Direct measurement of gap-state absorption in hydrogenated amorphous silicon by photothermal deflection spectroscopy

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We have measured the subgap optical absorption of undoped, singly doped, and compensated hydrogenated amorphous silicon down to 0.6 eV using the sensitive technique of photothermal deflection spectroscopy. We show that this absorption is due to silicon dangling-bond defects located ~1.3 eV below the conduction band. While doping also creates defects ~1.3 eV below the conduction band, compensation removes them. The results suggest that for the undoped material the density-of-states maximum found in field-effect measurements is due to silicon dangling bonds.

In amorphous semiconductors, the optical absorption of defects and impurities is most readily observed below the band edge since it is not obscured by the much larger band-to-band absorption. Consequently, subgap absorption spectra should provide information about the number and energy level of defects in these materials. Although such measurements have been made on chalcogenide glasses,[1] none of those made on hydrogenated amorphous silicon (a-Si:H) are reliable because of experimental limitations. The films are typically 1 μm thick and are not optically homogeneous, making conventional transmission and reflection measurements of absorption coefficients α unreliable[2] below 50–100 cm^{-1}. Derivation of the absorption from photoconductivity[3,4] requires reliance upon the experimentally unverified assumptions that the efficiency-mobility-lifetime product $\eta\mu\tau$ is independent of photon energy.[5] We have recently developed the highly sensitive ($\alpha l \sim 10^{-8}$) technique of photothermal deflection spectroscopy (PDS)[6] which directly measures the optical absorption, which is highly insensitive to scattering,[7] and which does not rely on the above assumption. We have found an absorption tail extending in the forbidden gap down to 0.6 eV. We show that the source of this absorption is silicon dangling-bonds defects which are located ~1.3 eV below the conduction band. Furthermore, we find that doping introduces defects at the same energy level and with approximately the same cross section.

A detailed description of PDS has been published elsewhere,[6] and our samples were 1–2-μm undoped, singly doped, and compensated films deposited by rf glow discharge as described in Ref. 8.

Figure 1 shows the effect of increasing the rf power density on the absorption tail of undoped material while keeping the substrate temperature fixed.[9] As the rf power increases, the strength of the subgap absorption tail increases in a monotonic fashion. A progressive decrease in the slope of the exponential edge as the rf power increases is also observed.[10]

The effects of doping and compensation on the absorption spectra are summarized in Fig. 2. In Figs. 2(a) and 2(b) we give the results for PH_3- and B_2H_6-doped films. The subgap absorption tail rises as the doping level is increased, while the slope of the exponential edge decreases as the dopant concentration is increased.

To separate those effects due to dopant incorporation from the effects due to shifts in the Fermi level, we measured α for a series of compensated films prepared by fixing the PH_3 concentration and gradually increasing the B_2H_6 concentration [Fig. 2(c)]. Note that the magnitude of the subgap absorption *decreases* as the degree of compensation increases. Concurrently, there is a pronounced shift to lower energies and a broadening of the exponential region.

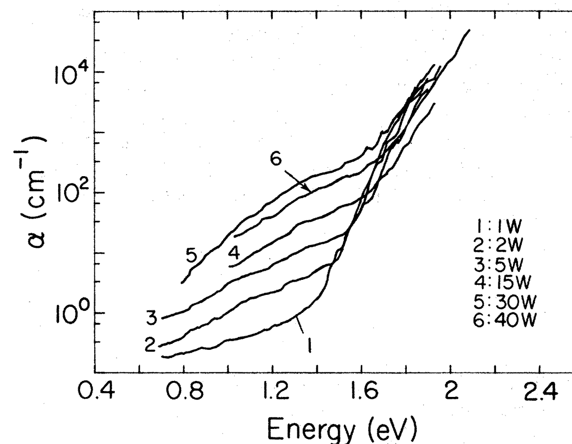

FIG. 1. Absorption coefficient vs energy for undoped a-Si:H for various rf powers, substrate temperature $T_s = 230\,°C$.

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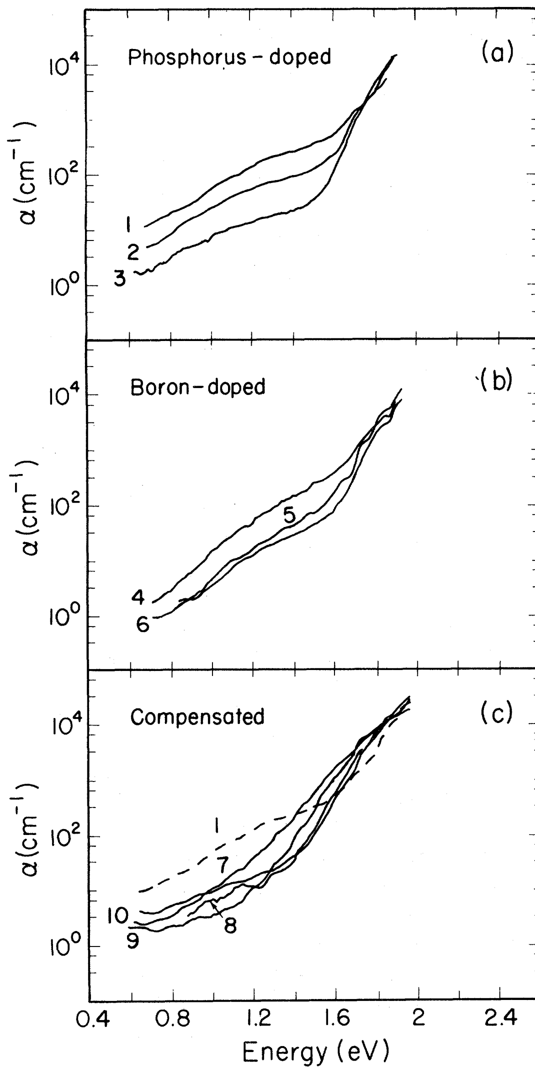

FIG. 2. Absorption coefficient vs energy for various dopants: (a) PH_3-doping concentration of the films is $1{:}1\times10^{-3}$, $2{:}3\times10^{-4}$, and $3{:}1\times10^{-5}$; (b) B_2H_6-doping concentration is $4{:}10^{-3}$, $5{:}3\times10^{-4}$, and $6{:}10^{-4}$; (c) compensated samples, all have 10^{-3} PH_3 and the B_2H_6 concentrations are 1:0, $7{:}2\times10^{-4}$, $8{:}4\times10^{-4}$, $9{:}2\times10^{-3}$, and $10{:}4\times10^{-3}$. All concentrations refer to the relative concentration of the dopant in the gas phase $T_s=230\,°C$ and rf power is 2 W.

If the gap-state absorption is due to dangling bonds, one would expect a positive correlation between the magnitude of the absorption and the number of dangling bonds as determined by electron-spin resonances (ESR). The excess absorption α_{ex} due to subgap states can be computed from $\alpha_{ex}=\alpha-\alpha_0\exp(\hbar\omega/E_0)$ where α_0 and E_0 are determined by a fit to the exponential region. We then can calculate the number of defects N_s from

$$N_s=\frac{cnm}{2\pi^2\hbar^2}\left[\frac{(1+2n^2)^2}{e^2 f_{0j} 9n^2}\right]\int \alpha_{ex}\,dE$$
$$=7.9\times10^{15}\int \alpha_{ex}\,dE \ , \qquad (1)$$

where c is the speed of light, $n(\simeq 3.8)$ is the index of refraction of the material, m is the electron mass, e is the electron charge, and f_{0j} is the oscillator strength of the absorption transition. The expression within the large parentheses is the inverse square of the effective charge of the defect when adjusted by the local-field corrections used in interpreting the infrared spectra of a-Si:H.[11,12] Assuming $f_{0j}=1$ and recognizing that the local-field corrections have been empirically determined to overestimate the correct local field by a factor of 2 in a-Si:H,[12,13] we get the numerical factor in Eq. (1). In the case of the undoped material, by plotting the equilibrium spin density N_s (ESR),[14] versus the defect density N_s (abs) as deduced by Eq. (1), we obtain an excellent agreement over three orders of magnitude, as shown in Fig. 3. Because ESR is a quantitative measure of the density of defects, the agreement suggests that the subgap tail is due to defects with spins. Unlike the case of unhydrogenated amorphous silicon,[15] we find no evidence of the absorption varying as N_s^2 (ESR).

For doped a-Si:H, there is no equilibrium spin density. However, the defect density may be estimated from the light-induced ESR (LESR), or from the quenching of luminescence.[16] If we compare such estimates with those deduced using Eq. (1), again we find excellent correlation (see Fig. 4). Our absorption estimates agree better with the luminescence ones than with those from LESR. This might be due to the fact that at high defect densities, LESR tends to underestimate the number of defects. The agree-

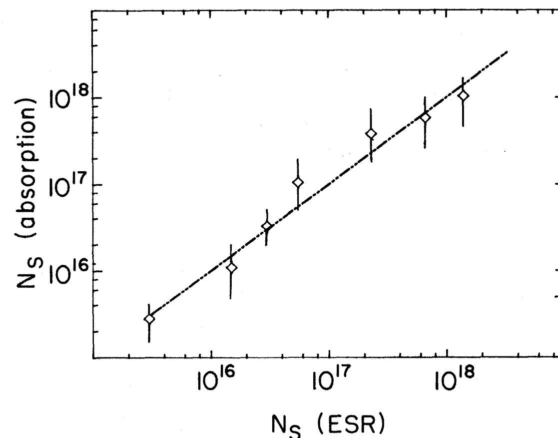

FIG. 3. Number of defects deduced from absorption by Eq. (1) vs number of spins measured by ESR.

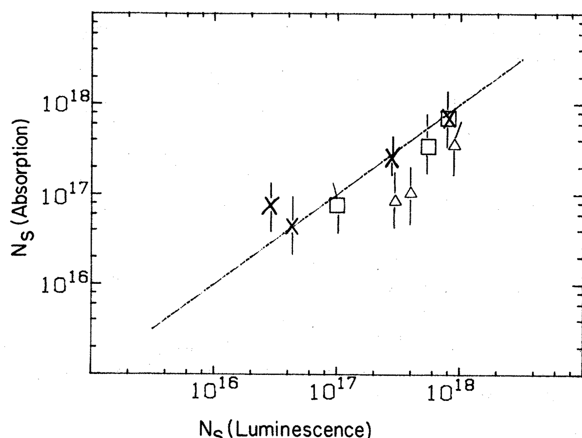

FIG. 4. Number of defects deduced from Eq. (1) vs number of spins estimated by luminescence (Ref. 16). □—phosphorous-doped samples, Δ—boron-doped samples, ×—compensated samples.

ment for B_2H_6 doping is not as good, perhaps because: (1) there is a different oscillator strength for this defect, or (2) Eq. (1) overcorrects for the exponential absorption for boron. For compensated *a*-Si:H, with low B_2H_6 concentrations, where there is a well-defined defect tail, Eq. (1) correctly predicts the number of defects centers, as estimated from luminescence and LESR results.

Using the agreement between absorption, ESR, LESR, and luminescence-deduced defect densities along with other data, the following picture emerges. For the undoped *a*-Si:H, as the rf power density and the substrate temperature increase, a maximum in the density of states (10^{15}–10^{18} states/cm^3), due to dangling silicon bonds appears ~1.3 eV below the conduction band. The evidence that the absorption is due to dangling silicon bonds is that the ESR and LESR lines used to calculate N_s (ESR, LESR) have $g = 2.0055$, which is known to be due to dangling silicon bonds.[17] This result supports the theoretical prediction of Joannopoulos, which places the Si dangling bond ~1.4 eV below the conduction band.[18] The fact that the energy of the absorption tail is the same as that of the maximum in the density of states, as determined by deep level transient spectroscopy (DLTS)[19] and field-effect measurements,[20] strongly suggests that this maximum is, in fact, due to Si dangling bonds. Since films with the lowest absorption tails have the highest luminescence, we conclude that dangling bonds quench the luminescence[21] rather than cause it, as previously had been hypothesized.[22] Furthermore, we estimate the optical cross section of the dangling bond to be 1.2×10^{-16} cm^2.

Doping with PH_3 introduces 10^{17}–10^{18} defects/cm^3 ~1.3 eV below the conduction band. The energy and cross section of these defects are nearly identical to that of dangling bonds. The absence of equilibrium ESR and the presence of a $g = 2.0055$ LESR line can be explained by the pairing of electrons at the defect center. Strong support for the increase in the number of defects with increasing level of doping comes from DLTS measurements of the density of states in the gap. For a 3×10^{-4} PH_3 concentration sample, we deduce 3.7×10^{17} states/cm^3 in a density-of-states maximum ~1.3 eV below the conduction band, indicating that DLTS may be more accurate than field-effect measurements. B_2H_6 doping also introduces defects. While boron-induced defects are probably near the valence band, as yet there is no clear evidence to support this hypothesis. Doping with PH_3 or B_2H_6 introduces defects, but doping with both removes the defects, as evidenced by the decrease in defect absorption. Finally, a general feature of *a*-Si:H is that defects tend to alter the shape of the band edge.[10]

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