can simulate a spectrum in the "incommensurate" region and show the substantial deterioration of the fit when we take γ to be either ten times or one-tenth the γ which gives the best fit. It is clear that the spectrum at 100 K gives a value of γ which we see from Fig. 2 exhibits a definite commensurate component. Thus we confirm McMillan's picture of the incommensurate phase.

Nakanishi and Shiba found that one should also include amplitude modulation. Moreover, it is possible that the width of $g(\omega;\vec{r}_i)$ is modulated. Such effects may account for the residual discrepancies between our line-shape theory and data. However, for the values of γ we obtain, the line shapes are insensitive to amplitude modulation (proportional to the phase modulation) of up to 50%.

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[1]J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. 24, 117 (1975); J. A. Wilson, Phys. Rev. B 15, 5748 (1977), and references therein.

[2]F. J. DiSalvo, in *Electron-Phonon Interactions and Phase Transitions*, edited by T. Riste (Plenum, New York, 1977), p. 107.

[3]J. A. Holy, M. V. Klein, W. L. McMillan, and S. F. Meyer, Phys. Rev. Lett. 37, 1145 (1976); J. A. Holy, thesis, University of Illinois, 1977 (unpublished).

[4]D. E. Moncton, J. D. Axe, and F. J. DiSalvo, Phys. Rev. B 16, 801 (1977).

[5]W. L. McMillan, Phys. Rev. B 12, 1187 (1975), and 14, 1496 (1976).

[6]K. Nakanishi and H. Shiba, J. Phys. Soc. Jpn. 44, 1463 (1978).

[7]C. Berthier, D. Jerome, and P. Molinie, J. Phys. C 11, 797 (1978).

[8]R. A. Craven and S. F. Meyer, Phys. Rev. B 16, 4583 (1977).

[9]R. M. Fleming, D. E. Moncton, D. B. McWhan, and F. J. DiSalvo, Bull. Am. Phys. Soc. 25, 199 (1980).

[10]R. A. Wind and S. Emid, J. Phys. E 8, 281 (1975). Note, however, that the *RC* filter distortion should be given by a complex transfer function.

Direct Measurement of the Bulk Density of Gap States in *n*-Type Hydrogenated Amorphous Silicon

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The first direct measurement is reported of the bulk density of deep states in n-type a-Si:H. The spectral distribution is considerably different from previous field-effect and C-V measurements and the overall density is much lower than has previously been reported. The states seen in these samples appear to be extrinsic and suggest that the extrapolated total density of deep states in pure a-Si:H may be less than 10^{15} cm^{-3}.

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Recently, there has been considerable interest in determining the concentration and energy distribution of states in the gap of hydrogenated amorphous silicon. This stems from the fact that nearly all of the important transport and optical properties of this material are influenced by these gap states. The most widely accepted techniques for obtaining such information have been field effect[1] and metal-oxide-semiconductor C-V measurements.[2] However, these methods are rather indirect and may be influenced by states located near the surface. In this Letter we report the first measurement of the spectral distribution of gap states in the bulk of n-type a-Si:H. Our results differ quite markedly from those of previous measurements.[1,2]

The techniques which we employ are well known in crystalline semiconductors and are generally referred to as space-charge spectroscopy.[3] Such techniques have recently been applied to a-Si:H,[4,5] but these early results were not definitive enough to yield a complete picture of the density of gap states. Since these methods as well as field-effect and C-V measurements are based on space-charge layers, it is essential to understand the differences between these techniques. In field-effect and C-V measurements one changes the bias voltage which simultaneously varies *both* the width of the space-charge layer and the intersection of the Fermi level with the density of states. The data are thus a convolution of the energy *and* spatial variation in gap states. All anal-

yses of these data have assumed without proof that the states are distributed uniformly in space. However, evidence from other experiments suggests that the regions near the surface are quite different from the bulk.[6-9]

Our technique separates the spatial and energy measurements. The energy is measured directly by observing the thermal emission of carriers initially trapped in gap states. The spatial variation can be independently measured by changing the bias voltage applied to the sample. In some samples the spatial variation in the density of states can be measured over a distance of 0.1 to 0.6 μm from the surface.

Our 1–2-μm-thick samples were grown by the standard method of rf decomposition of silane in a capacitively coupled system. The substrates were heavily doped n- or p-type crystalline silicon which were positioned during growth on the grounded rf electrode at a temperature of 250 °C. The pressure during growth was 0.36 Torr. Parameters intentionally varied were the SiH_4/Ar dilution ratio [(3–100)% SiH_4] and the PH_3 concentration (0–1500 vapor parts per million relative to the SiH_4). The rf power density (12–36 mW/cm^2) was chosen as a function of SiH_4/Ar ratio to yield growth rates of ~ 1 μm/h. The samples used for our measurements had a bulk resistivity less than 10^6 Ω cm at the temperature of measurement with resistivity activation energies, $\Delta E(\rho)$, of 175–290 meV. Semitransparent Schottky barriers of Pd or Cr were evaporated on the outer surface. The resulting structures were found from C-V and I-V measurements to have barrierlike contacts at both the metal and the substrate interfaces. All measurements were preceeded by a 5-min anneal at 200 °C at zero bias.

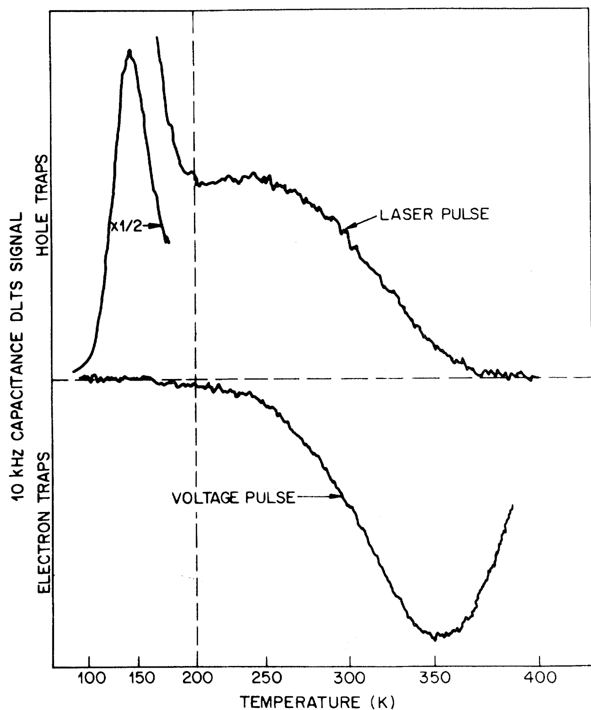

FIG. 1. DLTS hole and electron emission spectra of sample 1, typical of phosphine-doped a-Si:H (60 vapor parts per million PH_3). The rate window is 10 sec^{-1}. The dashed line at 200 K indicates the temperature below which the RC time constant of the sample is too large to follow the 10-kHz measurement frequency.

The specific forms of space-charge spectroscopy used in this work are (1) deep-level transient spectroscopy (DLTS),[10] (2) thermally stimulated capacitance (TSCAP), and (3) admittance spectroscopy. These are all well-known techniques which have been thoroughly described in the literature[3,10] and hence need not be discussed in detail here.

A typical set of DLTS spectra for a phosphine-doped sample is shown in Fig. 1. The electron trap spectrum is obtained in the standard manner by using voltage pulses to fill the traps. The hole trap spectrum is generated by a pulsed dye laser operating just above band gap at 6000 Å. If one assumes that the traps are completely filled by each pulse, the *relative* density scale is given to a good approximation by the DLTS spectrum divided by T (to take into account the variation of DLTS resolution with temperature).

The density of bound states in the gap, $g(E)$, corresponding to the spectra in Fig. 1 is shown in Fig. 2 (sample 1) along with the density of states for a sample grown without PH_3 (sample 2). The electron trap states in the upper half of the gap have energies measured from the conduction band while the hole trap states in the lower half of the gap have energies measured from the valence band. Figure 2 is the superposition of these two distributions on a scale which implies a gap of 1.6 eV. This is roughly the optical gap and is used to compare our results with previous densities of states.[1,2] However, since the thermal emission gap is not known for a-Si:H, the true point of overlap at the center of the gap in Fig. 2 is not yet precisely determined. [Note that $g(E)$ corresponds to the *sum* of the electron and hole emitting states in the overlap region.] The proper overlap will be important to deduce whether or not there is actually a peak at midgap in $g(E)$. Our data are consistent with a thermal

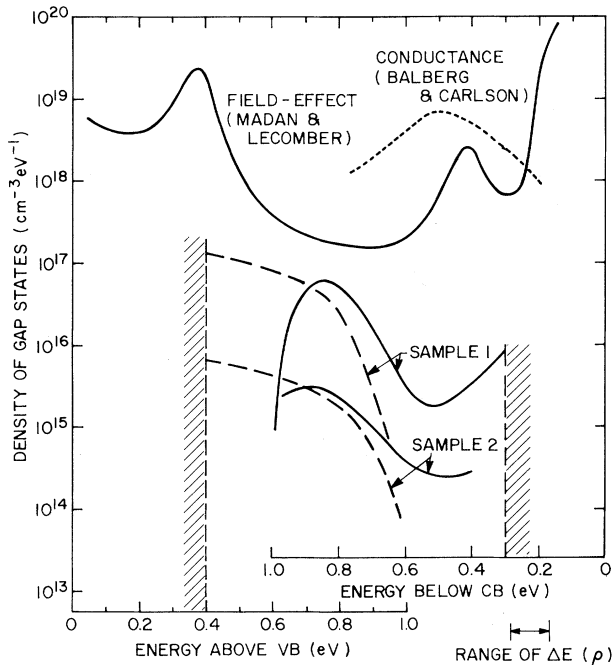

FIG. 2. Superposition of hole trap (dashed) and electron trap (solid) densities of states obtained from DLTS spectra for two of our samples. The vertical dashed lines correspond to the minimum energy observable. Also shown are published data for field-effect (Ref. 1) and conductance (Ref. 11) measurements.

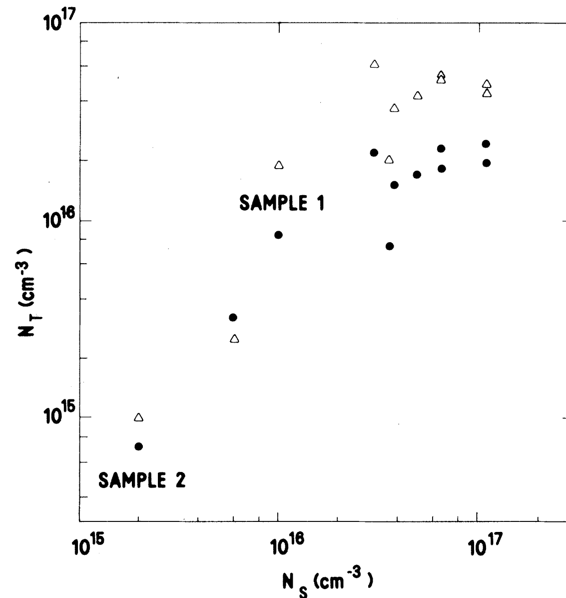

FIG. 3. Integrated deep-trap concentration N_T vs shallow level concentration N_s in various samples. Solid circles are electron traps; open triangles are hole traps.

emission gap of between about 1.6 and 1.8 eV.

The peaklike feature displayed by the voltage-pulse data may correspond to a cutoff in electron emission probability due to the change in equilibrium occupation near midgap. Nonetheless, one can demonstrate the measured activation energy of this feature (0.85 eV ± 10%) is a valid marker to define the energy scale displayed in Fig. 2. In general, the DLTS temperature scale is proportional to an energy scale, $E=\eta(\tau)T$, with the constant of proportionality for a particular DLTS rate window τ^{-1} given by $\eta(\tau)=k\ln(\tau\nu)$, where k is the Boltzmann constant and ν is the exponential prefactor in the expression for the thermal emission rate. The factor ν may often be expected to exhibit a weak temperature dependence. Our electron capture measurements indicate a variation of less than a factor of 10 over the temperature range of the electron emission peak in Fig. 1. Since η depends only logarithmically on ν, the effect on the energy scale is, therefore, at most 8%. Using the 0.85-eV energy marker, we obtain $\eta(100\text{ msec})=28k\pm10\%$ for Figs. 1 and 2. Thus our energies obtained from the DLTS spectrum are accurate to within 0.1 eV.

For any density-of-states determination there exist three different energy scales; namely, thermal activation energy, thermal equilibrium energy, and optical energy. For a rigid lattice these scales are identical, but if lattice relaxation is important these three scales may be quite different. The thermal activation energy scale shown in Fig. 2 is larger than the thermal equilibrium scale by an energy difference which is the height of the barrier to carrier capture.[3] Our electron capture measurements place an upper limit of 0.15 eV on this difference. Therefore our energy scale differs from the thermal-equilibrium energy scale (which would be obtained in an ideal field-effect measurement, for example) by no more than 0.15 eV. The optical energy scale could be significantly larger than either type of thermal energy.

The absolute density scale in Fig. 2 is quite accurate. The result of a capacitance spectroscopy measurement gives the *ratio* of the deep-level-trap concentration N_T to the uncompensated shallow-level concentration N_s.[3,10] Therefore, N_s must be measured to determine N_T. The value of N_s is easily obtained from C-V measurements via the well-known relation

$$N_s=-(C^3/\epsilon qA^2)(dC/dV)^{-1}, \quad (1)$$

where C is the capacitance, ϵ the dielectric constant, A the area of the sample, q is the electronic charge, and V is the bias voltage. In n-type crystalline semiconductors N_s corresponds to the net shallow-donor concentration, $N_D - N_A$. Even in the case of amorphous semiconductors Eq. (1) is a well-defined expression which can be used to obtain N_s. However, since the shallow states are expected to be smeared into a broad spectrum we must define the physical meaning of N_s more clearly. Namely, for the case of electrons

$$N_s = n(T) + \int_{E_c-\delta}^{E_c} g(E')f(E',T)\,dE', \qquad (2)$$

where $n(T)$ is the density of mobile electrons in conduction states above E_c, $f(E,T)$ is the Fermi distribution function for electrons, and δ is the energy of the deepest level which can thermally empty on the time scale of the measurement of dC/dV in Eq. (1). Thus as the time scale of the dC/dV measurement becomes very short δ approaches zero, and as the time to measure dC/dV becomes very long δ approaches midgap and $N_s \simeq n + N_T$. The values for $g(E)$ given in Fig. 2 are accurate to within better than a factor of 2, with the major uncertainty due to spatial variations of N_T and N_s within the sample.

Comparing samples 1 and 2 in Fig. 2 indicates the measured density of states is most likely not an intrinsic property of a-Si:H. This conclusion is strengthened by the integrated trap-concentration data in Fig. 3, which shows the results of TSCAP total–trap-concentration measurements on a number of different samples. In this figure N_T corresponds to the total density of hole or electron traps deeper than about 0.5 eV and N_s corresponds to Eq. (2) with $\delta \simeq 0.5$ eV. Note that *both* the electron and hole traps vary over nearly two orders of magnitude. The two samples with $N_s < 10^{16}$ cm^{-3} were not intentionally doped but had considerably lower resistivity than our normal undoped semi-insulating samples for which capacitance spectroscopy is impossible. The other nine samples were doped with phosphorous. While higher N_s values in this group usually correlated with higher PH_3 concentrations during growth, we found little correlation between N_T and the PH_3 concentration in this doping range.

It is apparent from Fig. 2 that our bulk density of states is totally different from those previously reported.[1,2] The major differences are (1) a maximum at midgap rather than a minimum, and (2) a much lower density in our case (by three to four orders of magnitude at $E_c - 0.4$ eV). Balberg and Carlson[11] have recently shown from conductance measurements (see Fig. 2) that the prominent feature at E $-$ 0.4 eV in the field-effect density of states[1] is characteristic of the surface region. Current transient and conductance measurements on our samples yield similar results, but we have no evidence that such states exist in the bulk. This strongly suggests that the reported densities of states were largely associated with the regions near the surface, in agreement with previous indirect evidence for substantial surface-state concentrations.[6,7]

In conclusion, we have measured for the first time the spectral shape and density of gap states in the bulk regions of n-type a-Si:H films. The density of states does not seem to be intrinsic in doped films with the extrapolated total density of states deeper than 0.5 eV expected to be less than 10^{15} cm^{-3} in undoped films. Our results suggest that the previous measurements of much larger densities of states with a different spectral shape must be associated with the regions near the surface of the film.

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[1] A. Madan, P. G. Lecomber, and W. E. Spear, J. Non-Cryst. Solids 20, 239 (1976).

[2] M. Hirose, T. Suzaki, and G. H. Döhler, Appl. Phys. Lett. 24, 234 (1979).

[3] D. V. Lang, in *Thermally Stimulated Relaxation in Solids*, edited by P. Bräunlich, Topics in Applied Physics Vol. 37 (Springer-Verlag, Berlin, 1979), p. 93.

[4] J. D. Cohen, D. V. Lang, J. C. Bean, and J. P. Harbison, J. Non-Cryst. Solids 35-36, 581 (1980).

[5] R. S. Crandall, to be published.

[6] J. C. Knights and D. K. Biegelson, Solid State Commun. 22, 133 (1977).

[7] C. R. Wronski and D. E. Carlson, Solid State Commun. 23, 421 (1977).

[8] I. Solomon, T. Dietl, and D. Kaplan, J. Phys. (Paris) 39, 1241 (1978).

[9] D. G. Ast and M. H. Brodsky, Bull. Am. Phys. Soc. 24, 399 (1979).

[10] D. V. Lang, J. Appl. Phys. 45, 3023 (1974).

[11] I. Balberg and D. E. Carlson, Phys. Rev. Lett. 43, 58 (1979).