Identification of the Dangling-Bond State within the Mobility Gap of a-Si:H by Depletion-Width-Modulated ESR Spectroscopy

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The first observation is reported of an absorption (dark) ESR signal specifically from unoccupied gap states within the space-charge region of n-type a-Si:H diode junctions. The detected resonance with $g = 2.0053 \pm 0.0003$ is associated with the singly occupied dangling-bond defect. The applied-bias and temperature dependence identifies this signal with the well defined midgap defect band observed in deep-level transient spectroscopy. The results also imply a positive correlation energy, $U \gtrsim 0.2$ eV, between the singly and doubly occupied centers.

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Observing and characterizing the electronic states within the mobility gap of hydrogenated amorphous silicon (a-Si:H) is of key importance in understanding the fundamental properties of this material. The presence of one or more distinct defect bands within the gap is most readily revealed by a variety of electron-spin-resonance (ESR)-related measurements,[1-5] by photoluminescence,[6] and more recently by deep-level transient spectroscopy (DLTS),[7,8] by infrared quenching,[9] and by some detailed photoconductivity measurements.[10] Of special interest is the ESR signal of g value near 2.0055 which, from its predominance in amorphous silicon samples with little or no hydrogen, together with results from ESR studies on crystalline silicon surfaces and grain boundaries, is associated with the singly occupied dangling-bond state.[1-3] However, apart from some estimates based on rather indirect arguments,[5,6] the electronic energies characteristic of this center in relation to the mobility gap have not yet been determined.

In this Letter we report the identification of this dangling-bond state within the mobility gap of a-Si:H by a new experimental technique: observing the changes in the dark absorption ESR signal as a result of modulating the width of the depletion region in n-type doped a-Si:H diode junctions. The temperature and bias dependences are compared to detailed admittance and DLTS measurements on the same samples. Such comparisons verify the bulk nature of the signal observed and, moreover, allow us to associate a spin signal with g value near 2.0055 specifically with the defect band observed in DLTS which lies near the center of the mobility gap.

Our PH_3-doped a-Si:H samples were prepared by the standard rf decomposition of SiH_4 as described elsewhere.[7,8] As in most of the samples studied in DLTS, a p^+ crystalline Si substrate was used which assured a diode p^+-n junction with a high intrinsic barrier. (This is required to vary the occupation of gap states near midgap.) Since the width of the space-charge region could only be varied by a few tenths of a micron, we employed the largest-area diodes compatible with the microwave cavity and Dewar geometry (4×10 mm^2) necessitating samples with large uniform areas of electrically defect-free material. These large-area diodes were defined by a Au/Cr contact evaporated on top of the a-Si:H layer. The ESR measurements were made in the X band (near 9.3 GHz) with a Varian E-4 spectrometer. The sample with its conducting substrate and electrical contacts was positioned within the low E field region of a TE_{102} mode resonant cavity. An inserted flow-through Helitran Dewar allowed the temperature of the sample to be varied between 10 and 400 K without affecting the cavity Q or overall microwave bridge sensitivity (the loaded cavity had a reasonable Q of about 2000). The calibration of the system was made by attaching a precalibrated dehydrogenated a-Si:H sample to the same probe assembly used in the diode measurements.

In addition to lock-in detection of a 100-kHz field modulation, a second phase-sensitive detector measured the signal synchronous with a 3.75-Hz square-wave voltage applied to the a-Si:H sample. The resulting signal is thus a derivative absorption spin signal from the *change* in occupation of gap states due to the changes in the applied voltage. Since the total change in the volume of the depletion region is $\sim 10^{-5}$ cm^3, many hours of signal averaging for each set of traces was required to observe the effect. During these long runs, the stability of the system was periodically monitored with a diphenylpicrylhydrazyl frequen-

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cy marker. Overall drifts were found to be small and are corrected for in the data reported here.

A series of measurements illustrating the temperature and applied voltage dependence of one sample, JH272, is shown in Fig. 1. In spite of the relatively low signal-to-noise ratio for each set of traces, we have determined $g = 2.0053 \pm 0.0003$ from the sum of all the high-temperature traces ($T \geq 320$ K) which is displayed as the bottommost curve of Fig. 1. The *sign* of the signal indicates a *larger* spin signal for *larger* reverse bias. This establishes that these unpaired spins are created by *removing* electrons from states normally filled below the neutral bulk Fermi level. ($E_F{}^0 = E_c - 0.15$ eV as determined by ac conductivity measurements.)

Each series of traces in Fig. 1, with the exception of 340 K (*b*), was generated by switching the bias applied to the p^+-n junction between 0 and -3.5 V. This resulted in a change in the depletion width, W, between 0.15 and 0.31 μm. Here $W = \epsilon A/C$ is defined operationally from the *measured* 100-kHz capacitance, C, where ϵ is the dielectric constant and A is the diode area. For the series of traces 340 K (*b*), the applied bias was switched between -1.25 and -3.5 V which resulted in a ΔW one half as large as the case described above. A comparison of the 340 K (*a*) and 340 K (*b*) traces shows indeed a drop in the signal by a factor of 2. This linear dependence of signal amplitude on ΔW attests to the bulk origin of the signal observed. Moreover, changes in surface-state occupation are unlikely to occur under the conditions used for 340 K (*b*) since the applied bias plus the intrinsic barrier height is never less than the mobility gap energy, E_g, at the diode interface.

Figure 1 indicates that the signal, which is within the noise below 200 K, increases monotonically with temperature to about 360 K and then "saturates." In Fig. 2 the temperature dependence of the signal amplitude is shown in more detail. The maximum signal for JH272, normalized to the change in depletion width volume, is $(4.9 \pm 0.6) \times 10^{16}$ spins/cm^3.

The density of states, $g(E)$, for sample JH272 derived from capacitance DLTS and thermally

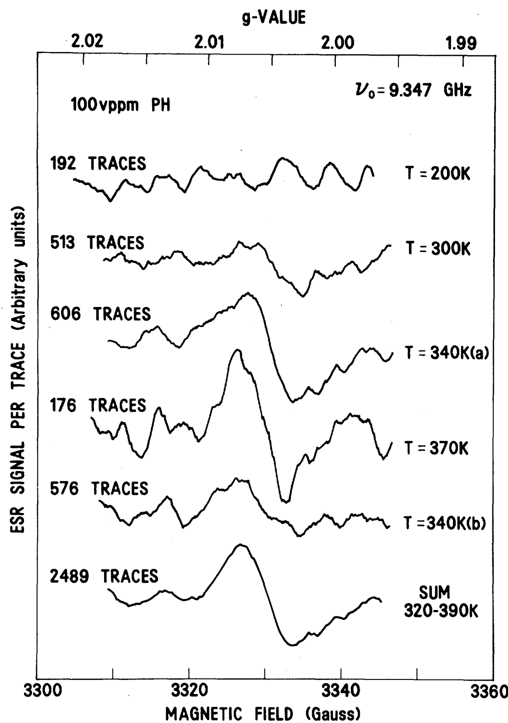

FIG. 1. Depletion-width–modulated ESR signal as a function of temperature, taken under the following conditions: a modulation amplitude of 5 G, a sweep time of 2 min, and a time constant of 3 sec. The detailed bias modulation conditions are explained in the text and are identical for all traces except 340 K (*b*), for which the resulting change in depletion width is one half that of the other curves.

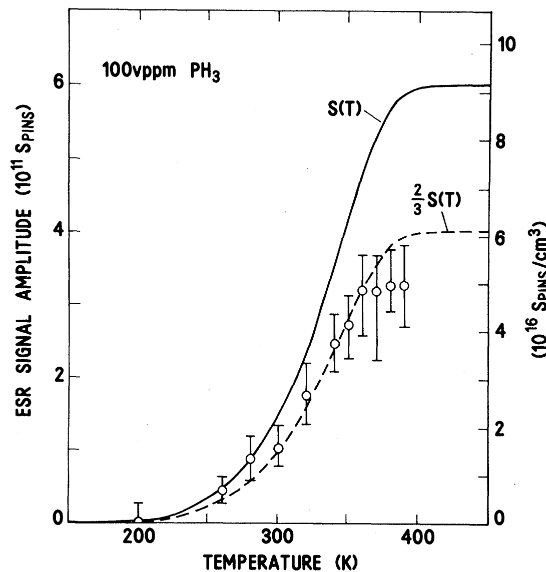

FIG. 2. ESR signal amplitude vs temperature: Experiment and theory. The solid line, $S(T)$, was computed from the DLTS/TSCAP-determined density of states with *no* adjustable parameters. The dotted line, $\frac{2}{3}S(T)$, has been added to aid in the comparison of the relative temperature dependences. The right-hand scale is normalized to the volume defined by the change in depletion width.

stimulated capacitance measurements (TSCAP) is shown in Fig. 3. Since the methods used to observe the ESR spectra in Fig. 1 can only vary the occupation of states above midgap, the spin signal can only result from defect bands above midgap. The temperature dependence furthermore rules out the shallower states from the exponential tail below the conduction-band mobility edge (E_c). If we assume that all unoccupied states deeper than 0.5 eV in Fig. 3 result in one unpaired spin, then this $g(E)$ predicts that the temperature dependence of the spin signal, $S(T)$, will be given by

$$S(T) = G\frac{T_0}{T}\int_0^{t=\pi/\omega} dt' \sin\omega t' \times \int_{E_F 0}^{E_c - E_g/2} dE\, R(E) \exp(-e_n t'), \qquad (1)$$

where ω is the lock-in (angular) frequency, G is the experimentally determined calibration factor at $T = T_0$, and $R(E)$ is the energy-dependent response function for the occupation deficit of states below 0.5 eV. The function R is numerically calculated directly from $g(E)$ and is described in detail by Cohen and Lang.[11] Here e_n denotes the usual electron emission rate from states to the conduction-band mobility edge from an energy E below E_c:

$$e_n(E,T) = \nu_n \exp(-E/k_B T). \qquad (2)$$

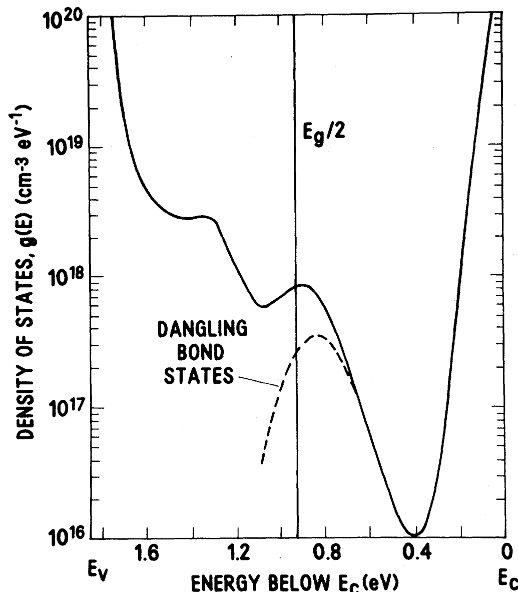

FIG. 3. Density of states for JH272, as determined from DLTS and TSCAP measurements. The dotted curve indicates the position of the states contributing to the spin signal, as deduced from Fig. 2.

Equation (1) assumes that the variation in gap state occupation is totally emission limited.

Using $\nu_n = 2\times10^{13}$ sec^{-1}, determined from DLTS measurements,[12] we predict the solid line shown in Fig. 2. The agreement for both the temperature dependence and magnitude is quite good considering that there remain uncertainties in determining absolute magnitudes from both kinds of measurements. These include possible differences in cavity loading conditions between the sample and our calibration standard, possible reduction of rf fields within the sample due to the conducting contacts, and a factor of 1.5 remaining systematic uncertainty in interpretating the DLTS signal in terms of an absolute $g(E)$.[8] We also mention that capacitance DLTS and the junction ESR measurements are most sensitive to different spatial regions within the depletion width, and that some eivdence exists for spatial variation of $g(E)$ is this sample (factor of ~1.5) from capacitance-voltage measurements.

Thus the fact that the maximum total spin density is about a factor of 1.5–2 below that predicted from DLTS is probably not significant. It is quite plausible, however, that because of overlapping defect bands, only a fraction of the DLTS $g(E)$ at midgap for JH272 is due to the dangling-bond state. [We note that a different sample indicated a spin signal from 80% of the DLTS $g(E)$ at midgap.] On the other hand, we believe that the saturation of the spin signal at a temperature below that predicted by DLTS *is* significant and indicates that the dangling-bond state actually lies slightly *above* midgap as shown in Fig. 3.

Two other conclusions regarding the nature of the dangling-bond defect can be made with reasonable confidence: (1) The very fact that the DLTS-deduced $g(E)$ near midgap produces a spin signal of comparable size implies a fairly large *positive* correlation energy, U, between the singly and doubly occupied center. A value of U smaller than the observed defect band width of ~0.2 eV would result in the spin centers in the upper half of the defect band losing a second electron before those in the lower half lose their first. Since the doubly ionized defect contains no unpaired spin, the signal shown in Fig. 2 would be expected to reach a maximum and then begin to fall off at the higher temperatures, rather than simply saturate. Therefore, the saturation of the spin signal at temperatures characteristic of less than $E_g/2$ implies $U \gtrsim 0.2$ eV. This is consistent with the value (U~0.4 eV) proposed by Dersch, Stuke, and Beichler[5] to explain the appearance and strength

of the dangling-bond ESR signal as a function of doping. (2) Since it has been shown that $g(E)$ increases dramatically near midgap as a result of PH_3 doping[7,8] we must conclude that part of the result of phosphorus doping is the creation of dangling-bond defects. The same conclusion has been reached by Street *et al.* from recent ESR and defect luminescence compensation doping studies in a-Si:H.[13]

In conclusion, the present experiments identify a defect center with ESR g value of 2.0053 ± 0.0003 with a characteristic energy of 0.85 eV below E_c. Such a defect band is readily apparent in the DLTS-determined $g(E)$ curves for all n-type doped a-Si:H samples studied thus far. This band is identified as the energy position of the second electron bound to the dangling-bond center in a-Si:H.

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[12] This value of ν_n was obtained experimentally in Ref. 7 for the electron emission DLTS peak near midgap which is the very feature we find associated with the observed spin effect. The value of ν_n for nearby energy has been shown not to deviate markedly from this value (Ref. 8), and, moreover, any such variation only enters into the calculated temperature dependence in a logarithmic fashion.

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