Study of gap states in hydrogenated amorphous silicon by transient and steady-state photoconductivity measurements

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The energy distribution of gap states in amorphous hydrogenated silicon has been investigated by transient photoconductivity (TPC) and steady-state photoconductivity (SPC) measurements. Both TPC and SPC measurements show that the shallow states decrease exponentially with energy away from the conduction-band edge with a characteristic temperature of 300 K whereas the deep states decrease with a characteristic temperature of about 1000 K. The transition energy is located around 0.3 eV from the conduction-band edge. The density of states at the Fermi level was obtained from frequency dependence of the capacitance (C-ω curve) of Schottky diodes. The derived density-of-states distribution as obtained from TPC, SPC, and C-ω measurements agrees with results obtained from field-effect and C-V measurements.

I. INTRODUCTION

It is now well established that amorphous hydrogenated silicon (a-Si:H) films are characterized by a distribution of states in the mobility gap. These states which originate from the tailing of the band edges due to the lack of long-range order[1] and also from dangling bonds, defects, and impurities in the material[2] have pronounced effect on the photovoltaic properties of the films. Study of these gap states has therefore received a great deal of attention in recent years.[3]

The most widely used method for determining gap-state distribution is based on the measurement of field effect.[4–6] The results show a density of around 10^{16}–10^{17} $cm^{-3}eV^{-1}$ near the midgap in good quality material; the density increases as one approaches the band edges. Estimates of density of states (DOS) have also been obtained from voltage dependence of capacitance (C-V) and temperature and frequency dependence of capacitance (C-T-ω) of Schottky diodes and metal-oxide–semiconductor (MOS) structures. C-V results[7] show a midgap density of around 2×10^{16} $cm^{-3}eV^{-1}$; the density increases as one approaches the conduction-band edge. C-T-ω studies[8–11] which provide only DOS at the Fermi level $g(E_F)$ give a midgap density close to 5×10^{15} $cm^{-3}eV^{-1}$. $g(E_F)$ has been found to be higher in films where the Fermi level is closer to the conduction-band edge again indicating that DOS increases as one moves away from the midgap.

Deep-level transient-capacitance spectroscopy (DLTS) has been used extensively for studying deep traps in crystals.[12] This technique which relies on the measurement of the time dependence of capacitance of Schottky diodes or p-n junctions as traps empty out has recently been used to obtain DOS in a-Si:H. In striking contrast to the results discussed earlier, DLTS studies[13,14] show a minimum in DOS at around 0.4 eV from the conduction-band edge with the gap states rising as one approaches the midgap. The minimum value obtained from DLTS is also much lower—less than 10^{15} $cm^{-3}eV^{-1}$. It has been argued[14] that the higher values of DOS obtained from field-effect, C-V, or C-T-ω measurements, may be due to the influence of surface states. On the other hand, interpretation of DLTS data in amorphous semiconductors with a continuous distribution of gap states is quite complex and is limited in its application only to samples which have been doped to increase their conductivity. Clearly there is a need for measurement of DOS by independent techniques to resolve this problem.

The study of transient photoconductivity of amorphous semiconductors provides a useful tool for obtaining information about the states in the gap. When electron-hole pairs are created by pulsed optical excitation, the photocurrent is found to decrease with time even when the carrier density remains a constant. This can be explained[15] by the

phenomenon of dispersive transport where the carrier mobility decreases with time because of multiple trapping at the localized sites. It has been shown[16,17] that the dependence of photocurrent on time is related to the energy distribution of the gap states and from a study of time and temperature dependence of the photocurrent, the energy spectrum of the gap-state distribution can be obtained.

Another interesting method for obtaining information about the gap state is from the study of intensity dependence of steady-state photoconductivity. If the trap distribution is exponential between the Fermi level and the quasi-Fermi level, it has been shown[18] that the intensity dependence of photoconductivity σ_{ph} obeys a relation $\sigma_{ph} \propto I^{\gamma}$ where γ is determined by the characteristic temperature for the exponential distribution. By changing the temperature and the intensity, the quasi-Fermi level can be moved and one can obtain the energy distribution over a wide energy range.

It is interesting to note that in slightly n-type material, steady-state photoconductivity (SPC) scans the energy range from the Fermi level upward where as the transient photoconductivity (TPC) explores the energy region from the conduction-band edge downward. We have therefore carried out measurements on the same sample of a-Si:H using both techniques and have thereby scanned a wide energy range in the upper half of the mobility gap. SPC or TPC measurements give the shape of the energy distribution only; in order to find out absolute values for the density, we have carried out C-T-ω measurements on Schottky diodes made on samples grown in the same run. A combination of these three techniques has, therefore, given a complete description of the density and energy distribution of the gap states in the upper half of the mobility gap for undoped a-Si:H samples (which are usually slightly n type) and the results are reported in this paper.

II. EXPERIMENTAL DETAILS

Undoped a-Si:H films, typically 6000 Å to 1 μm thick, were grown on Corning 7059 glass substrates by rf glow-discharge decomposition of silane. Typical deposition conditions were as follows: substrate temperature, 260 °C; pressure, 0.2 Torr; and rf power, 300 mW cm^{-2}. One section of the glass had predeposited NiCr film on which a heavily doped thin ($\sim$500 Å) n^+-type layer was first deposited to obtain the bottom Ohmic contact for the Schottky diodes used for the C-T-ω measurements. The top metal contact was made by evaporating Pd dots of 50% transmission.

For the photoconductivity experiments, coplanar structures, using NiCr or aqua-dag contacts spaced about 2 mm apart, were used. Both the dark and the photocurrent were found to be Ohmic up to 10 KV cm^{-1}, the highest field used in the experiments. Measurements were carried out in a vacuum system at a base pressure of 10^{-6} Torr. The samples were heat dried at 200 °C for 2 h and all measurements were carried out *in situ*. For the transient measurements, photocurrent was excited by a pulsed dye laser of 100 psec duration with a repetition rate of 10 Hz. The signal was amplified by PAR Model No. 113 preamplifier and recorded by a Biomation transient digitizer. Signal averaging by a Tracor signal averager was used before the data were analyzed by a computer to obtain the time dependence of the photocurrent. For all the experiments, the laser intensity was suitably attenuated so that it was more than 1 order below the intensity at which bimolecular recombination sets in.

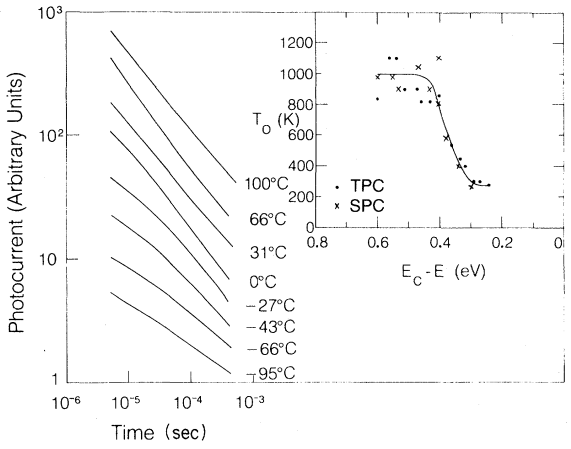

FIG. 1. Dependence of photocurrent on time at different temperatures. The inset shows T_0 as a function of energy away from the conduction-band edge as obtained from the transient and steady-state photoconductivity data.

For the steady-state photoconductivity experiments, a quartz-halogen lamp with suitable neutral density filters was used to obtain the intensity dependence of photocurrent. C-T-ω measurements were performed using a PAR lock-in amplifier in the frequency range 5—200 Hz. The temperature range of measurements was between 80 and 120 °C which is below the temperature at which saturation of capacitance takes place. The Schottky diodes used for the measurements had ideality factors better than 1.2.

III. RESULTS AND DISCUSSIONS

In Fig. 1 we show the variation of photocurrent with time at different temperatures. At room tem-

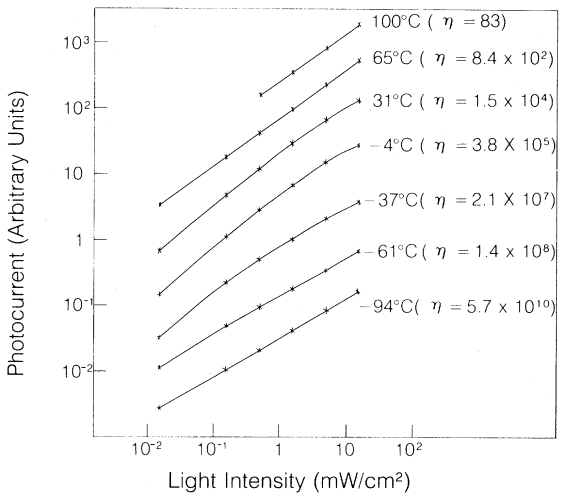

FIG. 2. Dependence of steady-state photocurrent on intensity at different temperatures. η is the ratio of light-to-dark conductivity at an intensity of 15 mW/cm^2.

perature and above, the double-logarithmic plot is found to be linear indicating a power-law dependence of photocurrent on time. As the temperature is lowered, the linearity is no longer maintained and the slope is smaller at shorter times. When the temperature is very low ($\sim$180 K), the plot is again linear but the slope is now smaller than at room temperature.

For an exponential distribution of localized states, dispersive transport is expected to give a power-law dependence of current on time as[19]

$$i(t) \propto t^{-(1-T/T_0)} , \tag{1}$$

where the gap states vary with energy as

$$g(E) \propto \exp[-(E_c - E)/kT_0] . \tag{2}$$

Here E_c is the position of the mobility edge. We also note that at any given time t, the carrier packet probes the localized states at an energy E_d, where

$$E_d = E_c - kT \ln(\nu_0 t) \tag{3}$$

and ν_0 is an escape frequency associated with the traps and is assumed to be a constant (5×10^{11} sec^{-1}). By using Eq. (1), T_0 can be obtained from the $\log_{10} i(t)$-$\log_{10} t$ plots shown in Fig. 1 at different times and use of Eq. (3) enables us to convert the time scale into an energy scale. The results are shown in the inset of Fig. 1 where T_0 as measured at different times and temperatures is plotted against $E_c - E$. Since our undoped samples are slightly n type, E_c is the conduction-band edge. We notice that closer to the conduction-band edge $T_0 \sim 300$ K whereas away from it $T_0 \sim 1000$ K with the transition taking place around 0.35 eV. We should mention that in converting time to energy by using Eq. (3) we assume that all the carriers are localized at $E_d(t)$ at a given time t. In reality the carriers form a packet of a finite energy width which depends on T_0 and this may give an uncertainty in the determination of the transition energy of about 0.05 eV.

The intensity dependence of steady-state photoconductivity is shown in Fig. 2. We notice that at around room temperature, $\sigma_{ph} \propto I^\gamma$ with $\gamma \sim 0.75$ over the entire range of intensity. As the temperature is lowered, the value of γ changes at high intensity and finally at the lowest temperatures ($\sim$200 K), γ is again a constant but has a lower value $\sim$0.6. These results are in essential agreement with the data of Wronski and Carlson[20] and Wronski and Daniel[21] who find values of γ equal to 0.7 and 0.5, depending on the intensity and temperature.

The steady-state photoconductivity data can be explained using the model of Rose[18] who showed that for an exponential distribution of traps as in Eq. (2), photoconductivity depends on intensity as $\sigma_{ph} \propto I^\gamma$ with

$$\gamma = T_0/(T + T_0) . \tag{4}$$

For the case of a-Si:H where traps at the valence-band tail are more numerous than at the conduction-band tail,[22] recombination takes place mostly at the valence-band tail. Charge neutrality enforces that Eq. (4) is still valid with the value of T_0 reflecting the slope of the density of states at the conduction-band tail.[23] Specifically, T_0 gives the slope at E_f^t, the trap-Fermi level for electrons which for undoped a-Si:H is the same as E_{fn}, the quasi-Fermi level for electrons. For the sample used for this experiment, the activation energy is 0.71 eV. This gives the relative position of the dark Fermi level $E_f(0)$ at 0 K with respect to the conduction-band edge and E_f at any temperature can be calculated using the relation

$$E_f(T) = E_f(0) - \beta T , \tag{5}$$

where β is the temperature coefficient of the shift of the Fermi level. If we assume[24] that the temperature coefficient of the shift of the optical gap, $\gamma = -4.4\times10^{-4}$ eV/K, is the same as that of the mobility gap and that $\beta \simeq \gamma/2$, we can determine $E_f(T)$. We neglect any statistical shift of the Fermi level or any movement of mobility edge with increasing temperature because of increasing wave-function overlapping as proposed by Spear *et al.*[25] All these assumptions may lead to an uncertainty of about 0.05 eV in the determination of $E_f(T)$. The quasi-Fermi level E_{fn} depends on the temperature

and the light intensity and can be obtained from

$$E_{fn}(T)=E_f(T)+kT\ln(\sigma_{\rm ph}/\sigma_{\rm dark}) \ . \qquad (6)$$

Use of Eqs. (4) and (6) enables us to find out the value of T_0 as a function of energy from the plots given in Fig. 2. The results are shown in the inset of Fig. 1. We find that in agreement with the results from TPC, there are two distinct regions in energy, closer to the conduction-band edge $T_0 \sim 300$ K and away from the conduction-band edge $T_0 \sim 1000$ K with the transition region around 0.35 eV. We have studied several samples prepared under similar conditions and the T_0 vs $E_c - E$ plots are very similar with the transition between the low-T_0 and high-T_0 regions taking place between 0.25 and 0.35 eV.

At this point we would like to compare our results with other TPC experiments on undoped a-Si:H. Time-of-flight measurements have been carried out by Tiedje *et al.*[16] who find for n-type samples $T_0 \sim 300$ K. In these experiments, since a Schottky structure is used, the transit time is small and since in dispersive transport, the photocurrent decreases rapidly with time after the transit time, the experiments were confined to a time region less than 10 μs. The energy region probed, therefore, was less than 0.3 eV away from E_c and in this region our results also show $T_0 \sim 300$ K. Transient photoconductivity experiments on coplanar structures have been carried out by Hvam and Brodsky[26] and by Street.[27] In the experiments of Hvam and Brodsky, the undoped sample was characterized by a short recombination lifetime and hence an unambiguous dispersive regime could not be observed. Street used undoped samples with longer recombination lifetimes and observed dispersive transport with $T_0 \sim 750$ K. The energy region probed in his experiments is deeper than 0.35 eV away from the conduction-band edge and this is the region where our data show $T_0 \sim 1000$ K. The fact that DOS is characterized not by a single exponential but with exponentials with different values of T_0 near the band edge and away from it allows one to speculate about the origin of these states. It is possible that the states near the band edge having $T_0 \sim 300$ K are disorder-induced and decay fast. The deeper states where $T_0 \sim 1000$ K are probably defect induced.

Using the T_0 vs $E_c - E$ plot given in Fig. 1, we can now draw the energy distribution of the localized states. We need to know the density at a given energy and this we obtain from C-T-ω measurements on the Schottky structure grown during the same deposition run. We find for this sample $g(E_f)=2\times10^{16}$ cm^{-3}eV^{-1}. The resulting density-of-states plot is shown in Fig. 3. Also shown in the figure are the data obtained from field effect by

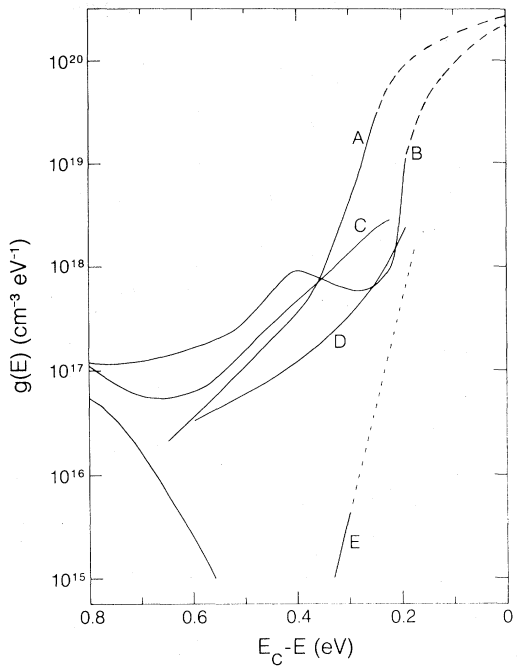

FIG. 3. Plot of density of states as a function of energy as obtained by (A) present experiment, (B) field-effect (Ref. 28), (C) field-effect (Ref. 24), (D) C-V measurements (Ref. 7), and (E) DLTS measurements (Ref. 14).

LeComber and Spear[28] and Fritzsche,[24] results of C-V measurements,[7] and the DLTS data.[14] We find that our results are in good agreement with the field-effect and C-V data with the density of states increasing as one moves from the midgap towards the conduction-band edge. The DLTS data, however, show the opposite trend. As we have mentioned earlier, it should be noted that the DLTS data are on P-doped sample whereas our results are on undoped materials. P doping, however, has been seen to increase the states in the gap, and recent experiments on P-doped a-Si:H using current transient spectroscopy[29] also do not show the minimum around 0.45 eV. We are now carrying out experiments using TPC, SPC, and C-T-ω on P-doped samples to resolve this anomaly.

A look at our DOS plot shown in Fig. 3 indicates that the extrapolated value at the mobility edge gives an unrealistically large value of $g(E_c)$, the density of states at the mobility edge. As we have pointed out earlier, because of various assumptions involved, we have an uncertainty of about 50 meV in fixing the energy scale. But this alone cannot account for the high value of $g(E_c)$ extrapolated from the plot. One may conjecture that DOS does not go

down exponentially just below the mobility edge. The parabolic band edge which is normally assumed for explaining the optical-absorption data continues up to a certain energy below the mobility edge. In that case, the slope of the DOS plot will decrease as one approaches the mobility edge as shown by the dotted line in Fig. 3. It is interesting to note that a similar assumption was made[30] in drawing the DOS plot from the field-effect data (curve *B*) where the DOS just below the mobility edge was assumed to be parabolic. TPC experiments carried out at shorter times and lower temperatures can give useful information about this region close to the mobility edge.

We should mention that the T_0 vs $E_c - E$ plot, shown in Fig. 1, has been derived by assuming that ν_0, the attempt to escape frequency, is a constant. It has been shown recently[31] that the capture cross section or the jump rate decreases away from the conduction-band edge in P-doped samples. The effect of an energy-dependent ν_0 as mentioned above will shift the energy scale for the TPC data whereas it will remain unaltered for the SPC data. Since our results give a good agreement in the transition energy obtained from the SPC and TPC data, any strong dependence of ν_0 on energy in undoped *a*-Si:H can be ruled out.

In conclusion, we have measured the gap-state density and energy distribution of *a*-Si:H by TPC, SPC, and *C-T-ω* measurements. Both TPC and SPC results show that the shallow states change exponentially with energy with a characteristic temperature of 300 K whereas the deep states have a characteristic temperature of about 1000 K. The transition energy is located about 0.3 eV from the conduction-band edge. The derived density-of-states distribution agrees with results obtained from field-effect and *C-V* measurements.

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