

Photothermal and photoconductive determination of surface and bulk defect densities in amorphous silicon films

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The sub-band-gap optical absorption spectra of high-quality hydrogenated amorphous silicon (*a*-Si:H) films are shown to be dominated by surface and interface state absorption when measured by photothermal deflection spectroscopy (PDS), while spectra determined using the constant photocurrent method (CPM) are not. For bulk defect states (both as-deposited and light-induced), the integrated subgap absorption is approximately twice as large for PDS as for CPM. Similarly, the conversion factor relating integrated subgap absorption with neutral dangling bond density is twice as large for CPM as PDS. This factor of 2 results from CPM seeing only transitions from below midgap into the conduction band while PDS sees transitions from the valence band into states above midgap as well.

Structural defects (under- and over-coordinated atoms, strained bonds, and impurities) with electronic states in the band gap control the electronic transport and recombination properties of many semiconductors. In hydrogenated amorphous silicon (*a*-Si:H), for example, material with neutral dangling bond densities N_s at or below 10^{16} cm^{-3} produces high-efficiency solar cells, while performance is quite poor for $N_s > 5 \times 10^{16} \text{ cm}^{-3}$. Thus accurate determination of gap-state defect density is critical.

Of the various experimental techniques for measuring the density of defect states in *a*-Si:H, optical absorption for photon energies less than the mobility gap determined by photothermal deflection spectroscopy (PDS)¹ offers several advantages. First, it is contactless, and can be performed on both doped and undoped films, requiring no special device structure. Second, it is "all-seeing," in the sense that any level that can have an electron lifted into or out of it, whether it is at the surface or in the bulk, should be observable. Third, unlike electron spin resonance (ESR), it does not require the state to be paramagnetic to be observable.

Unfortunately these same properties can be disadvantageous as well. Studies of PDS spectra versus film thickness^{2,3} indicate a density of defects at or near the surface (exposed surface or film/substrate interface) of $N_{ss} \sim 10^{12} \text{ cm}^{-2}$. Recently, Frye *et al.*⁴ published data showing N_{ss} to depend critically on post-deposition procedures. For common film thicknesses ($\sim 1 \mu\text{m}$), $N_{ss} \sim 10^{12} \text{ cm}^{-2}$ means that in high-quality films (with bulk deep defect density $N_{def} < 10^{16} \text{ cm}^{-3}$), there is more optical absorption due to surface states than bulk. In devices such as *p-i-n* solar cells, these surface states are irrelevant as it is the bulk states in the *i* layer which control collection efficiency.

Photoconductive techniques in general,^{5,6} and the con-

stant photocurrent method (CPM)⁷ in particular, offer an alternative to PDS for measuring subgap absorption. Because of the much greater mobility of electrons in *a*-Si:H than holes, the photocurrent is dominated by electron transport. This means that CPM sees primarily the transitions which contribute an electron to the conduction band, shown in Fig. 1(a) as (1). In contrast, we expect PDS to see transitions which leave behind a hole in the valence band [indicated as type (2)] with equal strength. Assuming a constant optical matrix element for all transitions,⁸ a density of states symmetric about midgap should produce twice as much defect absorption in PDS as CPM.

The second key difference between CPM and PDS is the sensitivity to surface states. When measured with the conducting path parallel to the plane of the insulating substrate (coplanar), the resultant CPM absorbance curve is similar in shape to the PDS curve with one important difference: the CPM curve drops as photon energies approach and exceed the band gap. The standard explanation for this is that high-energy photons are absorbed very near the top surface, and surface recombination reduces the density of carriers, reducing photocurrent.⁷ Since CPM assumes absorbance is in-

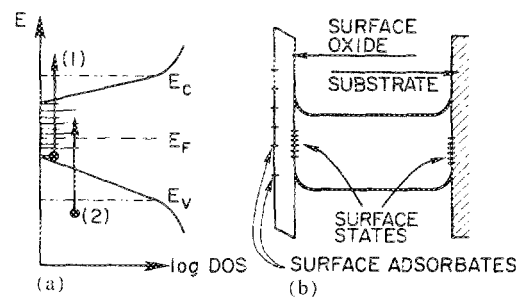


FIG. 1. (a) Energy diagram of subgap optical transitions in *a*-Si:H: (1) Electron lifted from occupied deep localized state to extended state in conduction band, (2) electron lifted from extended valence-band state to unoccupied deep state. (b) Band diagram (perpendicular to the conducting path during CPM).

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verse to the intensity required to maintain constant photocurrent, a fictitiously low absorbance will be calculated. This argument can be turned around: carriers generated near the surface have a reduced contribution to the photocurrent, and surface state absorption will hardly be seen at all. This means CPM will be relatively insensitive to surface states.

In general, the bands will be bent in the region near the surface. While the direction of band bending at the exposed surface can depend critically on the nature of surface adsorbates, an electron depletion layer is commonly found near the surface when well covered by a native oxide layer.⁹ This situation is shown in Fig. 1(b). To test the effects of surface adsorbates and surface depletion widths, we have performed CPM experiments with samples immersed in CCl_4 , and observed no change in the CPM spectra. Illuminating the sample with a dc bias of uniformly absorbed light can also be used to shrink the surface depletion widths, but it introduces a number of complications. First, the carriers generated by the bias light are trapped by states above the dark Fermi level (which was measured to be within 0.15 eV of midgap for all films studied), then type (1) transitions from these states can contribute to subgap absorption. Second, the occupation of the density of states under dc illumination can then undergo infrared quenching^{10,11} by the probe beam itself and produce complex effects which depend on bias intensity, wavelength, and the density of defects.¹² These experiments,¹² however, indicate that the CPM absorption spectrum is not significantly perturbed for above-band-gap absorbed carrier generation rates G below $10^{18} \text{ cm}^{-3} \text{ s}^{-1}$. Furthermore, we observe no change in PDS spectra over the available range of bias lights (up to $G = 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$). This at first surprising result is plausible if the dominant defect states are dangling bonds; any neutral dangling bond (below midgap) which captures an electron and becomes a doubly occupied state above midgap adds a type (1) transition to but subtracts a type (2) transition from the absorption spectrum at approximately the same photon energy.

The difference in sensitivity to surface states of PDS versus CPM is illustrated dramatically in Fig. 2, by the thickness dependence of PDS and CPM spectra for $a\text{-Si:H}$ films grown by chemical vapor deposition.¹³ The absorption coefficient is computed assuming the samples absorbed uniformly, so that the surface state absorption of PDS shows up as a higher effective bulk absorption coefficient. As expected, the spread between CPM and PDS drops to about a factor of 2 for very thick films.

The subgap absorption spectra are usually decomposed into two types of transitions, band/tail and band/defect. The first type is thought to be responsible for the exponential (Urbach) absorption edge, while the second shows up as the plateau at low photon energies. Jackson and Amer¹⁴ postulated that with a constant optical matrix element, the integral of this second type, "excess" absorption (shown schematically as an inset in Fig. 3) should be proportional to the defect density. Their data showed that $\int \alpha dE$ is proportional to the ESR-determined neutral dangling bond density N_s ,

$$N_s (\text{cm}^{-3}) = 7.9 \times 10^{15} \int \alpha_{\text{PDS}} (\text{cm}^{-1}) dE (\text{eV}). \quad (1)$$

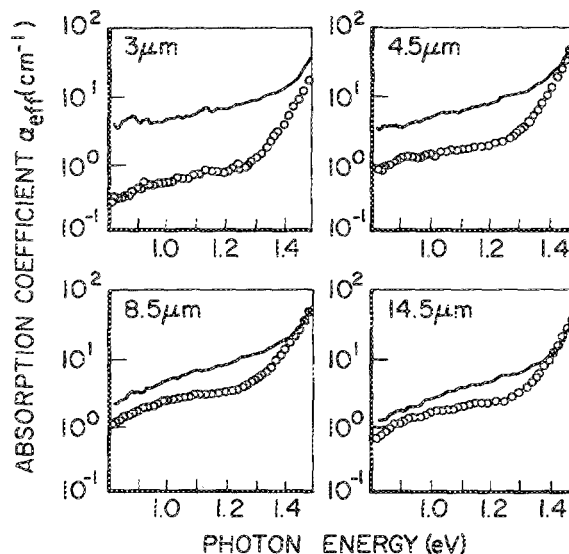


FIG. 2. Sub-band-gap optical absorption spectra for $a\text{-Si:H}$ films of four thicknesses as indicated. The solid-line spectra were measured using PDS, while the data points represented with circles were determined using CPM. The absorption coefficient plotted is that computed assuming all absorption in the bulk.

This correlation between PDS and ESR has been observed by other groups to hold in good-quality material, but not in material with large amounts of internal surface area.¹⁵ Band bending at surfaces and interfaces can alter the occupation of the dangling bonds, leaving them ESR silent,¹⁶ and there could also be defects unrelated to the dangling bonds at surfaces not found in the bulk. Again, CPM can be used to separate off the bulk states. Comparing CPM and ESR data on glow discharge $a\text{-Si:H}$ films^{17,18} (where the ESR densities were calibrated against samples provided by and measured at the same laboratory¹⁹ as used by Ref. 14) yields

$$N_s (\text{cm}^{-3}) = (1.9 \pm 0.3) \times 10^{16} \int \alpha_{\text{CPM}} (\text{cm}^{-1}) dE (\text{eV}). \quad (2)$$

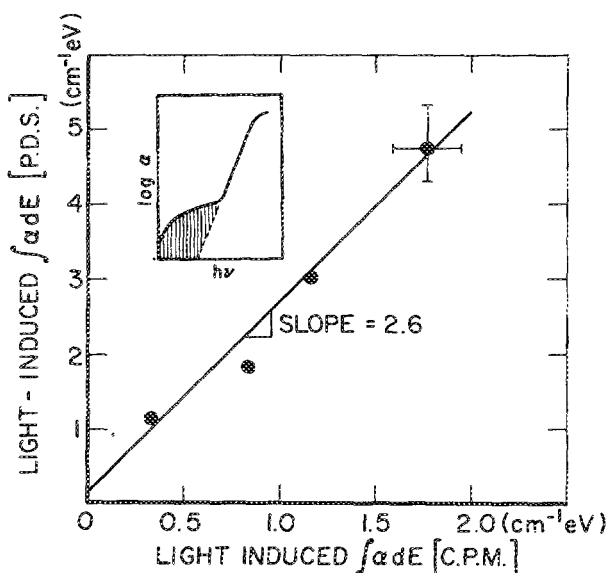


FIG. 3. Integrated light-induced subgap absorption for a single film measured at four points during light soaking. Value plotted is the difference between the integrated subgap absorption at a given time and its initial (annealed-state) value. Inset shows region of integration.

Comparing Eqs. (1) and (2), we find that the prefactor of N_s (CPM) is 2.4 times N_s (PDS), consistent with the expectation that PDS sees about twice as much absorption. We note in passing that neither (1) nor (2) requires that all deep defects be dangling bonds, merely that the total defect density be *proportional* to the dangling bond density.

A more precise comparison without the ambiguity of sample-to-sample variations can be made by using the Staebler–Wronski effect²⁰ to controllably introduce more deep defect states in a single sample. In Fig. 3 we show the integrated subgap absorption due to the light-induced states [$\int \alpha dE(t) - \int \alpha dE(t=0)$] for a high-quality *a*-Si:H sample for four different periods of light soaking. Again, PDS sees approximately twice (2.6 times) as much absorption for the same defect density. This result is consistent with the inference, drawn from ESR studies of light-soaking films of different thicknesses, that the Staebler–Wronski effect is predominantly a bulk effect^{21,22}; if surface states were added, PDS would see them and CPM would not.

Equations (1) and (2) give us a general program for separating out bulk and surface defect densities: Use the CPM spectrum and (2) to find the bulk defect density $N_{\text{def}}^{\text{bulk}}$; use the PDS spectrum to find the bulk and surface effective defect density $N_{\text{def}}^{\text{eff}}$; then the surface state density is

$$N_{\text{ss}} = (N_{\text{def}}^{\text{eff}} - N_{\text{def}}^{\text{bulk}})d, \quad (3)$$

where d is the film thickness. Such analysis on the data shown in Fig. 2 yields $N_{\text{ss}} = 3 - 8 \times 10^{12} \text{ cm}^{-2}$ and $N_{\text{def}}^{\text{bulk}} = 0.5 - 3 \times 10^{16} \text{ cm}^{-3}$. As one example of the value of separating bulk from surface states, the dc photoconductivity for above-band-gap light was found to be the highest in the sample with the lowest CPM defect spectrum, even though its PDS defect spectrum was the highest.

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