Spin-dependent recombination at dangling bonds in *a*-Si:H

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(Received 4 February 1982)

Studies of optically detected magnetic resonance (ODMR) provide detailed information about recombination in hydrogenated amorphous silicon. Two different spin-dependent effects are found which quench the luminescence. One process is identified as nonradiative recombination at dangling bonds. Time-resolved ODMR measurements confirm that the effect occurs at unthermalized spins and provide a new technique for measuring spin-lattice-relaxation times.

The technique of optically detected magnetic resonance (ODMR) is interesting because it directly links the structural information obtained by ESR to the electronic properties studied by luminescence.[1] ODMR occurs because the transition probability between two paramagnetic states depends on the spin orientations, and so the recombination rate will change when either spin is brought into microwave resonance. The present paper reports ODMR studies of dangling bonds in hydrogenated amorphous silicon. Amorphous silicon is well known to contain paramagnetic centers with a g value of 2.0055,[2] which have been identified as silicon dangling bonds,[2,3] and which are an important trapping and recombination center.[4] For example, the intensity of the dominant luminescence band at 1.4 eV is strongly reduced by the presence of dangling bonds, indicating that the defects are nonradiative states.[5] Previous ODMR measurements found at least three distinct resonances, and there have been several attempts to interpret the results in terms of specific models.[6–9] One recent study concludes that dangling bonds are in fact radiative centers.[1,9] If this were so, then a major reassessment of the luminescence data would be required. We report the ODMR of time-resolved luminescence and show that this is a powerful technique for investigating both the recombination and spin properties. The combined information from the time dependence and the defect density dependence of ODMR confirm that dangling bonds are indeed nonradiative centers in *a*-Si:H.

Our ODMR measurements are made in an X-band ESR spectrometer. The cavity contains a variable temperature cryostat and an optical access. The luminescence is measured in back reflection, perpendicular to the magnetic field, using a cooled Ge detector with a response time of 300 nsec. The luminescence consists of a single broad band at 1.3–1.4 eV, and all the measurements reported here use the total luminescence emission. Unlike Depinna and Cavenett,[1,9] we find no change in the ODMR line shape across the luminescence spectrum. $\Delta L/L$ does increase with decreasing luminescence energy, but this does not affect the interpretation of the data and is related to the distribution of radiative lifetimes, as discussed elsewhere.[10] In the samples used by Depinna and Cavenett there is a second luminescence band at 0.9 eV, which perhaps explains their different results. In ESR it is found convenient to modulate the magnetic field to obtain a derivative of the absorption line shape. This technique allows for a precise determination of the g value. We therefore use this technique for ODMR rather than the more conventional modulation of the microwave power.

The *a*-Si:H samples were prepared by plasma decomposition, as described elsewhere.[5] By varying the deposition conditions, the spin density, N_s, can be varied over about three orders of magnitude.[5] Figure 1(a) shows the magnitude of the spin-dependent change in luminescence intensity $\Delta L/L$ for a selection of samples at 85 K. In each case, the resonance results in a reduction of the luminescence intensity and is referred to as a quenching line. When N_s is less than $\sim 3\times 10^{16}$ cm^{-3}, $\Delta L/L$ is small and independent of N_s. The ODMR line shape [see Fig. 1(c)] contains two resonances and closely resembles the *light-induced* ESR spectrum of similar samples.[11] This pair of resonances, with g values 2.004 and 2.01, has been attributed to singly occupied electron and hole band-tail states, respectively.[11] The magnitude of $\Delta L/L$ increases when N_s exceeds about 10^{17} cm^{-3} and reaches a peak near 2×10^{18} cm^{-3}. For these samples, the ODMR spectrum changes and is similar to the dangling-bond ESR spectrum [see Fig. 1(b)]. However, the interpretation of the ODMR is complicated by the fact that two resonances should normally be present to give the spin-dependent effect. Evidently the broad band-tail hole resonance does not make a significant contribution to the ODMR spectrum of Fig. 1(b). The narrow band-tail electron resonance is too close in g value and width to be resolved from the dangling band. However, close inspection of the ODMR spectrum reveals a small reduction in g value and slightly increased asymmetry compared to the dangling-bond ESR. Both features are consistent with the addition of the

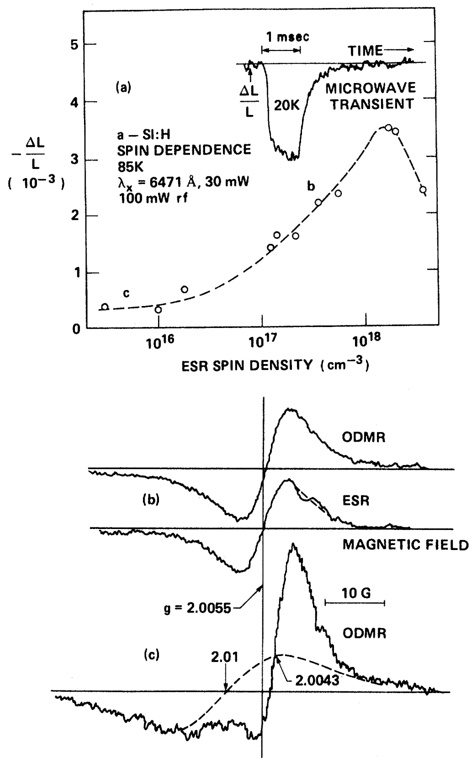

FIG. 1. (a) Dependence of $\Delta L/L$ on the dangling-bond spin density as measured by ESR. The insert shows the transient response of sample b to a microwave pulse. (b) Direct comparison of the ODMR and ESR line shape for the sample labeled b in (a). The weak resonance on the high-field side of the ESR spectrum is from the glass substrate. (c) ODMR line shape for sample c in (a), showing the estimated deconvolution into two lines.

electron resonance to that of the dangling bond.

We conclude both from the ODMR line shape and magnitude that the spin dependence occurs through dangling bonds when N_s exceeds 10^{17} cm^{-3}, but through a different mechanism involving only band-tail electrons and holes at lower N_s. This is the first time that two different quenching effects have been identified, and this may explain some of the conflicting interpretations in previous studies. In the remainder of this paper we focus only on the ODMR in samples with $N_s > 10^{17}$ cm^{-3}.

More specific information about the spin dependence at dangling bonds is obtained from time-resolved measurements. One technique uses continuous illumination and measures the response of $\Delta L/L$ to a microwave pulse. These data in Fig. 1 show that for a sample with $N_s = 3.5 \times 10^{17}$ cm^{-3}, there is a slow onset and decay of $\Delta L/L$ with time constant decreasing from 350 μsec at 15 K to ~ 30 μsec at 100 K. From an analysis of the recombination rate equations, the Hull group[1,9,12] has shown that this type of microwave response is the signature of a nonradiative process. A radiative transition has a qualitatively different response with a transient spike at the beginning and end of the pulse. The dangling-bond transition is therefore nonradiative.

A different type of time-resolved measurement is preformed with a short illumination pulse and by gating the detection of the transient luminescence response with a variable delay. Microwave power is applied continuously. Figure 2 shows the results of this experiment for the sample with $N_s = 3.5 \times 10^{17}$ cm^{-3} and several different temperatures. Because the luminescence decay has a broad distribution of time constants, we are able to observe ODMR over four decades in time. The data show two distinct features. One is an increase in $\Delta L/L$ with time for which the magnitude of $\Delta L/L$ is almost independent of tem-

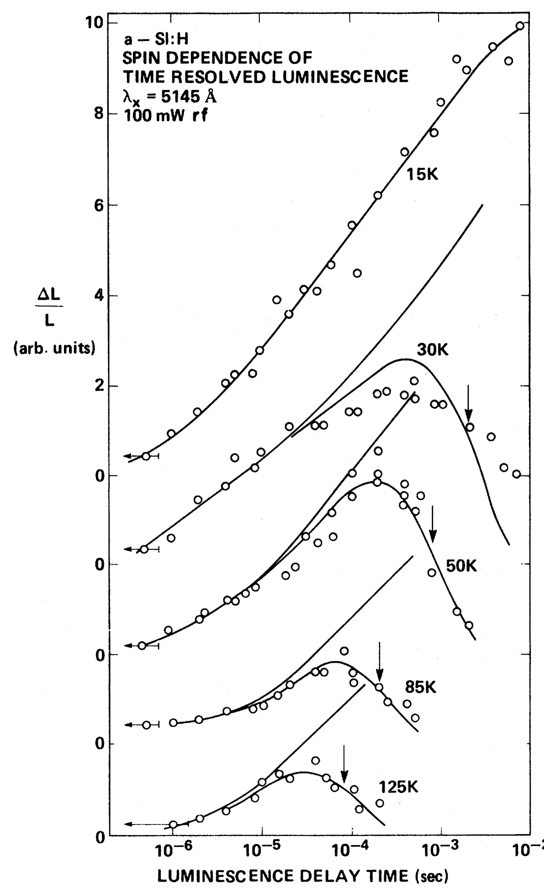

FIG. 2. Values of $\Delta L/L$ as a function of delay time from time-resolved luminescence in a sample with $N_s = 3.5 \times 10^{17}$ cm^{-3}. The vertical axis is the same for each set of data. Solid lines show the extrapolated $F(t)$ and the fit to Eq. (1) as described in the text. Arrows show the values of T_1 used in the fit.

perature. The second feature is a cutoff in $\Delta L/L$ at a time that decreases rapidly with increasing temperature.

The behavior at times below the cutoff demonstrates that the spins are unthermalized. Thermalized spins yield $\Delta L/L \sim (g\mu_B H/2kT)^2$ which has the wrong temperature dependence and a much smaller magnitude. Instead, the temperature-independent $\Delta L/L$ can only occur at times short compared to the spin-lattice relaxation time T_1. This result therefore suggests that the cutoff occurs because T_1 of either of the spins involved in the spin-dependent effect has been reached. T_1 is then found by assuming that $\Delta L/L$ is given by

$$\Delta L/L = F(t)\exp(-t/T_1) \quad , \tag{1}$$

where $F(t)$ is the response at time t for unthermalized spins. The procedure used to find T_1 was to extrapolate the short-time behavior based on the observed response at the lowest temperature. This yields an empirical $F(t)$ (shown in Fig. 2) which is then used to obtain a fit of Eq. (1) to the data. As shown in Fig. 2, this procedure yields a good fit except at 30 K. We speculate that the deviation here may be due to a distribution of T_1 values. At 15 K no cutoff is found in the range accessible to investigation, and so a lower limit on T_1 is taken to be 20 msec. To check these results, we have measured the ESR saturation properties of the dangling-bond resonance. Provided the magnetic field modulation frequency is kept low enough to avoid rapid passage effects, the ESR is observed to saturate like an ideal inhomogenous line. T_1 can then be obtained as described by Portis.[13] The ODMR sample did not contain enought total spins to perform the experiment at low temperature, and so a much larger volume of *a*-Si:H was used which had a spin density of $\sim 10^{16}$ cm^{-3}. Even so, the measurements could only be performed down to 100 K owing to the need to reduce the modulation frequency as T_1 increased. The room-temperature value of T_1 deduced for this sample agreed well with that of the ODMR sample using the same technique. The T_1 values obtained from ESR saturation are compared to the ODMR results in Fig. 3. The two sets of data have the same functional form, but the ESR values are smaller by about a factor of 2. However, this difference is probably within the inherent uncertainties of the two experiments. We conclude that the ODMR data are indeed measuring T_1, and that the values are probably specific to dangling bonds. Thus at high temperature $T_1 \sim T^{-2}$ with a stronger temperature dependence below 100 K. This behavior is as predicted for a Raman spin-lattice relaxation process as suggested by Hasegawa and Yazaki,[14] who also found approximately a T^{-2} dependence at high temperature.

Thus ODMR of time-resolved luminescence provides a novel technique for measuring T_1 of recombination centers. Although the method is not as

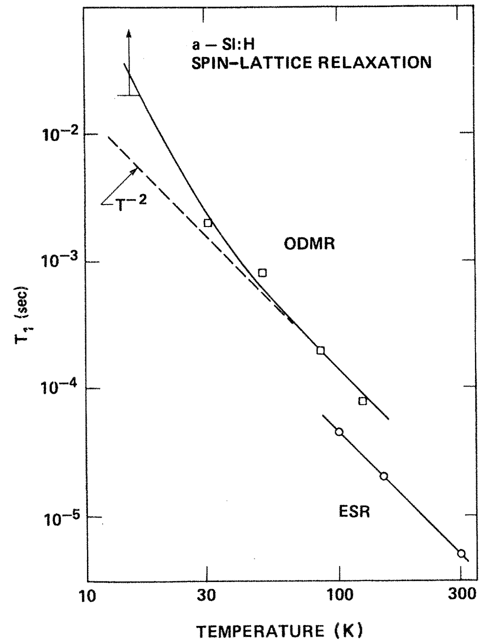

FIG. 3. Values of T_1 as a function of temperature obtained from the ODMR data of Fig. 2 and from ESR saturation measurements.

direct or as generally applicable as pulsed ESR techniques, it has an advantage of being very sensitive, particularly in measurements on thin films. In the present experiments, the excitation source has an absorption depth of ~ 1000 Å, and so the luminescence is emitted from a volume containing only about 10^{12} spins.

Our model[4] for nonradiative recombination is that the transition occurs by tunneling from the conduction-band tail to randomly distributed dangling bonds. Given an average Bohr radius for band-tail electrons of ~ 10 Å, it is predicted that low-temperature nonradiative recombination at dangling bonds dominates as spin densities greater than 10^{17} cm^{-3} (Ref. 5). We consider that the present results provide overwhelming confirmation of this model. We find that in samples with $N_s > 10^{17}$ cm^{-3} the ODMR is indeed dominated by the dangling-bond resonance, with an indication that the band-tail electron resonance is also present. In addition, the microwave pulsing experiment shows that the spin-dependent transition is definitely nonradiative. The spin dependence arises from unthermalized spins, as shown by Fig. 2. The model of Kaplan *et al.*[15] should apply to this case,[6] giving a quenching ODMR, as observed. The observation of $\Delta L/L$ over four orders of magnitude in time is indicative of a broad distriubtion of nonradiative rates, and in fact we show elsewhere that the tunneling model gives a reasonable quantitative description of the time-resolved $\Delta L/L$.

In summary, we have shown that ODMR provides detailed information about nonradiative recombination in *a*-Si:H. The time-resolved measurements are a particularly powerful technique. Finally, we also obtain new information about the spin-lattice relaxation times.

ACKNOWLEDGMENTS

We are grateful to J. C. Knights for providing samples and to B. C. Cavenett and S. Depinna for discussion and copies of their unpublished work. This work was partially supported by the Solar Energy Research Institute under Contract No. XJ-0-9079-1.

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