

Photoinduced absorption spectra in *a*-Ge:H and *a*-Si:H

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Measurements of steady-state photoinduced absorption in *a*-Ge:H and *a*-Si:H were extended to cover the energy range from 0.25 to 1.9 eV. The subgap photoinduced-absorption bands in both materials are interpreted in terms of four kinds of optical transitions of photogenerated carriers from traps in the gap into the bands; two transitions produce absorption and two bleaching. This model explains the approximately symmetric form of the photoinduced-absorption band in *a*-Ge:H previously ascribed to polaron absorption.

Illumination above the gap of amorphous tetrahedral semiconductors produces a subgap photoinduced-absorption (PA) band^{1,2} whose steady state and transient properties have been studied most extensively in *a*-Si:H.³ In this material, the PA band has been ascribed to photoionization of holes trapped in the tail of the valence band into the valence band.^{2,4-6} Compared to *a*-Si:H the PA band in *a*-Ge:H has a more symmetrical spectral shape and changes much less with temperature. It was shown¹ that these properties can be accounted for by ascribing the PA band in *a*-Ge:H to photoinduced hopping of polarons. However, this suggestion is in contradiction with the small difference between the electron phonon coupling strengths in amorphous Si and Ge.⁷ In this paper we present extended data on the PA band in *a*-Ge:H and show that they can be interpreted in terms of photoionization of trapped carriers, provided a bleaching mechanism is added that sharpens the high-energy side of the spectrum and makes the spectrum more symmetrical. We show that a similar bleaching effect may be present in *a*-Si:H as well.

The experimental setup³ for measuring photoinduced absorption uses two light sources: a pump beam (usually a laser) and a probe beam with a wide spectrum. An Ar⁺ ion laser with an intensity of about 50 mW/cm² at 514 nm was used as the pump. The probe beam was an incandescent infrared (IR) source followed by a monochromator. The changes in the probe beam transmission *T* were measured by various solid-state detectors (Si, Ge, PbS, or PbSe) depending on the energy range. The covered energy range was 0.25 to 1.9 eV. The *a*-Si:H films were prepared at Exxon Research (Linden) by the glow discharge process. Two samples were used in order to cover the entire photon energy range. At low energies the measurements were done on a sample with a crystalline silicon substrate while for high-energy measurements the film was on a quartz substrate. The *a*-Ge:H sample was prepared at IBM (San Jose) by glow discharge. All films were about 1.5 μm thick.

The PA spectra of *a*-Ge:H and *a*-Si:H are shown in Figs. 1 and 2. The dominant spectral feature is the subgap PA band which has a rather sharp onset and a slower decay at high energies. The decay is faster in *a*-Ge:H producing a PA band which is more symmetric than in *a*-Si:H. The PA band in *a*-Ge:H does not change much with temperature while in *a*-Si:H it shifts to lower energies as the temperature is decreased.⁸ The PA band strength decreases with increasing temperature; the decrease is much larger in *a*-Si:H than in *a*-Ge:H. The structures observed at the low-energy end could not be reliably identified because of the small *S/N* in

this region; however, they appeared in all our samples and often had sharp bandlike features. Finally, we note an onset of additional induced absorption at high energies, which is more dramatic at higher temperatures. We will discuss the origin of these spectral features and their temperature dependencies, with an emphasis on the subgap PA band shape.

It was shown by O'Connor and Tauc⁴ (OT) that the onset of the PA can be described by the formula

$$\Delta\alpha = (\hbar\omega - E_0)^{1/2}/\hbar\omega, \quad (1)$$

where $\Delta\alpha$ is the photoinduced change in the absorption coefficient α and E_0 is the threshold. This equation was interpreted as absorption due to transitions of photogenerated

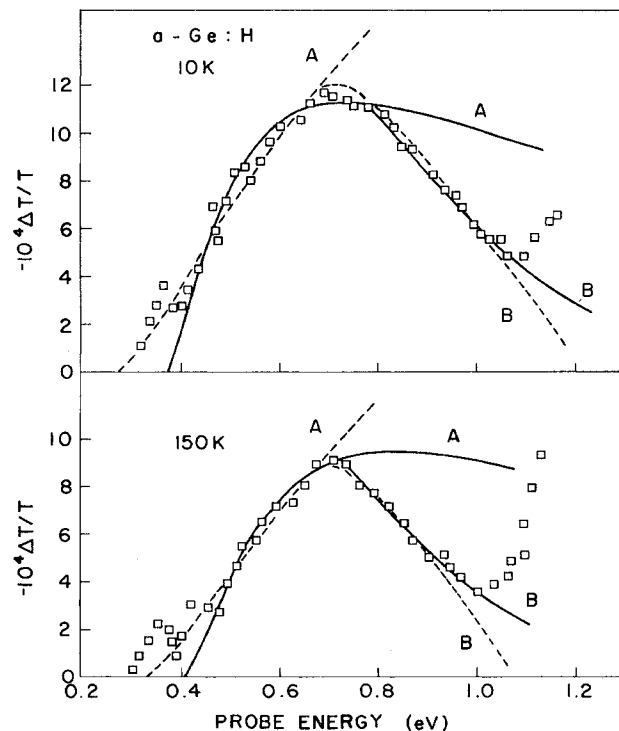


FIG. 1. PA spectra in *a*-Ge:H at 10 and 150 K. Curves A: Calculated absorption only. Curves B: The bleaching contribution subtracted from curve A. The same model was used for both absorption and bleaching. Solid lines: LUC model [Eq. (3)]. Dashed lines: IOT model [Eq. (2)].

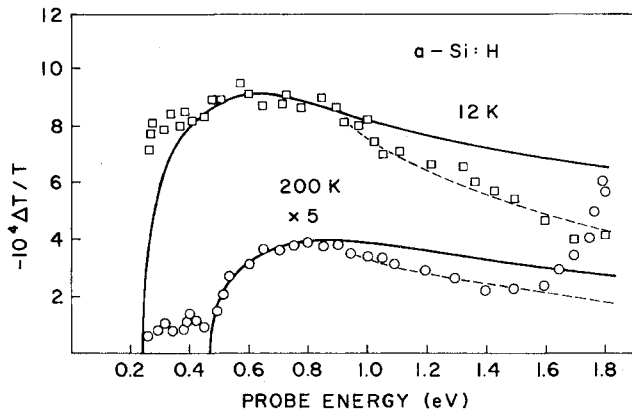


FIG. 2. PA in *a*-Si:H at 12 and 200 K. Solid lines: Fits using the OT model [Eq. (1)] for absorption only. Dashed lines: Bleaching described by the OT model was subtracted. The argon laser intensity was not the same as for the *a*-Ge:H spectra shown in Fig. 1.

holes trapped in the tail of the valence band into the valence band.^{3,4} The tail is assumed to have a density of states sharply decreasing into the gap and is filled with holes to the quasi-Fermi level F_p . Under these conditions most holes are concentrated in a narrow energy interval around F_p which we can approximate by a delta function $\delta(E - F_p)$. It was further assumed that the momentum-matrix elements are independent of energy and the density of states in the valence is proportional to $(E_v - E)^{1/2}$ where E_v is the mobility edge of the valence band; in this case, $E_0 = F_p - E_v$. The same formula was obtained by Inkson⁹ for transitions in a crystalline solid from a deep impurity into the adjacent band under the assumption that the transitions were allowed and nonvertical.

A slightly different equation for $\Delta\alpha$ can be deduced in a similar manner as Eq. (1), if the gap states have a flat distribution ($\approx \text{const}$) in the region around F_p , by integrating over the initial states as previously suggested by Persans.¹⁰ In this case

$$\Delta\alpha = (\hbar\omega - E_0)^{3/2} / \hbar\omega \quad (2)$$

Equation (2) [integrated OT (IOT)] is identical to the formula that Inkson⁹ obtained for nonallowed nonvertical transitions from deep impurities.

Finally, Hirabayashi and Morigaki⁶ have used a different formula which was deduced by Lucovsky¹¹ (LUC) for carrier photoionization from delta function impurity potentials in crystals:

$$\Delta\alpha = (\hbar\omega - E_0)^{3/2} / (\hbar\omega)^3 \quad (3)$$

These formulas fit reasonably well the data on *a*-Si:H but not those on *a*-Ge:H. Equation (1) describes well the onset of the PA band in *a*-Si:H (Fig. 2),⁴ but at higher energies Eq. (3) gives a better fit. This equation does not fit the high-energy data in *a*-Ge:H (Fig. 1) because $\Delta\alpha$ decreases much faster than in *a*-Si:H. Equations (2) or (3) give good fits to the onset of PA in *a*-Ge:H while Eq. (1) does not. None of the proposed equations fit the high-energy data in *a*-Ge:H.

This discrepancy could be removed by making suitable assumptions about the matrix element for optical transitions which depends on the nature of the trapping potential.

These choices are completely arbitrary unless they can be justified on theoretical grounds. Instead, we propose a simple explanation which is based on considering additional transitions that produce bleaching (reduction of α by illumination).

The valence-band tail is filled with electrons in the dark. These electrons produce ordinary absorption associated with their transitions into the conduction band and contribute to the absorption below the absorption edge as observed in *a*-Si:H.¹² When illumination introduces holes into the valence-band tail, the density of initial states of electrons is reduced and so is the absorption associated with electron transitions into the conduction band. Once this effect sets in it reduces the PA produced by hole transitions into the valence band and produces a sharper decrease of the high-energy side of the PA band.

A simple model shown in Fig. 3 is based on the assumption that the signal measured by the lock-in amplifier corresponds to variations of photoinduced carrier densities close to the quasi-Fermi levels. The processes are PA absorption by holes (transition 1) and bleaching of the electron transitions (transition 2). There are two analogous processes, absorption by electrons (process 3) and bleaching of hole transitions (process 4). The onsets E_0 of these processes are $E_1 = F_p - E_v$, $E_2 = E_c - F_p$, $E_3 = E_c - F_n$, and $E_4 = F_n - E_v$; it holds $E_1 + E_2 = E_3 + E_4 = E_g$.¹³ If the hole density at F_p is p_i and the electron density at F_n is n_i , the total photoinduced change in the absorption coefficient is

$$\Delta\alpha = [\sigma_1(\omega) - \sigma_2(\omega)]p_i + [\sigma_3(\omega) - \sigma_4(\omega)]n_i \quad (4)$$

where $\sigma_i(\omega)$ ($i = 1, 2, 3, 4$) are absorption cross sections; their magnitude is proportional to the density of the final states in the respective bands. For their frequency dependencies we used Eq. (1) (OT model), Eq. (2) (IOT model) and Eq. (3) (LUC model).

At this time, there is no evidence that the origin of the PA band in *a*-Ge:H is produced by trapped holes transitions in the valence band, as in *a*-Si:H, but we assume that this is the case. If it was eventually found that the effect in *a*-Ge:H is due to electrons, essentially the same arguments would apply. We obtained good fits to the data in Fig. 1 us-

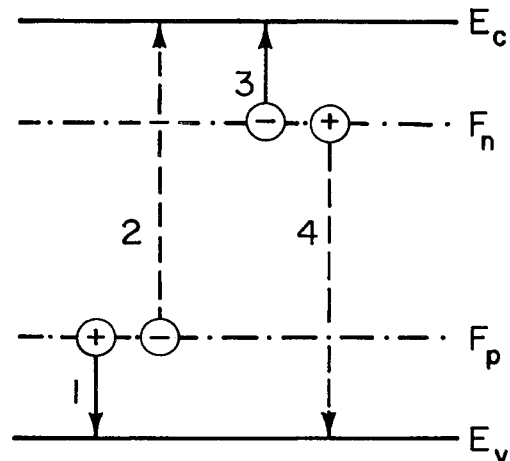


FIG. 3. Energy levels used for describing the PA absorption processes (transitions 1 and 3) and bleaching processes (transitions 2 and 4).

TABLE I. Parameters for PA absorption and bleaching in *a*-Ge:H. (Notation explained in text.)

Model	<i>T</i> (K)	<i>E</i> ₁ (eV)	<i>E</i> ₂ (eV)	<i>E</i> ₁ + <i>E</i> ₂ (eV)	<i>E</i> _g (eV)	<i>C</i> ₁ / <i>C</i> ₂
IOT	10	0.28	0.68	0.96	1.15	0.57
	150	0.32	0.67	0.99	1.00	0.53
LUC	10	0.37	0.76	1.13	1.14	0.66
	150	0.41	0.73	1.14	1.07	0.65

ing the IOT and LUC models, applying the same model for absorption (transition 1 in Fig. 3) and bleaching (transition 2). These transitions are illustrated in Fig. 1 by curves A and B. The parameters of the fit are shown in Table I. It is seen that $E_1 + E_2 \approx 1$ eV which was, within the precision of the measurement, the gap in our sample (the way it was determined is described below). The last column in Table I gives the ratio of the strength of the bleaching process 2 to the absorption process 1. The constants C_i ($i=1, 2$) are defined by equations

$$\sigma_i(\omega) = C_i(\hbar\omega - E_i)^{3/2}/\hbar\omega$$

or

$$\sigma_i(\omega) = C_i(\hbar\omega - E_i)^{3/2}/(\hbar\omega)^3$$

for IOT and LUC models, respectively.

The introduction of the bleaching process explains the shape of the PA spectrum in *a*-Ge:H without introducing arbitrary assumptions. In *a*-Si:H, it is not necessary to introduce a bleaching process because the Lučovský formula [Eq. (3)] appears to describe sufficiently well the high-energy part of the spectrum.⁶ There is, however, an alternative explanation of the spectra. We may use Eq. (1) for the PA band and account for the difference between the calculated curve by introducing a bleaching process with a threshold $E_0 = 0.9$ eV. In this case, the sum of the onsets of the PA band ($E_1 = 0.25$ eV) and of the bleaching process (0.9 eV) is much smaller than the gap ($E_g \approx 1.7$ eV). The bleaching in this case may be due to transition 4 for which $E_0 = E_4 = F_n - E_v = 0.9$ eV in *a*-Si:H.

Transition 3 has been proposed by Hirabayashi and Morigaki⁶ for explaining their observation of an additional photoinduced absorption with an onset at $E_3 = 0.6$ eV in *a*-Si:H with a high density of D^- states. We note that $E_3 + E_4$ is close to E_g .

It has been observed¹⁴ that the recombination in *a*-Ge:H is stronger and less temperature dependent than in *a*-Si:H. Consequently the steady-state trapped carrier concentration in *a*-Ge:H is less temperature dependent and therefore the strength of the PA band and its onset $E_0 \approx F_p - E_v$ changes less with temperature than in *a*-Si:H, as seen in Figs. 1 and 2.

Having explained the main PA band shape in *a*-Ge:H, its temperature dependence and its similarity with the PA in *a*-Si:H, we will now focus on the other features of the PA spectra. The sharp structures below the onset of the PA band such as those seen in Fig. 1, may be due to transitions of trapped holes from the ground state into an excited state of the trap. However, a reliable identification of these very

weak features would require an increase in the signal to noise ratio.

As seen in Table I, the bleaching process in *a*-Ge:H is stronger than the absorption process and therefore could be positively identified if the induced absorption turned into induced transmission. However, before this happens, another process contributes to the photoinduced absorption. The chopped pump photon absorption produces heat and consequently thermomodulation. This effect is small in the region below the gap where $d\alpha/d\theta$ is small (θ is temperature). However, in the region of the absorption edge it can be a strong effect if E_g shifts with temperature. The rise of $-\Delta T/T$ seen in Fig. 1 at the high-energy end of the spectra is ascribed to the thermomodulation of the gap. In this region, after subtracting the extrapolated $\Delta T/T$ due to the PA band, one obtains a linear energy dependence for $\Delta\alpha$ which we interpreted as the thermomodulation contribution. This is in accordance with the equation

$$\frac{-\Delta T}{T} \sim \frac{d\alpha}{d\theta} \sim \frac{d(\hbar\omega - E_g)^2}{dE_g} \frac{dE_g}{d\theta} \sim (\hbar\omega - E_g) \quad (5)$$

from which the E_g values given in Table I were determined. They depend somewhat on the PA model used, but within the accuracy of the procedure, are in agreement with the E_g values determined by direct-optical measurements.¹⁵ It was observed that both in *a*-Ge:H (Ref. 7) and *a*-Si:H (Ref. 16) the gap has a nonzero temperature coefficient even at low temperatures. We note in Fig. 2 an indication of the onset of the thermomodulation effect in *a*-Si:H at 12 K which presumably could be more clearly identified if our photon energy range was broader.

In conclusion, we showed that the spectrum of subgap photoinduced absorption in both *a*-Ge:H and *a*-Si:H can be understood in terms of four transitions from the gap states into the bands, two of which produce absorption and the other two bleaching. At the high-energy side of the spectrum a contribution of gap thermomodulation was identified and used to determine the band gap.

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