent dark conductivity of n-type a-Si:H (1 vol % PH_3 in the gas phase). Note that the spin dependence is enhancing (positive derivative of the absorption signal) rather than quenching as in SDPC.

not for the more interesting case of n-type a-Si:H where, in particular, details of donor-band hopping at low temperatures may be addressed with this technique.

The hyperfine-split lines of the donor band also appear in the SDPC spectrum of compensated a-Si:H, as shown in Fig. 5. Once more, a decrease of photoconductivity at resonance is observed. The central line can be decomposed by phase-shift analysis[7] into a line at $g = 2.0055$, arising from the neutral-silicon DB and the line at $g = 2.011$, again the hole in the h tail. No line corresponding to electrons in the conduction-band tail could be found in SDPC of that sample. This is corroborated by light-induced electron-spin-resonance (LESR) measurements[13] of compensated a-Si:H, which show a steady decrease of the spin density of the e signal with increasing compensation level. At compensation levels above 10^{-4} the hyperfine line clearly dominates the trapping of excess electrons. As could be expected from these results, we also find in SDPC that electrons in the conduction-band tail do not contribute to the recombination process in compensated a-Si:H, in contrast to undoped material.

Indicated by the arrows in Fig. 5(b) is a second hyperfine-split resonance in compensated a-Si:H, also observed in LESR and ODMR.[13] This paramagnetic state can be understood as an exciton formed by an electron at the neutral donor and a hole trapped nearby; it is characterized by a hyperfine splitting (125 G) which is exactly $\frac{1}{2}$ of the donor hyperfine splitting. The same conditions for the observability discussed above for the broad resonance in undoped a-Si:H then apply to this hyperfine pair as well. The donor-bound exciton in compensated a-Si:H is the counterpart of the weak-bond–bound exciton in undoped *a*-Si:H (i.e., the 200-G broad resonance described above). The transfer of exciton trapping from weak bonds in undoped *a*-Si:H to donors in compensated *a*-Si:H has been proposed as the origin of the increase in stability in compensated samples as compared to undoped material.[12]

To summarize, the main results of our study on spin-dependent transport in *a*-Si:H are as follows:

(1) In undoped *a*-Si:H a broad resonance previously seen in ODMR and attributed to triplet excitons is also observed in SDPC with an integrated intensity similar to that of the dangling-bond–tail-state signals. This indicates that recombination via such excitons contributes appreciably to carrier lifetimes in high-quality material in the temperature range 100–300 K. The relative contribution of the exciton signal in SDPC decreases strongly during light soaking in a reversible manner.

(2) The phosphorus-donor hyperfine signal has been observed in spin-dependent *dark* conductivity of *n*-type *a*-Si:H at low temperatures, showing that for high-doping levels tail states and donor states both contribute to hopping at the Fermi level in a comparable way. In addition, the same donor states are shown to provide an important contribution to photocarrier trapping and recombination in *n*-type and compensated amorphous silicon.

The experimental results presented here suggest that spin-dependent transport measurements in amorphous silicon can be applied to a much broader range of problems than has been realized so far. This should provide interesting perspectives for future work.

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