PHOTOCONDUCTIVITY AND PHOTOINDUCED ABSORPTION IN a-Si:F AND a-Si:H

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ABSTRACT

The photoconductivity (PC) and photoinduced absorption (PA) of RF glow discharge a-Si:F and a-Si:H samples is reported. The value of the room temperature PC of a-Si:F is lower by some four orders of magnitude relative to that of a-Si:H, but the PA of a-Si:F is found to be significantly higher than that of a-Si:H. This indicates that the recombination rate of excess carriers is lower in a-Si:F than it is in a-Si:H, yet a larger fraction of the excess carriers are trapped in the band tails of a-Si:F, leading to its low PC. From the analysis of our PA data, we also determine the position of the mobility edge with respect to the extrapolated band edge in a-Si:H.

INTRODUCTION

RF glow-discharge a-Si:F and a-Si:H films of low-spin densities (below $3x10^{16}cm^{-3}$) were prepared in two separate, similar reactors under similar plasma conditions from the plasma of SiF_2 and SiH_4 gases, respectively. The deposition temperatures were 225°C for the a-Si:F and 250°C for the a-Si:H samples. The a-Si:H films had similar optical and electronic transport properties to those of non-doped, high quality GD a-Si:H films reported in the literature.[2] The a-Si:F films contained about 8 at.% fluorine, bonded predominantly in the monofluoride (Si-F) form.[1,3] The optical band-gap was 1.75±0.1 eV, the dark conductivity at room temperature (RT) was about 10^{-10} $(\Omega\cdot cm)^{-1}$, and the activiation energy of the dark conductivity above RT was 0.78±0.04 eV for the a-Si:F films. The undoped a-Si:F films were n-type and could be doped by either phosphorous or boron, indicating that there is no large density of mid-gap defect states pinning the Fermi level.

While the optical properties and the equilibrium carrier transport properties of the RF GD a-Si:F samples were similar to those of the a-Si:H samples, we found significant differences in the excess carrier transport properties of both types of films.

Below, we present a comparative study of the steady state excess carrier behaviour of a-Si:F and a-Si:H, as derived from PC and PA measurements of non-doped films. The results are used to estimate the difference in the density of tail states of both types of materials.

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PHOTOCONDUCTIVITY (PC)

The steady state PC was measured in co-planar electrode geometry with an interelectrode spacing of 0.3 mm, and an applied voltage of 20V. The light intensity was 25mW/cm^2, the wavelength was 5461 Å, and the chopping frequency was 170Hz.

Figure 1 shows the PC of one of the a-Si:H samples (#H-5) and four of the a-Si:F samples (#F-191, F-174, F-176 and F-170). The PC is presented in terms of the product $\eta\mu\tau$, where η is the quantum yield, μ the mobility, and τ the mean carrier lifetime.[4] The figure also indicates the spin density of the samples, N_s. The spin density of samples F-176 and F-191 was higher than that of the other samples as a result of postdeposition thermal anneals, at 325°C and 425°C, respectively.[1] There are a few interesting points presented in figure 1. First, the room temperature PC of the a-Si:F samples appears to be some four orders of magnitude lower than that of the a-Si:H sample. Second, there seems to be no correlation between the magnitude of the PC of the a-Si:F samples and their spin density, unlike the results reported for a-Si:H.[2] We received similar values for the PC of the a-Si:F samples up to spin densities of 10^{18}cm^{-3}. Third, there seems to be a significant difference in the magnitude of the temperature dependence of the PC of both types of samples above RT.

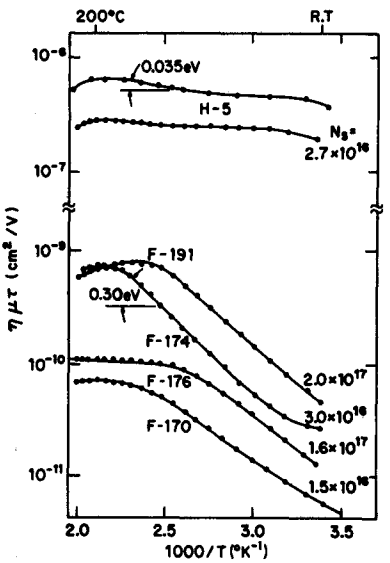

Fig. 1: PC of a-Si:H and a-SiF vs. temperature.

PHOTOINDUCED ABSORPTION (PA)

In order to understand the origin of the difference in the excess carrier transport properties of the a-Si:F and a-Si:H samples of equal spin densities, we performed PA measurements. PA measurements give information on the trapped fraction of the photocarriers, while PC measures the mobile photocarriers, so the two experiments are complementary. The results reported below were obtained on samples H-5 and F-174, which had similar values of spin density and equilibrium (dark) transport properties.

Our experimental set-up was similar to that used by O'Connor and Tauc for steady-state PA measurements.[5,6] Excitation of photocarriers (pumping) was done with an Ar^+ laser at a power of 0.1 W/cm^2, and at a wavelength of 5145 Å. The laser beam was chopped at a frequency of 160 Hz. The films were thick enough to completely absorb the pump beam. The PA was probed with ir

light coming from a monochomatized tungsten lamp at a power of 50 $\mu W/cm^2$. The wavelength varied between 1 and 4 μm. The samples for the PA experiment were deposited on crystalline silicon substrates, so that interference effects in the probe beam were eliminated. The amorphous structure of these samples was verified by Raman spectroscopy. The PA results are presented in terms of $\Delta\tau/\tau$, where τ is the transmittance of the samples at the probe-beam wavelength in the absence of pumping, and $\tau + \Delta\tau$ is the transmittance of the sample during laser excitation ($\Delta\tau$ is negative).

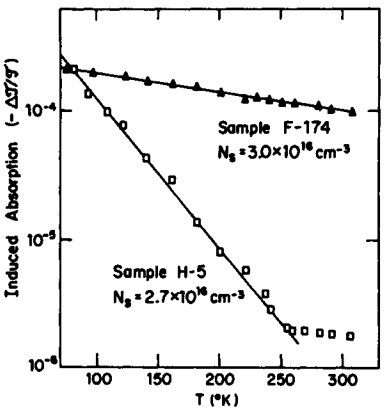

Fig. 2: PA vs. temperature

Figure 2 shows the temperature dependence of the PA for both samples in the temperature range 80 to 310°K. The probe beam was set at a photon energy of 0.75 eV. We can see from the figure that the PA decreases exponentially with increasing temperature. In the temperature range $60°K \leq T \leq 260°K$, we found that the slope of the PA curve on the semi-log plot for the a-Si:H sample is 8 times steeper than the slope for the a-Si:F sample. In the temperature range below 60°K (not shown in the figure), the PA of the a-Si:H sample reached a steady value. In the temperature range above 270°K, the PA of a-Si:H became, again, much less temperature-dependent.

For our present discussion, perhaps the most interesting point in figure 2 is the absolute value of the PA signal of the a-Si:F sample near RT, which is almost two orders of magnitude higher than that of the a-Si:H sample. We note that this result was obtained for the two samples measured with the same pump and probe beam intensities, respectively.

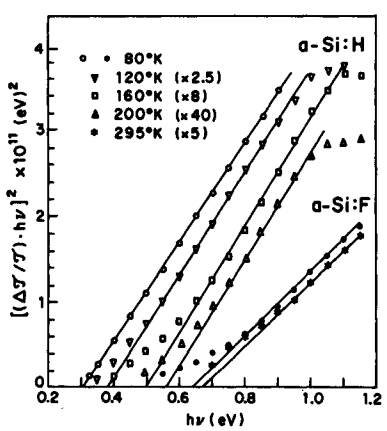

Fig. 3: PA vs. photon energy

Figure 3 shows plots of $[(\Delta\tau/\tau)h\nu]^2$ vs. the photon energy of the probe beam, $h\nu$, at various temperatures. The solid lines in the figure are the fits of the linear portion of the data to the function

$$(\Delta\tau/\tau)h\nu = A(h\nu - h\nu_0)^{1/2}, \qquad (1)$$

where $h\nu_0$ is the (extrapolated) threshold photon energy for the PA process. As discussed by Tauc,[6] eq. (1) is consistent with the assumption that the major contribution to the PA signal in the corresponding range of photon energies is due to the transitions of trapped photo-

carriers from a narrow energy region in the band tail, into the parabolic energy band. If the density of states in the energy band away from its edge is given by

$$D_u(E) = N_u|E - E_u|^{1/2}, \quad (2)$$

and if the trapped photocarriers are excited from the quasi-Fermi level E_{qF} into the band,[6] then $h\nu_0$ is given by

$$h\nu_0 = |E_u - E_{qF}|, \quad (3)$$

where E_u is the band-edge energy (see fig. 5). E_u should not be confused with the mobility edge $E_{\mu u}$, which lies lower in the band tail, as we shall show in the discussion below. The subscript u in eqs. (2) and (3) may denote either the conduction or the valence band; we can not determine which band tail makes the dominant contribution to the PA from PA measurements alone.[7]

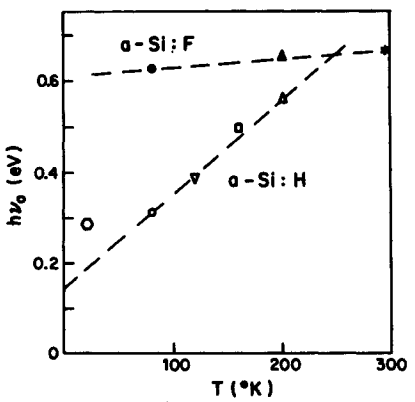

Fig. 4: $h\nu_0$ vs. temperature

Figure 4 presents the values of $h\nu_0$ for a-Si:F and a-Si:H as a function of temperature. In the case of a-Si:H, $h\nu_0$ has a relatively strong dependence on T. It indicates that, with increasing temperature, the quasi-Fermi level sinks rapidly down into the band tail. For a-Si:F, on the other hand, the quasi-Fermi level lies deep in the tail at all temperatures. Under our experimental conditions, E_{qF} of the a-Si:F sample was about 0.65 eV in the tail away from E_u.

DISCUSSION

The low PC of a-Si:F with respect to a-Si:H could be explained by one or more of the following reasons:

(a) Low microscopic mobility (that is, low value of the mobility of the carriers at energy states above the mobility edge),

(b) Low macroscopic mobility (that is, a relatively large fraction of photocarriers are trapped in the band tails), and

(c) Fast recombination rate, which would cause a low steady-state value of the density of photocarriers in a-Si:F.

As to (a), the close similarity of the values of the dark conductivity of a-Si:F and a-Si:H over five decades[1] suggests that their microscopic mobilities are, most likely, the same. The third possibility, that a shorter photocarrier

lifetime in a-Si:F is the reason for the low PC of this material, is unlikely. We saw, above, that the value of the PA in a-Si:F is higher than in a-Si:H. With the assumption of similar matrix elements for optical transitions from the tail into the band in both types of samples, the higher PA of a-Si:F near RT implies a higher density of trapped photocarriers in this sample. If the trapped photocarriers at E_{qF} are in thermal equilibrium with the free photocarriers, the total number of steady-state photocarriers must be higher in a-Si:F, and hence their average lifetime must be longer.

We conclude, then, that the lower PC of a-Si:F is due to the larger density of trapping states at the band tails of this material. For an order-of-magnitude calculation of the difference in density of tail states between a-Si:F and a-Si:H, we write the ratio of free photocarriers, n_f, to trapped photocarriers, n_t, as

$$n_f/n_t \approx [D_f(E_{\mu U})/D_t(E_{qF})] \exp[-|E_{\mu U} - E_{qF}|/kT] , \quad (4)$$

where D_f and D_t are the densities of states (in $eV^{-1}cm^{-3}$) of free and of trapped carriers at the mobility edge and at the quasi-Fermi level, respectively. From the PA and PC data presented above, we obtain, near RT:

$$[n_f/n_t]_{a\text{-}Si:H} / [n_f/n_t]_{a\text{-}Si:F} \approx 10^6 . \quad (5)$$

Let us describe the density of tail states by the equation[6,8]

$$D_t(E) \approx 10^{21} \exp[-|E - E_{\mu U}|/E_0] , \quad (6)$$

where E_0 is the characteristic width of the band tail. From figure 4 we obtain, near RT, $|E_u - E_{qF}| \approx 0.65$ for both materials. We shall show below that for a-Si:H, $|E_u - E_{\mu U}| = 0.15$ eV, so that, near RT, $|E_{\mu U} - E_{qF}| = 0.5$ eV. (For a-Si:F, $|E_u - E_{\mu U}|$ may be larger, but for the sake of comparison we take the same value for both materials.) We further assume that $D_f(E_{\mu U})$, for both a-Si:F and a-Si:H, is about the same. If we take the value $E_0 = 0.03$ eV for a-Si:H, then from eqs. (4), (5), and (6) we get $E_0 = 0.18$ eV for a-Si:F. As we discuss elsewhere,[9] this large value of E_0 for a-Si:F in eq. (6) is inconsistent with the low density of spins in our a-Si:F samples; with $E_0 = 0.18$ eV, the predicted density of overlapping tail states alone comes out to the order of 10^{18} cm^{-3}. This inconsistency can be explained in several ways. As we show elsewhere,[9] one of the possibilities is that the density of tail states is given by a Gaussian distribution, rather than by eq. (6). A Gaussian distribution will have an exponential appearance near $E_{\mu U}$,[9] but it decays much faster towards mid-gap, and gives consistent results with our observed spin density.

Our model for the PA of a-Si:H and a-Si:F is schematically presented in figure 5, below. In a-Si:H, at the temperature range $60°K \leq T \leq 270°K$, the multiple-trapping model may be applied.[6,10,11] Then, the dominant mechanism by which the band tails get depleted of photocarriers is thermal excitation to the mobility edge, and the subsequent drift of the carriers to recombination centers.

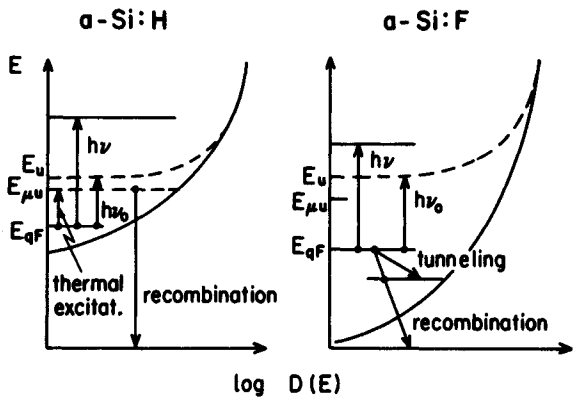

Fig. 5: Schematic diagram of the density of tail states and the dominant transitions in the PA of a-Si:H and a-Si:F

In this case, the quasi-Fermi level stabilizes at an energy level given by

$$|E_{qF} - E_{\mu u}| = kT \ln \nu t , \qquad (7)$$

where ν is the "attempt to escape" frequency[6,10,11] ($\nu = 10^{12}$ sec^{-1}) and t is the time scale of the experiment. The value of t should be equal to the chopping period, since states deeper than E_{qF} given by eq. (7) would not empty during the dark part of the chopping period.

From eqs. (3) and (7), $h\nu_0$ should be given by

$$h\nu_0 = |E_u - E_{\mu u}| + kT \ln \nu t . \qquad (8)$$

Indeed, the slope of the curve $h\nu_0(T)$ of the a-Si:H sample (fig. 4) is 2×10^{-3} eV·°K^{-1}, in very good agreement with the predicted value $k \ln \nu t = 8.5 \times 10^{-5}$ eV°K^{-1} x $\ln(10^{12}/160) = 1.9 \times 10^{-3}$ eV·°K^{-1}.[12] From the figure, we also find that, at T = 0, $|E_u - E_{\mu u}| = 0.15$ eV. Hence, we find that, in a-Si:H, the mobility edge lies 0.15 eV in the tail relative to the extrapolated band edge E_u. (As mentioned before, we can not say whether the value we found refers to the conduction or to the valence band, or to both.) We should point out that if one assumes a linear dependence of $D_u(E)$ in eq. (2),and the data of figure 3 is fitted accordingly, the last result is modified, and we get $|E_u - E_{\mu u}| \simeq 0$. The rest of our analysis remains unaffected. For a-Si:H, however, particularly at low T, where the PA signal was large and clear, we found that the fit to a parabolic density of states holds over a wider energy range than the fit to a linear density of energy states.

In a-Si:F (as well as in a-Si:H at temperatures below 60°K), the dominant mechanism of tail depletion is probably tunneling and direct tail-to-tail

recombination. The temperature dependence of E_{qF} is then expected to be much weaker than that given by eq. (8). The domination of a tail-to-tail recombination process in a-Si:F is probably the reason for the independence of its photoconductivity on spin density, as mentioned above.

CONCLUSION

We have presented PC and PA data of a-Si:F and a-Si:H samples of equal spin density. We have shown that in the temperature regime where the total density of photocarriers of a-Si:F is about two orders of magnitude higher than that of a-Si:H, the PC of a-Si:F is four orders of magnitude lower. We attributed this result to the relatively wide band tails of a-Si:F, which trap a significantly higher faction of the photocarriers than the trapped fraction in a-Si:H. We have re-interpreted the steady state PA results of a-Si:H, suggesting that the position of the quasi-Fermi level depends on the chopping frequency of the pump beam. We have also claimed that in a-Si:F the major recombination mechanism is not via thermal release of the trapped carriers and their subsequent drift to recombination centers, but tunelling and recombination through tail states. Such a tunneling mechanism is consistent with the large density of tail states found in this material. Finally, our results indicate that fluorine can eliminate deep spin centers in a-Si, but it does not eliminate the tail states. We thus conclude that the unique property of hydrogen in a-Si:H is not the elimination of spin centers (which flourine does, too), but the elimination of tail states, which gives the material its good photoconductive quality.

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REFERENCES

1. M. Janai, R. Weil, B. Pratt, submitted to Phys. Rev. B.
2. H. Fritzsche, Solar Energy Mater. 3, 447 (1980).
3. M. Janai, L. Frey, R. Weil and B. Pratt, Solid State Commun. 48, 521 (1983).
4. W.E. Spear and P.G. LeComber, in "Photoconductivity and Related Phenonema," ed. J. Mort and D.M. Pai (Elsevier, NY 1976) p. 185.
5. P. O'Connor and J. Tauc, Phys. Rev. B25, 2748 (1982).
6. J. Tauc, in "Advances in Solid State Physics," ed. P. Grosse Aachen, 22, (Vieweg, Braunschweig, 1982) p. 85.
7. In Ref. 6 it is suggested that the PA is due to holes trapped in the valence band tail.
8. T. Tiedje, T.M. Celbulka, D.L. Morel and B. Abeles, Phys. Rev. Lett. 46, 1425 (1981).
9. M. Janai, submitted to Phys. Rev. Lett.
10. T. Tiedje and A. Rose, Solid State Commun. 37, 49 (1981).
11. J. Orenstein and M.A. Kastner, Phys. Rev. Lett. 43, 161 (1981).
12. Our interpretation to fig. 4, which is based on eq. (8), differs from that given in ref. 6.