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Determination of the gap-state distribution of hydrogenated amorphous silicon alloys from sub-band-gap absorption measurements

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The sub-band-gap absorption of undoped hydrogenated amorphous silicon alloys has been measured to obtain the distribution of gap states. Since the absorption is governed by the convolution of the initial and final densities of states for the optical transitions, it was found that small structures in the gap-state distribution cannot be discerned from these measurements. A good fit to the experimental data can be obtained both with and without a peak in the gap-state distribution. This explains the discrepancies in the literature regarding the location of the dangling-bond peak in undoped samples as obtained from sub-band-gap absorption measurements.

I. INTRODUCTION

There is a great deal of interest[1] in the study of the gap-state distribution of amorphous silicon alloys. These states, which originate from tailing of band edges because of absence of long-range order[2] and also from dangling bonds, defects, and impurities in the material,[3] are distributed over the entire mobility gap and a large number of techniques have been developed to study these gap states. Measurement of sub-band-gap absorption has been used extensively for obtaining information about the states in the lower half of the mobility gap. Using photothermal deflection spectroscopy (PDS), Amer and Jackson[4] measured sub-band-gap absorption in undoped and phosphorus-doped hydrogenated amorphous silicon alloys (a-Si:H) and derived the gap-state distribution (GSD) of these materials. They showed that there is a peak in the GSD about 1.25 eV from the conduction-band edge (E_c) in the undoped material. In P-doped material, the peak moves upward in the gap appearing at 0.9 eV below E_c. The peaks were identified, respectively, as singly and doubly occupied dangling bonds and a correlation energy of 0.35 eV was determined.

Wronski, Abeles, Tiedje, and Cody[5] obtained sub-band-gap absorption from measurement of photoconductivity. They interpreted their data in terms of transitions to states above E_c from the exponential valence-band tail and a peak in GSD at 0.8 eV above the valence-band edge for undoped a-Si:H, which was attributed to the singly occupied dangling-bond states. In P-doped samples also, a peak was observed in the same position indicating that the defect band remains fixed with respect to the valence-band edge.

If the optical gap for the undoped and P-doped samples measured by the authors[5] is used to locate the peak, it is found that incorporation of phosphorous moves the dangling-bond peak downward towards the valence-band edge — an observation which is in total disagreement with the results of Amer and Jackson.[4] Measurements of photoconductivity have also been carried out by Vaněček *et al.*[6] to obtain GSD from sub-band-gap absorption. In contradiction to both of the previous results, they find the dangling-bond level to be fixed at 1 eV below E_c in both undoped and P-doped samples. It is apparent that there is a need for further investigations to understand these anomalies.

We have used PDS to determine sub-band-gap absorption of undoped a-Si:H alloys deposited at different substrate temperatures. Since the variation of absorption coefficient α, as a function of photon energy $h\nu$, is governed by a joint density of states, we find that it is not possible to derive a unique density of state distribution from an analysis of the optical-absorption data. Specifically, we use two different models of GSD, one with a peak and the other without, and show that both these distributions can explain the optical data equally well.

II. EXPERIMENTAL DETAILS

For this study, undoped a-Si:H films typically 1 μm thick, were grown on Corning 7059 glass substrates by radio-frequency glow-discharge decomposition of silane-hydrogen (1:1) mixture. Typical deposition parameters were as follows: pressure 0.2 torr, rf power 300 $\mathrm{mW\,cm^{-2}}$. Two different substrate temperatures were used, 250 °C for good quality material (sample no. ECD I) and 100 °C to provide a highly defective material (sample no. ECD II).

Activation-energy measurements were carried out in a vacuum system with base pressure of 10^{-6} torr using coplanar structures where the contacts were made of colloidal graphite approximately 2 mm apart. Optical-absorption measurements were also performed on each sample using a standard transmission and reflection apparatus. In the absorption region, 5.10^3–10^5 $\mathrm{cm^{-1}}$, both PDS and the standard technique measure absorption with good accuracy and the normalization factor for PDS was determined from that measurement.

PDS was used to measure sub-band-gap absorption. A 150-W Xe source chopped at ~6 Hz coupled with a double monochromater was used as a pump source, and the pump-beam intensity was monitored with a thermopile detector. A 1-mW He-Ne laser was used as the probe beam which was detected with a laterally sensitive position detector. The signal was amplified and synchronously detected using a Princeton Applied Research (PAR)124A lock-in amplifier and the data were collected and averaged by a Cyborg 91A data-acquisition system coupled to an Apple IIe computer.

The entire optical system was placed on an optical table which was completely enclosed with Plexiglas to reduce noise due to convection currents in the ambient air. The measurements were performed at room temperature and carbon tetrachloride was used as the deflecting fluid.

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III. ANALYSIS OF DATA

The interpretation of optical-absorption data is complex and requires certain assumptions if one is to derive information about the density of states. The curve of absorption versus incident photon energy yields a joint density of states which must be deconvoluted. In accordance with earlier work[4–6], we have assumed that the matrix element for transitions from a localized state to an extended state is constant with respect to incident photon energy, and that the matrix element for transitions from localized to localized states is negligible. For photon energies less than E_g, we assume that only transitions from occupied localized states below the Fermi level to unoccupied extended states in the conduction band takes place. This implies that the conduction-band edge is sufficiently steep[5] to ignore transitions from occupied extended states in the valence band to unoccupied states in the conduction-band tail. The optical absorption then is given by[3]

$$\alpha\hbar\omega = \text{const}\times\int N_v(E)N_c(E+\hbar\omega)\,dE \ , \qquad (1)$$

where $N_c(E)$ corresponds to the conduction-band extended states and $N_v(E)$ to the occupied states below the Fermi level.

At this point, the absorption is modeled with various functions. $N_c(E)$ is usually taken to be parabolic of the form $a\sqrt{E}$. N_v is the sum of two terms; a term describing the exponential distribution of the valence-band tail states and a term describing the density of mid-gap states. Several distributions of mid-gap states have been used by various workers. Wronski *et al.*[5] have used a hyperbolic secant as the mid-gap states, and have ignored the population of the localized states by assuming that the integrand falls sufficiently fast as one integrates towards the conduction-band edge. This model has been used to explain the results of phosphorous-doped and undoped amorphous silicon. Vaněček *et al.*[6] used a Gaussian distribution and were able to adequately fit their absorption curves for P-doped and undoped *a*-Si:H. Amer and Jackson[4] also used a peaked mid-gap function.

In order to test the sensitivity of the chosen density of state distribution to explain the observed optical-absorption data, we have used a model in which the mid-gap distribution is not peaked and is described by an exponential function. We have also carried out the integration in Eq. (1) taking into account the position of the Fermi level. We may mention that the relevant parameter here is the electron-trap quasi-Fermi-level E_{Fn}, under illumination, beyond which the electron population in the localized states falls to zero. We have also made an additional assumption regarding the distribution of conduction-band extended states. In accordance with several experimental results,[7,8] we have assumed that the conduction band is parabolic of the form $A(E+E_0)^{1/2}$ with $E_0 = 0.2$ eV. We may mention that the shape of the derived absorption spectrum is quite insensitive to the magnitude of E_0 and if we choose[5] $E_0 = 0$, the shape of the curve shows insignificant change.

Under these conditions (using the nomenclature of Wronski *et al.*[5])

$$\alpha\hbar\omega = K\int_0^{E_F} A(E+E_0)^{1/2}\left[N_v \exp\frac{(-E-E_g+\hbar\omega)}{E_{0V}} + N_m \exp\frac{(-E-E_g+\hbar\omega)}{E_1}\right]dE \ , \qquad (2)$$

where K is a constant. E_{0V} is the slope of the valence-band tail states and E_1 is the slope of the mid-gap states. N_m is the extrapolated value of the intercept of the mid-gap states at the optical edge. We have also assumed that the mobility gap is equal to the optical gap, E_g. At each $E+\hbar\omega$, one must integrate through the density of states to get the optical absorption. We may mention that the energy from the valence-band edge up to which the tail states are characterized by E_{0V} depends on how large the density of mid-gap states is and in a highly defective material, the energy range is very small.

IV. RESULTS AND DISCUSSIONS

In Fig. 1, we present the optical absorption of a normal good sample of *a*-Si:H (sample No. ECD I). As is evident, there is an area, $1.4 < E < 1.7$ eV, where the absorption is exponential with a characteristic temperature of ~ 650 K. Below 1.4 eV, the absorption is flatter with a slightly faster decrease below 0.9 eV. As we have explained earlier, for the analysis of the data, we have used two different models, one a peaked mid-gap distribution as used by the Exxon group,[5] and the model of two exponentials. In this sample,

TABLE I. Parameters needed to obtain the best fit to the experimental data for the model with two exponentials (the symbols are defined in the text).

Sample	E_g (eV)	N_m ($\text{eV}^{-1}\,\text{cm}^{-3}$)	E_1 (eV)	$E_c - E_F$ (eV)	E_{0V} (eV)
ECD I ($T_s = 250\,°\text{C}$)	1.70	1.3×10^{17}	15	0.5	0.055
ECD II ($T_s = 100\,°\text{C}$)	1.91	6.0×10^{18}	0.3	0.65	0.050
Wronski *et al.* I (Ref. 5)	1.70	5.6×10^{16}	10	0.68	0.047
Wronski *et al.* II (Ref. 5)	1.72	9.0×10^{17}	0.7	0.69	0.053
Amer and Jackson (Ref. 4) (30 W)	1.84	7.0×10^{19}	0.2	0.74	0.050

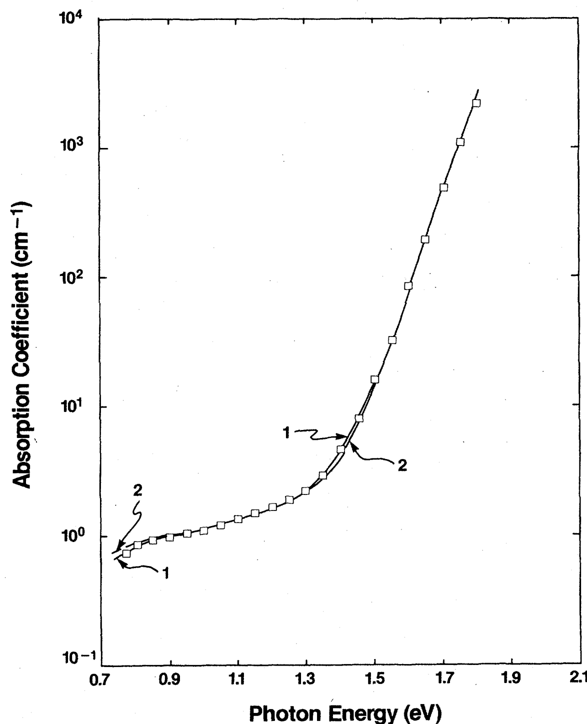

FIG. 1. Absorption spectrum of sample No. ECD I. 1 and 2 refer, respectively, to the fits obtained using exponential and a peaked mid-gap distribution.

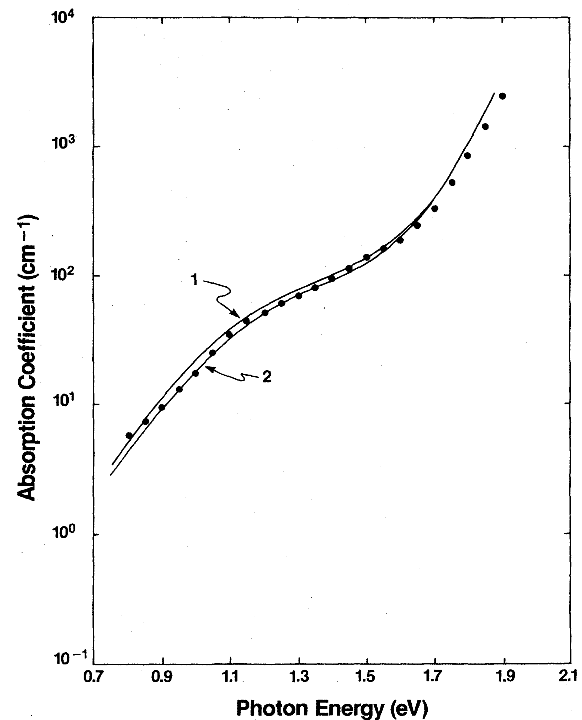

FIG. 2. Absorption spectrum of sample No. ECD II. 1 and 2 refer, respectively, to the fits obtained using exponential and peaked mid-gap distribution.

we have set E_F at 0.5 eV, whereas from the measurement of activation energy, the dark Fermi level was found to be at 0.7 eV below the conduction-band edge. The photoconductivity of this sample was measured *in situ* and showed that in our PDS setup there was approximately a 200 meV shift of the quasi-Fermi-level due to the scattered light from the probe laser.

As one can see, both models fit these data very well. For the two exponential models, we find from Table I that a flat deep-state distribution gives good fit to the experimental data.

A highly defective sample (sample No. ECD II) was also measured ($T_s = 100\,°\mathrm{C}$), to compare with the defective sample measured by Amer and Jackson.[4] Again, the purpose of this experiment was to see if one needed a peaked mid-gap function to describe the absorption. In Fig. 2, we present this data. Here, for the best fit, we find $E_F = 0.65$ eV, which is also in agreement with what we measure for this sample. For this defective sample, the mid-gap distribution has a characteristic temperature of ~ 3500 K, again, a fairly flat distribution. If we use the model of Wronski *et al.*[5] (Table II) to calculate the absorption we find that we need a peak position at $E_c - 0.8$ eV for the good quality sample and at $E_c - 1.12$ eV for the defective sample to obtain the best fit.

We have also used our model to fit the data of Wronski *et al.*[5] for their undoped material, and Amer and Jackson's[4] data on an undoped sample grown at 30-W rf power. In Figs. 3 and 4, we show that both the exponential and peaked distributions fit the data equally well. We also find from Table II, which gives parameters for obtaining the best fit, that there is a large scatter in the position of the peak

TABLE II. Parameters needed to obtain the best fit to the experimental data for the model with a peaked mid-gap distribution [the symbols are as defined by Wronski *et al.* (Ref. 5)].

Sample	E_g (eV)	N_r ($\mathrm{eV^{-1}\,cm^{-3}}$)	E_r (eV)	E_{r0} (eV)	E_{0V} (eV)
ECD I ($T_s = 250\,°\mathrm{C}$)	1.70	1×10^{17}	0.80	0.2	0.055
ECD II ($T_s = 100\,°\mathrm{C}$)	1.93	2×10^{18}	1.12	0.13	0.088
Wronski *et al.* I (Ref. 5)	1.70	3.1×10^{16}	0.84	0.1	0.047
Wronski *et al.* II (Ref. 5)	1.72	1.7×10^{17}	0.95	0.1	0.053
Amer and Jackson (Ref. 4) (30 W)	1.84	7.2×10^{18}	1.30	0.14	0.068

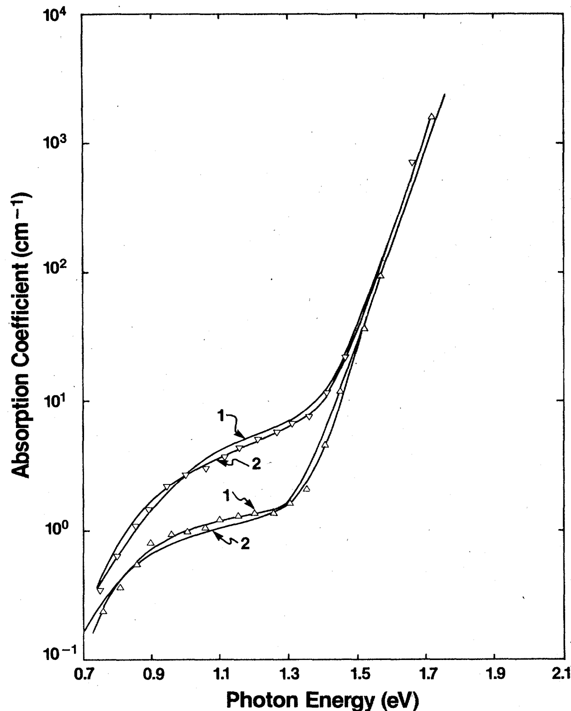

FIG. 3. Absorption spectrum for two undoped samples of Wronski *et al.* (Ref. 5). 1 and 2 refer, respectively, to the fits obtained using exponential and peaked mid-gap distribution.

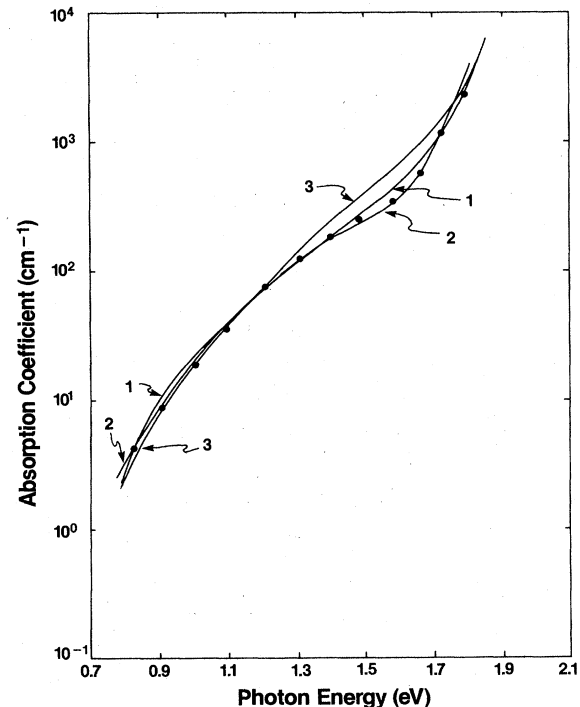

FIG. 4. Absorption spectrum for an undoped sample grown at 30 W rf power (Ref. 4). 1, 2, and 3 refer, respectively, to fits obtained using an exponential mid-gap distribution, the peaked mid-gap distribution function of Wronski *et al.* (Ref. 5) and the peaked mid-gap distribution used by Amer and Jackson (Ref. 4).

for the different samples.

We thus find that the optical absorption for undoped *a*-Si:H data can be explained equally well using either a peaked or a flat mid-gap GSD. Similar conclusions for undoped samples were also arrived at by Moddel, Anderson, and Paul.[9] Although there is some experimental evidence[10] that the GSD in the range $1.2 < E_c - E < 1.3$ eV is reasonably flat, we are not claiming that our experimental data give that information. The main contention is the fact that although sub-band-gap absorption is very useful for obtaining qualitative information about the gap-state density below the Fermi level, small features in the GSD cannot be derived unambiguously from the data. This accounts for the wide discrepancy that exists in the literature regarding the position of the peaks in the undoped samples.

V. CONCLUSIONS

We have measured the sub-band-gap absorption of undoped *a*-Si:H alloys deposited at 250 °C and 100 °C by PDS. We find that the data can be fitted equally well with gap-state distributions with or without a peak. The same conclusions hold for absorption data obtained by other groups[3–5] on undoped *a*-Si:H. We conclude that since the optical absorption is governed by a convolution of density of states, small features in the gap-state distribution cannot be discerned from the data and this explains the different values for the position of the peak that have been reported in the literature based on optical-absorption data.

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