OPTICALLY DETECTED MAGNETIC RESONANCE STUDIES OF UNDOPED a-Si:H

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ABSTRACT

Photogenerated carrier dynamics in undoped a-Si:H have been studied by photoinduced absorption (PA), photoluminescence (PL) and their respective optically detected magnetic resonances: PADMR and PLDMR. We have detected for the first time the "$g = 4$" resonance in PADMR, in addition to the previously measured narrow and broad resonances at $g \approx 2$. We compare the PADMR and PLDMR resonances over a broad spectral range of detection energies and conclude from the similarities that they share a common underlying mechanism. The PADMR spectra of the narrow and the broad resonances at $g \approx 2$, measured in the spectral range of 0.7 to 1.7 eV, suggest that a correlation exists between the two resonances and PA.

INTRODUCTION

The application of electron spin resonance (ESR) using photoluminescence (PLDMR) to investigate radiative and nonradiative recombination processes in a-Si:H is well established.[1-6] In this method changes in photoluminescence (PL) intensity induced by magnetic resonance are detected as the magnetic field is swept. Resonances occur when the microwave photon energy equals the Zeeman splitting of the two levels, i.e., $h\nu_0 = g\beta H$, where ν_0 is the microwave frequency, g is the gyromagnetic ratio, β is the Bohr magneton, and H is the magnetic field. Boulitrop[1] has observed three PL enhancing resonances and one PL quenching resonance. Morigaki et al.[7] have identified one enhancing and two quenching resonances attributed to holes at acceptors (A center) and electrons at two kinds of donors (D_1 and D_2 centers). Street[3] has identified a quenching resonance, which he attributes to tunneling of band tail electrons to dangling bonds. In samples with a low density of deep defects (silicon dangling bonds), he found an additional quenching resonance tentatively attributed to Auger recombination and an enhancing resonance due to trapped carriers in band tail states. Depinna et al.[5] found two enhancing resonances, which they attribute to recombination of distant electron-hole pairs, and one quenching signal attributed to recombination of close pairs.

As is evident from the attributions mentioned above, there is not a consensus on the interpretation of the results, in part due to the use of films deposited using different experimental conditions and in part due to the complex spectra consisting of overlapping resonances with similar g-values. In contrast to PLDMR, ESR detected photo-induced absorption (PADMR) measures changes in the transmission of a probe light due to changes in the recombination rates of the photogenerated carriers. This technique has several advantages over PLDMR as it is not constrained by the relatively weak PL intensity or by the limited range of the PL spectrum. PADMR uses an external light source, and is therefore sensitive to a broader spectral range and a higher probe intensity as compared to PLDMR. In addition, PADMR can also examine nonluminescent materials or materials where the PL is very weak. The first PADMR measurements in a-Si:H were performed by Hirabayashi and Morigaki,[8] who observed a resonance at $g \approx 2$ at nearly the position as their D_2 line identified in PLDMR. A comparison of the spectral dependence of PADMR with the photo-induced absorption (PA) spectrum has been presented for energies above 0.8 eV.[9]

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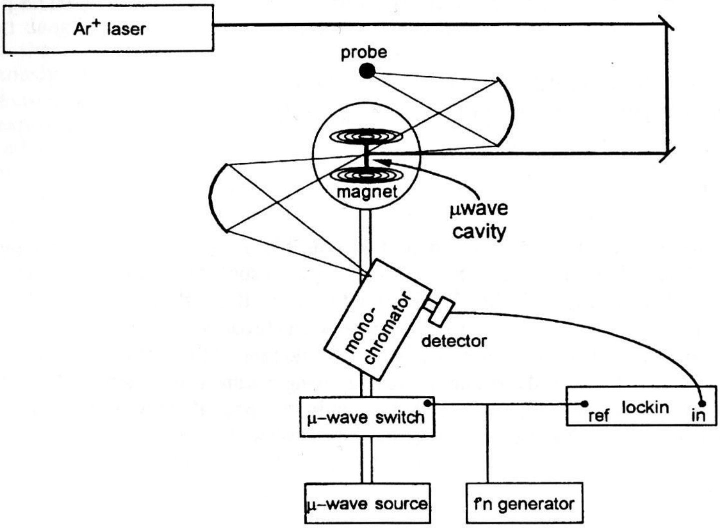

Fig. 1. The PADMR spectrometer. The Ar$^+$ laser is the pump beam and the probe beam is a tungsten incadescent lamp followed by a monochromator. The lock-in amplifier is referenced to the microwave modulation frequency.

We have performed PLDMR and PADMR measurements on a-Si:H to elucidate the origin of the $g \approx 4$ resonance previously detected in PLDMR and to find correlations among the narrow and broad resonances at $g \approx 2$ and $g \approx 4$.

EXPERIMENTAL

The PADMR spectrometer is shown in Fig.1. The sample is mounted inside a high-Q (~ 300) microwave cavity (3 GHz) and constantly illuminated with a pump laser beam (from an unfocused Ar$^+$ laser, 514.5 nm line), and an incandescent probe light beam (from a tungsten lamp). The cavity is installed in a cryostat equipped with optical windows and cooled with liquid helium. A superconducting magnet produces the magnetic field and a UHF-generator provides the microwaves. The microwaves are square-wave modulated at about 700 Hz, and the PL and transmission (T) signals are detected with a Si diode or a cooled Ge detector using phase sensitive techniques. The a-Si:H sample used in this work was prepared by glow discharge deposition on a sapphire substrate. The sample had a thickness of about 7 μm. In the data presented in this paper interference fringes due to internal reflections have been spectrally averaged.

Magnetic field swept PLDMR and PADMR spectra (at fixed probe wavelength) are presented as well as energy-dependent PADMR at fixed H. We refer to δPL and δT as changes induced by magnetic resonance in PL and T, respectively, and to ΔT as a changes in transmission due to PA. N is the density of steady state photoexcited charge carriers and δN its resonant change. The following equations hold for ΔT and δT:

$$-\frac{\Delta T}{T} = N\sigma d \qquad (1)$$

$$\frac{\delta T}{\Delta T} = \frac{\delta N}{N} \qquad (2)$$

RESULTS AND DISCUSSION

Figures 2 (a) and (b) show the PLDMR and PADMR spectra as functions of H for undoped a-Si:H over the range from 0 to 2000 G. In both spectra three resonances are identified, a weak resonance at approximately 525 G (A), a narrow peak at 1070 G (B), and a broad resonance (FWHM ≈ 200 G) centered around 1070 G (C). The positive sign of δdPL corresponds to an enhancing PL at resonance, the negative sign of δN shows a decrease of excited charge carriers at resonance. Overall the PLDMR and PADMR spectra shown in Fig. 2 are quite similar. We therefore conclude that these features share a common origin due to the same subset of excited electrons and holes. For δPL/PL and δN/N at the three resonances A, B and C we find approximately:

	δPL/PL	δN/N
A	0.8×10^{-3}	1×10^{-3}
B	4×10^{-3}	8×10^{-3}
C	0.5×10^{-3}	0.9×10^{-3}

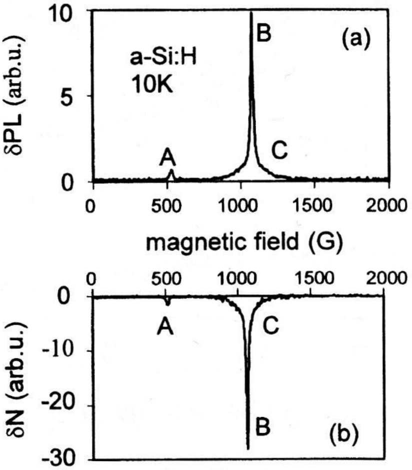

Fig. 2. The PLDMR (a) and the PADMR (b) spectra as function of magnetic field for a-Si:H at 10 K for magnetic fields up to H = 2000 G. The three resonances are designated A, B and C.

The similarities between δPL/PL and δN/N shown in the above table may ultimately allow for a quantitative measure of the low temperature quantum efficiency for radiative recombination, a parameter that is difficult to measure by other means. Under resonance conditions the total number of excited charge carriers decreases both radiatively and non-radiatively. The δPL and δT spectra are measures for changes of radiative or non-radiative recombination and the total number of excited charge carriers, respectively. Therefore, a comparison of δPL/PL and δT/ΔT could lead to a quantitative estimate of the relative efficiencies of the recombination paths.

To examine the nature of the two "g = 2" PADMR resonances we performed energy dependent PADMR measurements at both resonances B and C over the probe range from 0.8 eV to 1.7 eV as shown in Fig. 3. For the resonances B and C we set the magnetic field to 1070 G and 1020 G, respectively. (See inset to Fig. 3.) We observe a decrease in the featureless spectra B and C of about a factor of 2 between probe energies of 0.8 eV and 1.7 eV. Furthermore, if we scale the spectrum of resonance C by a factor of 4.7 we find a good correspondence between the spectra of resonances B and C (Fig. 3). We have also measured the PADMR spectrum of resonance A and found it to be similarly broad.[10] There exists a strong similarity between the spectrum of resonance B and the PA spectrum (Fig. 4), although the decrease below about 0.9 eV remains to be confirmed. We were not able to measure the PA above 1.4 eV due to thermal modulation artifacts. The featureless PADMR spectra are not surprising for a-Si:H since optical spectra of amorphous semiconductors are known to be much broader than their crystalline counterparts.

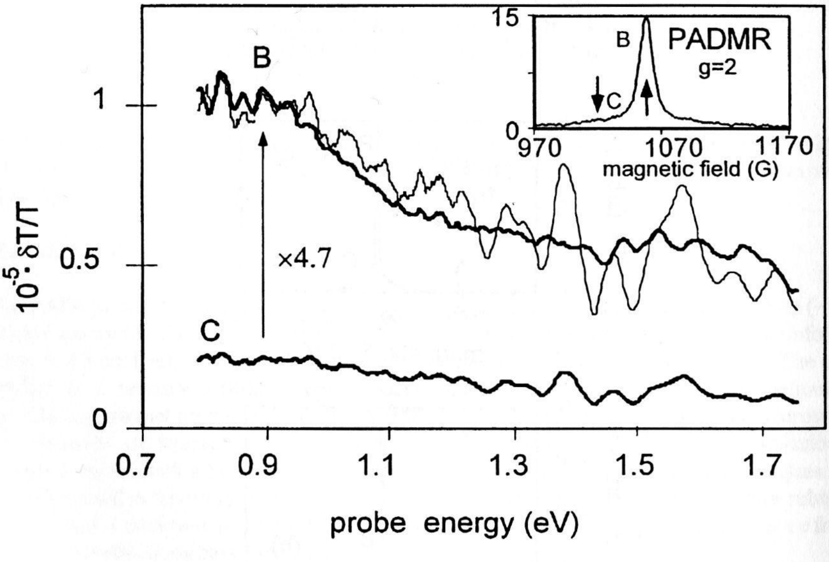

Fig. 3. The probe frequency dependences of the PADMR spectra of resonances B (H = 1070 G) and C (H = 1020 G) as defined in the inset. Resonances C is also shown scaled by a factor of 4.7 for ease of comparison.

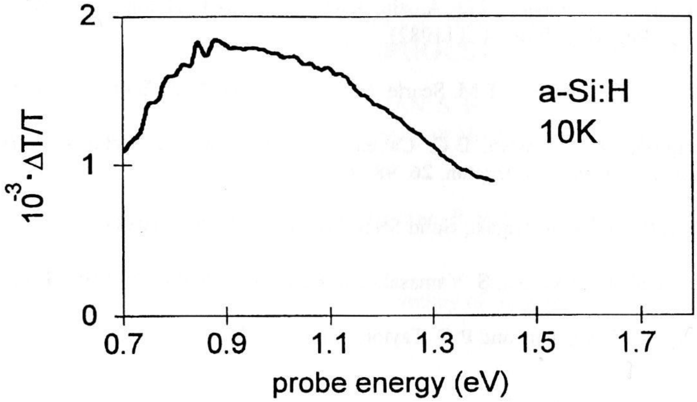

Fig. 4. The PA spectrum of a-Si:H at 10 K measured with the same PADMR spectrometer as in Fig. 1.

SUMMARY

We have detected the "g = 4" resonance in PADMR and were therefore able to compare the magnetic spectrum of PLDMR with PADMR. The similarity suggests a common underlying physical mechanism that will probably allow us to estimate the quantum efficiency of radiative recombination at 10 K in a-Si:H. From the spectral similarities of the narrow and the broad g ≈ 2 resonances seen in PADMR and the similar lineshapes between the probe energy dependence of the PADMR and PA spectra over the probe range of 0.8 to 1.4 eV we conclude that there exists a similar origin for the two resonances, namely spin-dependent recombination of photogenerated electron-hole pairs.

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