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Radiation-induced paramagnetism in *a*-Si:H

W. M. Pontuschka, W. W. Carlos, and P. C. Taylor
Naval Research Laboratory, Washington, D.C. 20375

R. W. Griffith
Brookhaven National Laboratory, Upton, New York 11973

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Several paramagnetic centers have been observed in doped and undoped *a*-Si:H after x irradiation at 77 K. The paramagnetic responses in nominally undoped *a*-Si:H include (1) an increase in the Si "dangling-bond" line, and (2) trapped NO_2 molecules. In O- and N-doped hydrogenated *a*-Si [*a*-Si:(H,O,N)] at least four responses are observed: (1) an increase in the Si "dangling-bond" line, (2) an oxygen-associated hole center which is probably a singly coordinated oxygen bonded either to a silicon or to another oxygen, (3) an sp^3-hybridized dangling bond on a silicon which is bonded to three oxygens (E' center), and (4) neutral, atomic hydrogen trapped in the *a*-Si:(H,O,N) matrix.

I. INTRODUCTION

The successful doping of hydrogenated amorphous silicon (*a*-Si:H) with controlled amounts of impurities[1,2] has led to the use of these materials in photovoltaic devices. Although the incorporation of intentional dopants in layers at ohmic contacts and at junctions is beneficial to device performance, the presence of inadvertent impurities in the active bulk material can often be deleterious. Two of the most pervasive of the unwanted impurities are oxygen and nitrogen. Most device quality films[3] contain on the order of 0.1 and 0.01 at. % of O and N, respectively.

Previous studies have shown that the device performance of solar cells made from *a*-Si:H is degraded when impurities such as O_2 and N_2 are present in the silane discharge.[4,5] At low concentrations, the presence of both O_2 and N_2 together produces synergistic effects.[5,6] In films prepared on high-temperature substrates ($T_s \sim 300\,^{\circ}\mathrm{C}$) the incorporation of both O and N (e.g., from 3000 ppm air in the silane plasma) results in *n*-type doping,[5] but the donor species has not been conclusively identified.

It has long been established that in unhydrogenated amorphous silicon (*a*-Si) there exists a large density ($N_s \sim 10^{18}-10^{20}$ cm^{-3}) of unpaired electronic spins.[7] This ESR response is commonly attributed to Si "dangling bonds." Recently several authors[8-10] have demonstrated that in O-doped *a*-Si there is no appreciable change in either the ESR spin densities or line shapes from the corresponding undoped samples. A similar insensitivity of both the dark and the optically-induced ESR to the presence of oxygen has been observed[11-13] in hydrogenated amorphous silicon which has been intentionally doped with oxygen, provided that the oxygen concentration is $\lesssim 1$ at. %. Although different defect densities are obtained for different preparation conditions, there is no significant correlation with oxygen impurity content.[10] There is also no appreciable shift in the band edge[12,14] for oxygen concentrations below about 1 at. %.

Although general agreement exists concerning the effect of oxygen on the ESR, there remains some disagreement as to the role of oxygen in the photoluminescence (PL) processes. Some authors[11] have suggested that the PL is associated with defects while others[12,13] have invoked the presence of self-trapped excitons which are bound to localized states in the band tails.

Infrared absorption measurements indicate[11,12] that the bulk of the oxygen goes into the films doubly coordinated to silicon atoms (bridging oxygen) and that very few, if any, O—H bonds are formed. Recent LCAO model calculations[15] support these observations and suggest that interactions between defect centers may become important in heavily oxygen-doped samples.

The purpose of this study is to investigate the impurity-associated defects which can be rendered paramagnetic through x irradiation both in nominally undoped films of *a*-Si:H and in films doped by the addition of oxygen and nitrogen to the silane discharge [*a*-Si:(H,O,N)]. A comparison of the present ESR results with evidence gained from a previous examination of solar-cell performance in undoped and air-doped cells[5] suggests that several O- and/or N-related defects may be responsible for the observed *n*-type doping and associated degradation in performance.

II. EXPERIMENTAL DETAILS

The samples of *a*-Si:H employed in this study were obtained from several sources (see Table I), but we shall concentrate on a pair of films made at Brookhaven National Laboratories which differed only in their respective oxygen and nitrogen contents. All films investigated contained between 5 and 15 at. % H and were deposited at relatively slow rates ($\lesssim 350$ Å/min) on high-temperature substrates ($T_s \gtrsim 230\,^{\circ}\mathrm{C}$) at relatively low powers ($\lesssim 1$ W/cm^2). The two Brookhaven samples were annealed in vacuum ($P \lesssim 10^{-6}$ Torr) at 150 °C for 30 min.

Samples were removed from the substrates and placed in evacuated quartz tubes. Several methods of removing the films from the substrates were employed, but the resulting ESR responses exhibited no apparent dependence upon the method of substrate removal which was employed. Some films were removed by flaking off the substrate or by scraping with a knife. For other samples the substrates were removed by etching in hydrochloric or hydroflouric acid. Samples were placed in standard ESR quartz tubes which were flushed with dry nitrogen, evacuated, and sealed. The sample sizes ranged from ~10 to ~50 mg.

Samples were x irradiated at 77 K (copper target with 100 mA at 40 kV). Irradiation times varied from 10 to 100 min, but the intensities of most ESR responses appeared to saturate at times $\lesssim 50$ min. Care was taken to eliminate any possible ESR response which might be induced in the quartz sample tube by the x irradiation. The x irradiation was performed with the *a*-Si:H sample at one end of the tube, and the ESR spectrum was taken with the sample in the unirradiated end of the tube. In addition, after x irradiation the unirradiated end of the tube was annealed with a hydrogen-oxygen torch while the sample was maintained at 77 K.

ESR spectra were taken on a standard *X*-band Varian E-9 spectrometer with an optical-access cavity. Variable temperautures (4–500 K) were obtained using either helium or nitrogen continuous flow systems. Signal averaging and background subtraction capabilities were provided by a Nicolet 1080 system. Intensity measurements were made by comparison to a standard sample of pitch supplied by Varian.

III. RESULTS

The samples employed in this study were characterized using several different techniques. Infrared (ir) absorption measurements, which were routinely performed on all samples, showed mainly those vibrational features attributed to the monohydride species[16–18] ($\bar{\nu}=2000$ cm^{-1}) and in some cases ($\bar{\nu}=2100$ cm^{-1}). Photoluminescence (PL) spectra were also routinely obtained for all samples at 77 K. The PL measurements, which provide a rough comparative characterization of the densities of defect states lying within the optical band gap, were performed both on the films before removal from the substrate and on the large, powdered ESR

TABLE I. Growth parameters of *a*-Si:H films used in ESR measurements.

Supplier	Thickness (μm)	Substrate temp. (°C)	Growth rate (Å/min)	Pressure (Torr)	Power W/cm^2	System type	Gas mixture (% silane)	Approximate substrate area (cm^2)
NRL	0.4–10	250	~350	0.1–1.0	≤ 1	inductive[a]	1.5	46
RCA	~1	330	~300	0.5	0.1	dc proxim.	100	81
University of Chicago	~10	~230	~150	0.2	~0.4	capacitive	100	~25
BNL	~6	225	~100	0.25	0.1	capacitive	100	500

[a] Coupling is nominally inductive but because of large diameter there are substantial capacitive effects.

samples in evacuated quartz ampoules. Equivalent results were obtained from both types of samples and both the line shapes and peak energies (~ 1.25 eV) of the spectra compare well with published results for good, low-defect-density materials.[19,20]

In addition to the ir absorption and PL measurements, small angle x-ray scattering (SAXS) experiments were performed[21] on most samples. The SAXS measurements indicated the presence of observable (10–20 Å) voids in some samples but not in others. However, the appearance of voids in the SAXS experiments does not correlate with any changes in the PL, ir absorption, ^{1}H NMR measurements, or the ESR measurements to be described below. Similar conclusions have been drawn from recent small-angle neutron scattering experiments.[22]

Because the sample sizes employed in this study were larger than those commonly employed for measurements of a-Si:H films on substrates, the usual silicon "dangling-bond" ESR response could be observed down to densities below 10^{15} cm^{-3} at low temperatures. The ESR responses of all samples were characterized before x irradiation, and the results are listed in Table II. The unirradiated spin densities were on the order of 10^{16} cm^{-3} for all samples. Because of differing sample masses and packing factors, the relative errors between samples in Table II are approximately factors of 2. The absolute values of the spin densities N_s in Table II are correct to within a factor of about 3. The ESR signal of the a-Si:(H,O,N) sample of Table II (BNL:O,N) was easily saturated at low microwave power due to an increase in the spin-lattice relaxation time T_1 upon oxygen doping. A similar effect has been reported by Kubler *et al.*[9]

After x irradiation at 77 or 300 K both in the nominally undoped samples and in the a-Si:(H,O, N) sample, the intensities of the Si dangling-bond line increased by factors of between 2 and 10. This increase, which was stable at 300 K, varied from sample to sample in no predictable way. No discernible changes were observed in either the g values or the linewidths of the ESR responses before and after x irradiation. These results are similar to those reported earlier by Dersch, Stuke, and Beichler[23] who employed intense optical excitation for several hours; however, the increases by Dersch *et al.*[23] were limited to a factor of 2.

TABLE II. Spin densities, N_s, for unirradiated samples of a-Si:H as described in the text.

Sample	Linewidth ΔH (G)	g	N_s (spins/cm^3)
NRL	6.7	2.0057	7×10^{15}
RCA	6.7	2.0054	5×10^{15}
BNL	6.7	2.0056	8×10^{15}
BNL: O,N	8.0	2.0057	2×10^{16}
University of Chicago	6.7	2.0056	4×10^{16}

Optically induced ESR has been studied in a-Si:H by several authors,[23–28] and we have observed similar effects in the samples listed in Table II. After x irradiation, the intensity of the optically induced ESR is increased over the unirradiated value. Both this increase and the increase in the dark ESR signal, which is observed after x irradiation, can be annealed by heating to temperatures of ~ 200–250 °C. Annealing at higher temperatures yields an increase in the dark ESR line (with the same g value and linewidth as listed in Table II) and a decrease in the optically induced ESR in general agreement with the results of several other studies.[29–31]

A. x irradiation of nominally undoped a-Si:H

After x irradiation at 77 K, some samples of a-Si:H display an ESR spectrum at 77 K as shown in Fig. 1(a). This spectrum is a superposition of the Si dangling-bond response near 3245 G, which is greatly over modulated, and a three-component resonance which, as we will demonstrate, is attributable to paramagnetic NO_2 molecules trapped in the a-Si:H matrix. The spin density N_s corresponding to the NO_2 ESR response is estimated to

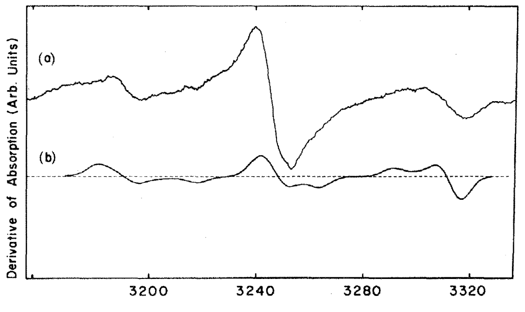

FIG. 1. (a) Experimental and (b) computer-simulated ESR derivative traces of NO_2 radicals in a-Si:H after x irradiation at 77 K. The additional feature near 3240 G in the experimental trace is due to the usual "dangling-bond" signal as explained in the text.

be $\lesssim 10^{16}$ cm^{-3}.

The spin Hamiltonian which describes this spectrum contains both electronic Zeeman and hyperfine terms:

$$\mathscr{H}=\beta\vec{S}\cdot\overleftrightarrow{g}\cdot\vec{H}+\vec{S}\cdot\overleftrightarrow{A}\cdot\vec{I} \ , \tag{1}$$

where $\overleftrightarrow{g}$ is the gyromagnetic tensor for the electronic spin, $\overleftrightarrow{A}$ is the hyperfine tensor, $\vec{H}$ is the applied magnetic field, and $\vec{S}$ and $\vec{I}$ are, respectively, the electronic and nuclear spin vectors. The eigenvalues can be calculated by considering the hyperfine term as a perturbation. If it is assumed that $S=\frac{1}{2}$ and that the principal axes of $\overleftrightarrow{g}$ and $\overleftrightarrow{A}$ are coincident, then to first order the resonant condition is given by[32]

$$h\nu=g\beta H+Am \ , \tag{2}$$

where

$$g^2=g_a^2\sin^2\theta+g_3^2\cos^2\theta \ ,$$

$$g_a^2=g_1^2\sin^2\phi+g_2^2\cos^2\phi \ ,$$

$$g^2A^2=g_a^2B^2\sin^2\theta+g_3^2A_3^2\cos^2\theta \ ,$$

$$g_a^2B^2=g_1^2A_1^2\sin^2\phi+g_2^2A_2^2\cos^2\phi \ .$$

In Eq. (2), the angles θ and ϕ are Euler angles of rotation, A_i and g_i are the principal components of $\overleftrightarrow{A}$ and $\overleftrightarrow{g}$, respectively, and m is the nuclear magnetic quantum number.

In a polycrystalline or glassy sample one must average over all equally probable orientations of the principal axes of $\overleftrightarrow{A}$ (and $\overleftrightarrow{g}$) with respect to the applied magnetic field $\vec{H}$. This average, which is called a powder pattern,[32] has been evaluated numerically[33] for the parameters of molecular NO_2 as found[34] in $NaNO_2$ after x irradiation at 77 K, and the derivative of the resulting spectrum is plotted in Fig. 1(b). An isotropic (angularly independent) Gaussian broadening of 4 G has been used in the computer simulation of Fig. 1(b) to account for unresolved interactions with nuclear spins in the *a*-Si:H network surrounding the NO_2 molecule. The magnitude of this broadening is consistent with the occurrence of $\sim$10 at. % hydrogen in the amorphous silicon.

The spin-Hamiltonian parameters used for NO_2 in Fig. 1(b) are[34] $g_1=2.0057$, $g_2=2.0015$, $g_3=1.9910$, $A_1=47$ G, $A_2=49$ G, $A_3=68$ G. As mentioned above, the discrepancies between the experimental and computer-simulated traces of Fig. 1 near 3245 G are caused by the presence of the Si dangling-bond signal which has been greatly saturated in order to display the less saturable NO_2 signal as clearly as possible. Although the agreement between traces (a) and (b) of Fig. 1 is not perfect, it is apparent that the characteristic signature of the paramagnetic NO_2 molecular in an amorphous or polycrystalline matrix has been observed in this sample of *a*-Si:H.

Because the NO_2 signal in *a*-Si:H is weak, it is not possible to evaluate the spin-Hamiltonian parameters precisely or even to determine whether there is more than one preferred site for the NO_2 molecules in the *a*-Si:H matrix. The anistropy in the g and A tensors does, however, indicate that these molecules are stationary (i.e., not rotating or nutating) at 77 K. In crystalline hosts the g and A tensors of NO_2 become axially symmetric when the molecules are free to rotate.[35] The x-ray-induced ESR signal in *a*-Si:H decays upon heating above 77 K and can be completely annealed by cycling to 300 K. In addition, the signal can be optically bleached at 77 K with a tungsten lamp although the spectral dependence of the bleaching process has not been investigated.

We attempted to enhance the NO_2 signal by deliberately introducing 1000 ppm O_2 and 1000 ppm N_2 into the silane gas stream during deposition of the material. Unfortunately, as we will demonstrate below, the incorporation of $\sim 2-4\,\%$ oxygen and 500 ppm nitrogen in the resulting *a*-Si:(H,O,N) films produces strong ESR responses due to oxygen (see Fig. 2) that mask any possible increases in the NO_2 spectrum. By comparison, measurements of secondary-ion mass spectroscopy (SIMS) show that the nominally undoped material contains 0.2 at. % O and 20 ppm N when produced under otherwise identical plasma processing conditions (BNL samples, Table I).

B. X irradiation of *a*-Si:(H,O,N)

Because the introduction of oxygen[5,6,9–13] and/or nitrogen[5,6,36] impurities into the vacuum chamber during deposition produces O- and N-doped *a*-Si:H whose properties are considerably modified from those of the nominally undoped material, we x irradiated the aforementioned *a*-Si:(H,O,H) samples at 77 K. The general features of a representative ESR spectrum at 110 K are shown in Fig. 2. We will show that the doublet (lines near 3000 and 3500 G) is due to neutral atomic hydrogen trapped in the *a*-Si:(H,O,N) matrix and that the structured response near 3200 G is the superposition of at least three resonances due

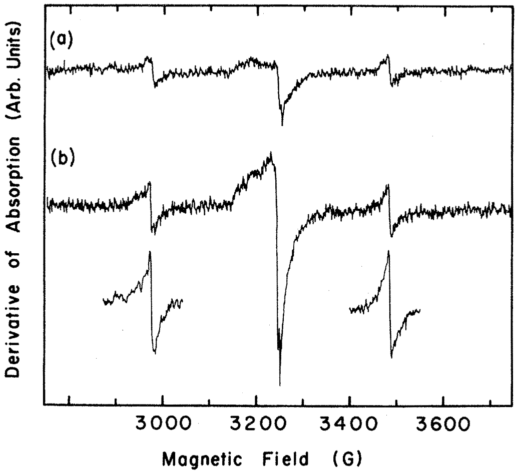

FIG. 2. (a), (b) ESR deivative spectra for two different samples of O-doped *a*-Si:H (BNL:O,N). The bottom traces are due to atomic hydrogen and are run under conditions to minimize the distortion in these line shapes due to excess microwave power and magnetic field modulation. The features near 3200 G are due to overlapping signals from the oxygen-related hole centers, the usual "dangling-bond" signal and silicon *E*′ centers, but the line shapes are distorted.

to (1) a Si dangling bond in the *a*-Si network, (2) an oxygen-associated hole center which is probably a singly coordinated oxygen bonded either to a silicon or to another oxygen, and (3) an sp^3-hybridized dangling bond on a silicon which is bonded to three oxygens (*E*′ center).

We consider first the center attributed to atomic hydrogen in *a*-Si(H,O,N). Because the signal attributed to atomic hydrogen was not observed in several samples of nominally undoped *a*-Si:H which were x irradiated under identical conditions, we conclude that the oxygen is needed to stabilize these centers in *a*-Si:H. Atomic hydrogen is a well known paramagnetic species in many crystalline and amorphous solids including both crystalline[37] and glassy[38] SiO_2 as well as other glasses.[39] In order to evaluate the doublet portion of the spectrum of Fig. 2, one needs to add to the spin Hamiltonian of Eq. (1) the nuclear Zeeman term, which is of the form $-\gamma\vec{I}\cdot\vec{H}$ where γ is the nuclear gyromagnetic ratio. Because the hyperfine term for atomic hydrogen is large, one usually employs the Breit-Rabi approach,[40] but the spin Hamiltonian may also be evaluated by exact matrix diagonalization of all three terms.[41] Because the two lines attributed to atomic hydrogen are symmetric in *a*-Si:H, we have assumed that both $\overleftrightarrow{g}$ and $\overleftrightarrow{A}$ are isotropic. Using an iterative method[42] we calculate $g=2.003\pm0.001$ and $A=504\pm1$ G independent of temperature from 4.2 to 300 K. These values compare favorably with those obtained for atomic hydrogen in glassy SiO_2 where the *g* and *A* values are 2.0025 and 503 G, respectively.[37,38] There is an anisotropy in both $\overleftrightarrow{g}$ and $\overleftrightarrow{A}$ for atomic hydrogen in crystalline quartz, but the magnitudes of these anisotropies are less than 0.1 of the errors quoted above for *a*-Si:H. For atomic hydrogen in free space[43] the isotropic hyperfine coupling constant is 506.8 G.

The magnitude of the ESR response due to atomic hydrogen in *a*-Si:H yields as estimate of $\sim 10^{15}$ spins cm^{-3} which is independent of the temperature from 4.2 to ~ 100 K. This estimate is complicated by the fact that at these temperatures it is not possible to observe an unsaturated signal without overmodulating the sample. Above ~ 100 K there is a gradual decay in the ESR signal. The stability of the atomic hydrogen defects is indicated in the isochronal annealing curve of Fig. 3. In these experiments the sample was x irradiated at 77 K for one hour after which an ESR measurement was taken at a base temperature (either 110 or 300 K). The sample was then annealed for 15 min at progressively higher temperatures inbetween each of which the signal was remeasured at the base temperature. The triangles represent data taken at 110 K and the circles represent data taken at 300 K after excursions to the indicated temperatures. It is apparent from this figure that most of the atomic hydrogen, once created by x irradiation, is stable at temperatures up to about 300 K. This behavior contrasts with that generally observed in oxide glasses and crystals where atomic hydrogen anneals[37] near 200 K. The slow decays below 300 K and the more rapid decay above this temperature indicate that there are at least two decay rates

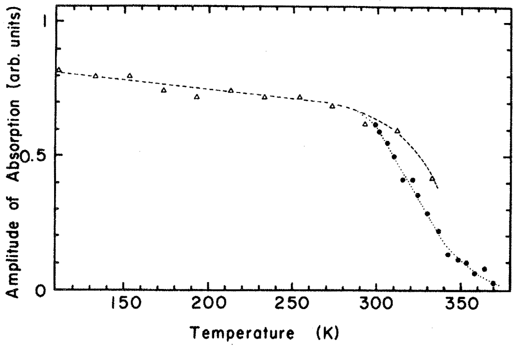

FIG. 3. Isochronal decay of atomic hydrogen ESR signal after 10-min excursions to the temperature indicated by the data points. Triangles were measured at 110 K and circles at 300 K.

for the atomic hydrogen sites.

A series of ESR measurements was performed to study the isothermal decay rates of the atomic hydrogen defects. The sample was x irradiated at room temperature for one hour after which the decay of the atomic hydrogen ESR signal was monitored as a function of time at a given temperature. The sample was then annealed at 363 K for 10 min after which it was again x irradiated and the procedure repeated at a different temperature. The results at five different temperatures are shown in Fig. 4 normalized by a decay time $\tau(T)$. It is apparent from Fig. 4 that all of the decay curves are essentially the same shape after normalization.

The most likely decay mechanism for these particular paramagnetic defects is for two hydrogen atoms to combine and diffuse out of the sample as H_2. This mechanism is a bimolecular decay process of the form

$$\frac{dI}{dt} = -f(T)I^2 , \tag{3}$$

where I is the ESR intensity and the rate $f(T)$ is given by

$$f(T) = f_0 \exp(-E_a/kT) . \tag{4}$$

In Eq. (4), f_0 is the preexponential factor and E_a is a thermal activation energy for release of the hydrogen atom. Equation (3) predicts that a plot of I^{-1} as a function of time should yield a straight line of slope $f(T)$. Such a plot is shown in Fig. 5 for five different temperatures. In these experiments the sample was x irradiated at 300 K for one hour and the decay of the ESR signal at an elevated temperature was immediately monitored. The sample was annealed at 363 K for 10 min before the cycle was repeated. One can see that except at high temperatures and long times the data are well fitted by bimolecular kinetics. The temperature dependence of the slopes yields the activation energy for the process ($E_a \cong 0.5$ eV) as shown in Fig. 6. Because of the slow decay rates below 300 K similar data could not be obtained in this regime.

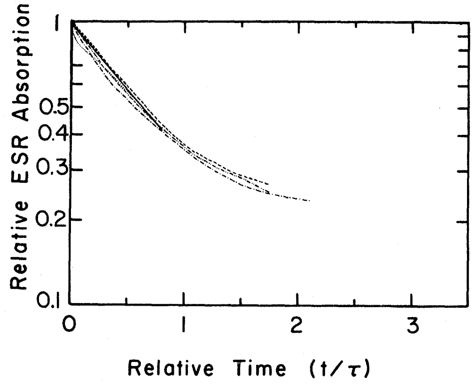

FIG. 4. Normalized isothermal decay of atomic hydrogen ESR signal as a function of time. Curves represent data taken at 310, 319, 323, 332, and 343 K.

A closer examination of the hydrogen doublet reveals the presence of two different sites with different linewidths which saturate at very different microwave power levels. Figure 7 indicates the "apparent" changes in line shape which appear as a function of temperature under constant operating conditions. A narrow line appears unsaturated at 60 °C but at −140 °C a broad line is enhanced because the narrow line is saturated. At 4.2 K (not shown in Fig. 7) only the broad component is observable because the narrow component has been completely saturated. The saturation behavior of the narrow line is indicated explicitly in Fig. 8 at two characteristic temperatures. Similar measurements for the broad line could not be made reliably both because this line saturates at much higher microwave powers and because the signal-to-noise ratios were not great enough. As the isochronal measurements of Fig. 3 would indicate, the (unsaturated) intensities of the broad and narrow lines do not change appreciably up to about 0 °C.

Figure 9 presents two more detailed traces from which the separation of the two components can be effected. The weaker signal shows the narrow line with appropriate values of microwave power and magnetic field modulation, H_1. The stronger curve was run with greater H_1 so that the narrow line is broadened (overmodulated), but the presence of an underlying broad line in the wings is apparent. The dashed curve is an estimate of the broad line with the remnants of the narrow line removed.

The linewidths of these two atomic hydrogen sites are determined mostly by dipolar interactions with neighboring bonded hydrogen. In glassy SiO_2 where there is little dipolar broadening from neighboring nuclei, the linewidth of the atomic hydrogen doublet[37] is 0.5−1.0 G. The ESR measurements in *a*-Si:(H,O,N) yield linewidths for the two sites of 3.4 and ~10 G, respectively. These linewidths are independent of temperature from 4.2 to ~360 K. The line shape of the narrow component is essentially Lorentzian. It is difficult to establish a line shape for the broad line because of the poor signal-to-noise ratio and the interference of the narrow line, but the wings appear to be more Gaussian than Lorentzian.

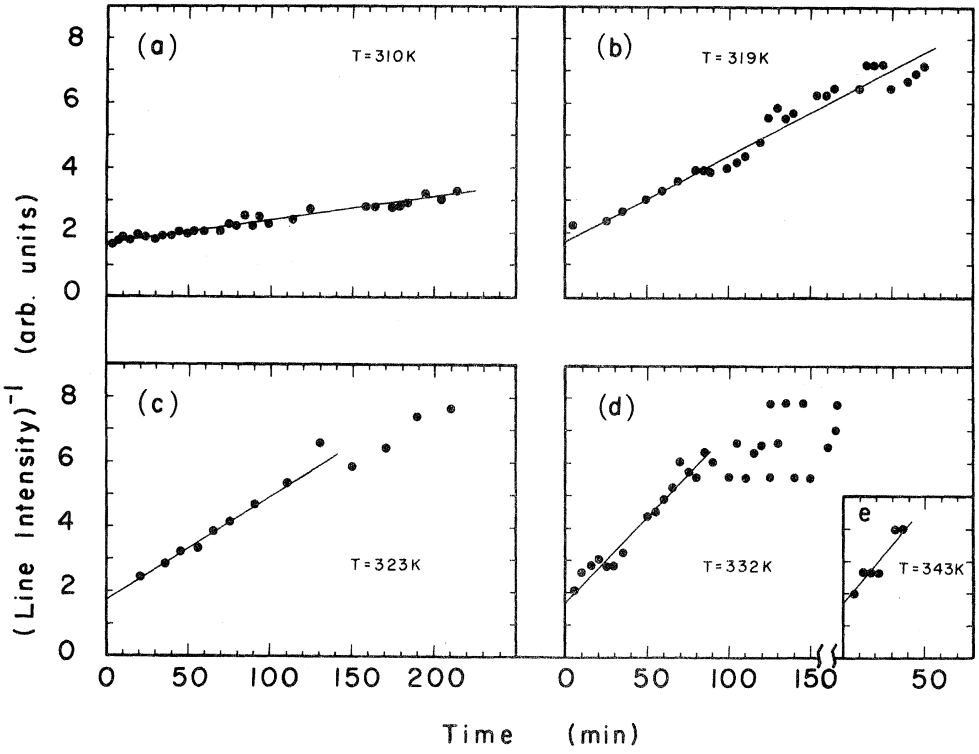

FIG. 5. Bimolecular (second-order kinetics) decay of atomic hydrogen ESR signal as a function of time at several temperatures.

We next consider the oxygen-related defects which are rendered paramagnetic by x irradiation at 77 K in *a*-Si(H,O,N). The ESR spectrum near $g=2.0$ is shown in Fig. 10. The spectrum consists of three distinct components which can be separat-

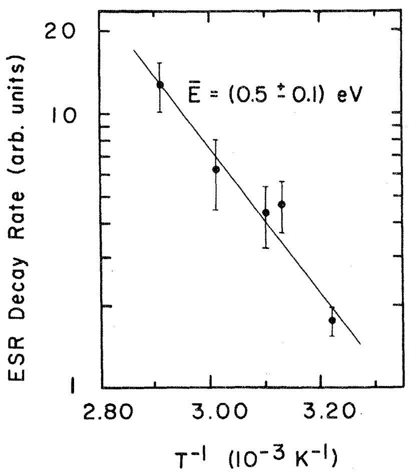

FIG. 6. Activation energy for (bimolecular) decay of atomic hydrogen centers in *a*-Si:(H,O,N). The straight line represents a weighted least squares fit to the data.

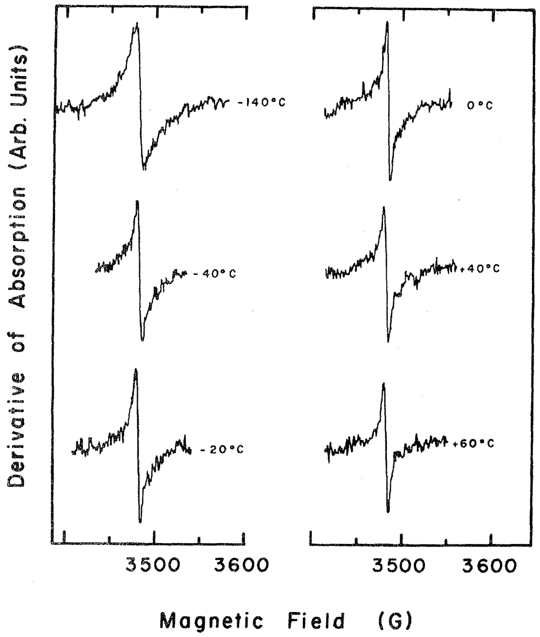

FIG. 7. Temperature dependence of one component of the atomic hydrogen hyperfine doublet. All traces were run at the same microwave power, and the narrow feature is saturated at the lower temperatures.

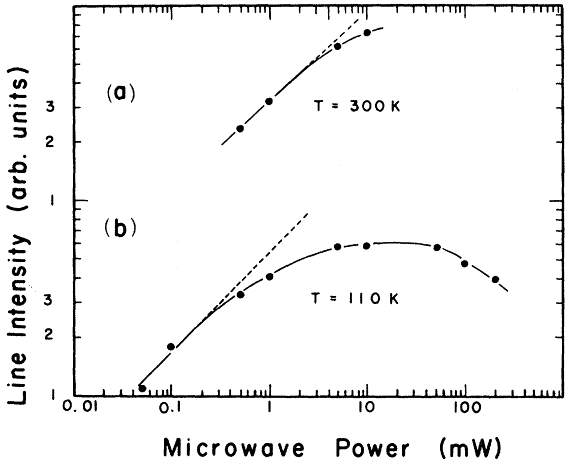

FIG. 8. Microwave power saturation of the narrow component of the atomic hydrogen centers at two representative temperatures. The dashed line represents the unsaturated response.

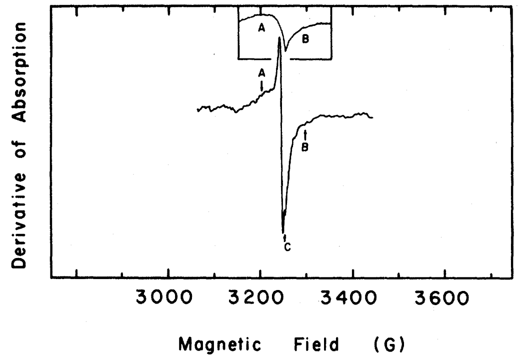

FIG. 10. Central portion of the ESR response in O-doped *a*-Si:H after x irradiation at 77 K. The strong central line is the Si dangling-bond signal; the features labeled *A* and *B* correspond to an oxygen-related defect (hole center); the feature labeled *C* corresponds to a silicon *E′* center. The inset shows the same spectrum run at much higher microwave power (100 mW) such that nearly all of the reponse is due to the signal from the oxygen-associated hole center. See text for details.

ed unambiguously through the use of microwave saturation and thermal annealing studies. The strong sharp central feature is due to the Si dangling-bond resonance which occurs also in undoped samples and was described above.

The broad underlying features labeled *A* and *B* on the low-field and high-field portions, respectively, are due to an oxygen-associated hole center (OHC). The inset at the top of Fig. 10 shows the spectrum run at high microwave power (100 mW). At this power level the Si dangling-bond line is nearly completely saturated and the remaining line shape is essentially due to the oxygen-related center which saturates less easily. The lack of influence of the Si dangling-bond lines was checked by observing that the optically induced enhancement of this line, which also saturates easily, was essentially unobservable at these high power levels even though the optically induced contribution dominates the spectrum at low power levels. The spectral feature attributed to an oxygen-associated hole center is too weak to be observed in nominally undoped *a*-Si:H, and the presence of oxygen (or perhaps nitrogen) is necessary for its production. In addition, the line shape is consistent with a variety of OHC's which have been observed in oxide glasses.[44,45] For example, in glassy SiO_2 two hole centers appear. One center, which appears more readily in SiO_2 containing OH impurities, is associated with a hole trapped on a singly coordinated oxygen atom which is bonded to a silicon atom[46] ($g_1=2.0010$, $g_2=2.0095$, average $g_3=\langle g_3\rangle=2.068$). This center, which is frequently stabilized on surfaces of metal oxide catalysts,[47] is often called on O^- ion. A second center, which occurs in "OH-free" SiO_2, is associated with a hole trapped on a singly coordinated oxygen atom which is bonded to another oxygen atom[48] (peroxy radical where $g_1=2.0014$, $g_2=2.0174$, $\langle g_3\rangle=2.068$). This center, which is also frequently stabilized on surfaces of metal oxide catalysts,[49] is usually referred to as an $O_2{}^-$ or a superoxide ion. The spectrum of Fig. 10 does not warrant a detailed line-shape calculation, but the asymmetry indicates that $g_1\sim2.00$ and $g_2\sim2.02$. The feature

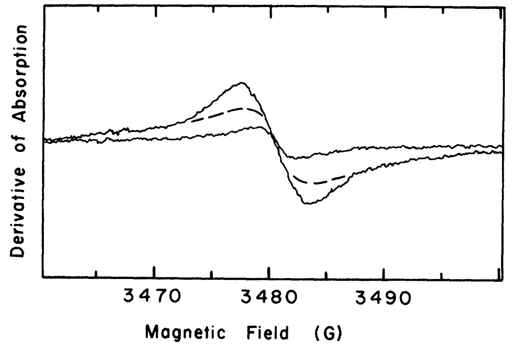

FIG. 9. Detailed ESR derivative trace of one component of the atomic hydrogen doublet. In the more intense trace the central portion has been overmodulated to emphasize a second broad component in the wings which is attributed to a second environment for atomic hydrogen in these samples. The dashed curve represents an estimate of the broad component.

associated with g_3 is washed out and no estimate for this parameter can be made.

The hole centers in SiO_2 both exhibit ESR spectra which are much more structured than the broad line in Fig. 10, but unstructured responses are observed for hole centers in the oxide glasses wherever nuclei with nonzero magnetic moments are present. For example in alkali silicate glasses,[50] two hole centers, HC_1 ($g_1=2.0026$, $g_2=2.0090$, and $g_3=2.0210$) and HC_2 ($g\sim 2.01$) are present for various alkali concentrations. The specific model for HC_2 has not been established, but there is little doubt that HC_1 is the analog of the hole center which appears in SiO_2 containing OH impurities. Furthermore, in sodium rubidium and cesium silicate glasses the spectrum attributed to HC_1 is very similar to the broad peak in Fig. 10 which displays a positive derivative peak near 3230 G and a negative derivative peak near 3250 G. Because of the presence of hydrogen in the *a*-Si:H one would expect the unresolved dipolar interactions to produce a structureless line similar to those encountered in some of the alkali silicate glasses.

Although a good case can be made for the attribution of the broad line seen in Fig. 10 to a hole center partially localized on a singly coordinated oxygen, it is not possible to determine whether the oxygen is bonded to a silicon or another oxygen because the g tensors are relatively insensitive to the details of the oxygen bonding.[44,45] These oxygen centers, which we estimate to be $\sim 10^{16}$ cm^{-3}, anneal at temperatures above ~200 °C although no detailed measurements have been performed. Preliminary experiments at room temperature also indicate that these centers can be induced optically by light with energies near the band gap.[51]

The narrow feature labeled *C* in Fig. 10 is attributed to an unpaired electron on a silicon atom which is bonded to three oxygen atoms (*E'* center). A more detailed trace of this response is shown in Fig. 11 where the broad line is the Si dangling-bond signal and the sharp feature between 3245 and 3250 G is the *E'* center.

The Si *E'* center has been extensively studied in glassy SiO_2 and related oxide glasses.[52] Comparisons with *E'* centers in crystalline α-quartz[53] and the use of samples of glassy SiO_2 which were enriched[54] in ^{29}Si have provided a definitive identification of the *E'* center in the oxide glasses ($g_3=2.0017$, $g_2=2.0006$, $g_1=2.003$). The hybridization of the wave function of the unpaired spin is essentially sp^3 for the *E'* center[54] in glassy SiO_2. Although the resolution of the line in Fig. 11 is not as good as that which is commonly observed in glassy SiO_2, the linewidth, the asymmetry, and the microwave saturation properties are such that one can clearly identify this feature as due to *E'* centers in the *a*-Si:(H,O,N) material. We estimate the number of these centers to be $\sim 10^{15}$ cm^{-3}.

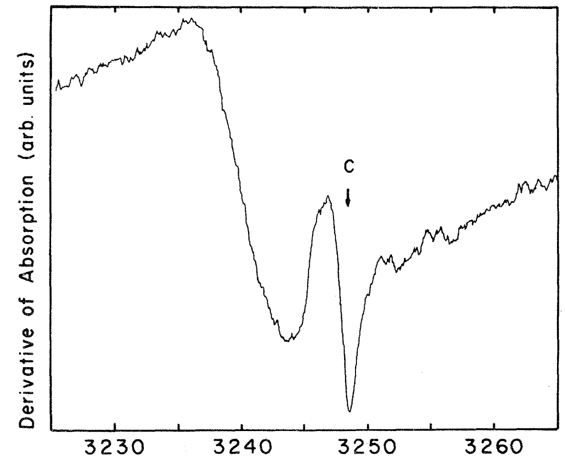

FIG. 11. Detailed ESR derivative trace of the central region of the spectrum. The broad line is due to the Si dangling-bond line which can be increased by the application of light. The narrow line near 3247 G (labeled *C*) is due to a silicon *E'* center which is similar to those which occur in oxide glasses.

IV. DISCUSSION

Since the original observation by Staebler and Wronski[55] of a metastable decrease in both the dark conductivity and the photoconductivity in undoped *a*-Si:H after prolonged exposure to light at 300 K, there is additional evidence which ties these optically-induced metastabilities (Staebler-Wronski effect) to the influence of electronic states which lie deep in the gap.[23,56,57] Although some authors have suggested that surface effects may be responsible for the Staebler-Wronski effect,[58] we believe the early work of Staebler and Wronski[55,56] has demonstrated that the observed conductivity changes represent a bulk effect. This effect can be annealed in the dark above ~150 °C with an annealing activation energy of 1.5 eV. Pankove and Berkeyheiser[57] discovered that exposure to light enhances the photoluminescence (PL) near 0.8 eV and slightly decreases the photoluminescent response near 1.2 eV. These changes in the PL were observed to anneal near 220 °C. Recently, Dersch *et al.*[23] have shown that long exposure to light produces an increase in the Si dangling-bond ESR signal. As described in Sec. III we have observed similar increases in both the dark and optically-induced Si ESR after x irradiation. The changes observed upon x irradiation also anneal between 200 and 250 °C.

Both Pankove and Berkeyheiser[57] and Dersch *et al.*[23] attribute the Staebler-Wronski effect to the production of additional Si dangling bonds after prolonged exposure to light. The present results on x-irradiated samples certainly do not contradict these earlier conclusions, but the measurements on *a*-Si:(H,O,N) do suggest that there may be some ambiguity in the previous results. For example, an extrapolation of the results on O_2-doped films suggests that in nominally undoped *a*-Si:H, where the oxygen impurities are usually on the level of ~ 0.1 at. %, one would expect the number of oxygen-related hole centers to be on the order of 10^{15} cm^{-3}. (One would anticipate the density of E' centers to be considerably smaller because these centers require a silicon bonded to three oxygen atoms.) Although cluster calculations by Ching[15] and Laughlin *et al.*[59] indicate that an isolated, *diamagnetic*, singly coordinated oxygen in the amorphous silicon network or on an *a*-Si internal surface does not create a state in the gap, the present ESR results show that the *paramagnetic* oxygen-associated hole center is a very stable gap state. It is therefore probable that these oxygen-associated centers occur on greatly relaxed surfaces or in oxygen-rich regions in *a*-Si:H because the heterogeneous nature of *a*-Si:H has been well documented. For example, extensive NMR investigations[60,61] always reveal two distinct and spatially separated hydrogen environments.

Whether the oxygen-associated hole center occurs on an internal surface, in an SiO_x-rich region or on an isolated Si—O bond in the *a*-Si network, it is certainly possible that this deep hole trap is responsible for the light-induced conductivity changes observed by Staebler and Wronski. There are also indications from deep-level transient spectroscopy (DLTS) experiments[62] that traps associated with impurities such as oxygen may be linked with the metastable optical properties in *a*-Si:H films.

Another paramagnetic defect which can potentially affect both the optical and the transport properties of *a*-Si:H is the trapped NO_2 molecule described in Sec. III. By analogy with the situation in crystalline hosts, the NO_2 molecule probably originates[35,63] from NO_2^- radicals trapped in the amorphous Si matrix or in SiO_x-rich regions. Because the paramagnetic NO_2 molecule is not moving or rotating (the g tensor is anisotropic), it is unlikely to be trapped on internal surfaces.[34,35] The optical and thermal annealing experiments of NO_2 in *a*-Si:H suggest that NO_2^- may be a shallow hole trap and as such could inhibit minority carrier diffusion in some devices.

The present ESR results suggest what is perhaps an important caution. There are a number of defects, which are not due to Si or H atoms bonded in the *a*-Si:H network but which may be important in controlling the optical and transport properties. Ultimately, the traps which limit minority carrier diffusion lengths in solar-cell devices made from *a*-Si:H may not be Si dangling bonds but rather impurity species. The oxygen hole centers and the trapped NO_2 molecules just discussed are merely two of many possibilities.

Parallel optical and transport experiments have been performed on identical *a*-Si:(H,O,N) films, as well as on similar films alternatively doped by the addition to the plasma of air or nitric oxide (NO).[6,64] Device performance of solar cells fabricated from such materials has also been evaluated.[5] These parallel measurements have shown that the presence of O_2 and N_2 in the plasma during film growth results in *n*-type doping (as a strong function of substrate temperature) and severely degrades the $\mu\tau$ product for holes. (Here μ is the hole mobility and τ is the hole recombination lifetime.) As mentioned in Sec. III, the PL spectrum and efficiency, as well as the Si dangling-bond dark ESR and optically induced ESR, do not change appreciably with O and N doping. For these and other reasons, the degradation in solar-cell performance was attributed to doping associated (i.e., N or O associated) defects whose energies were located at ~ 0.8 eV below the conduction band in the bulk.[5] These deep-lying donorlike states could be the oxygen-associated hole centers seen in x-irradiated ESR, but this explanation does not naturally explain the synergistic effects of O_2 and N_2 that reduce the short-circuit current density in *a*-Si:H solar cells. The defects could also be traps related to nitrogen-oxygen complexes such as NO_2^- and NO^-, or NO_3^- (or perhaps NO^+ or NO_3^+) which can be rendered paramagnetic by hole trapping (or in the cases of NO^+ or NO_3^+ also by electron trapping). In addition, one can envision a diamagnetic defect involving nitrogen bonded to the silicon network, such as $\equiv Si-N=0$, which can be transformed into a paramagnetic species by electron or hole trapping. These nitrogen-associated centers are masked in the *a*-Si:(H,O,N) samples by the oxygen-associated ESR response. We estimate that the density of such nitrogen-associated centers must be less than $\sim 5\times 10^{16}$ cm^{-3} (within a factor of 3) in order for the response to be unobservable in the doped films. This bound is reasonably consistent with a density of hole traps that could account for the observed collapse of the space charge width at solar-cell junctions.[5]

The preceding discussion has centered on defects directly associated with impurities such as oxygen and nitrogen; however, even in the case of atomic hydrogen which is a defect involving a major constituent atom, an impurity, namely oxygen, plays an important role in stabilization. Because the line shapes do not change with temperature, the hydrogen atoms are trapped in the lattice, but because the *g* and *A* values are so close to the free atomic hydrogen values, the bonding to the lattice must be weak. Two possibilities exist to explain this weak trapping of atomic hydrogen in *a*-Si:H. Firstly, the atomic hydrogen might be bonded to a cage via weak van der Waals forces.[37,42] Alternatively, the hydrogen might be held electrostatically[65] near surface oxygen atoms due to the large electric fields near oxygenated internal surfaces. Atomic hydrogen is not found in nominally undoped *a*-Si:H. For reasons which we shall now discuss we consider the electrostatic interpretation as the most plausible, although the larger atomic radius of oxygen, as compared to silicon, is consistent with the van der Waals explanation.

As noted in Sec. III, the hyperfine couping constant for the atomic hydrogen centers in *a*-Si:H is less than that for free hydrogen. This decrease is a result of a reduction in the *s* character of the wave function which is expected for either the van der Waals[66] or the electrostatic[65,67,68] mechanism. Using methods similar to those discussed by Papp and Lee,[69] we can estimate the electric field strength necessary to produce the observed reduction in the isotropic coupling constant $A=504$ G from the free hydrogen value $A_s=506.8$ G. Using a perturbation approach[69,70] one obtains

$$A=(1-\gamma^2)A_s\ , \tag{5}$$

where

$$\gamma=\frac{eE\langle 1s\,|\,z\,|\,2p\rangle}{\Delta E}\ .$$

In Eq. 5, $\Delta E=10.2$ eV is the energy separation between the ground *s* state and the first excited *p* state of the hydrogen atom and the matrix element $\langle 1s\,|\,z\,|\,2p\rangle=1.245\times 10^{-8}$ cm for atomic hydrogen.[71] From the ESR results $\gamma^2\sim 5\times 10^{-3}$, and one obtains $E\sim 6\times 10^7$ V/cm. This field strength is consistent with that observed[65] on porous glass surfaces. We are thus led to the suggestion that the atomic hydrogen is trapped electrostatically on internal oxygenated surfaces of *a*-Si:(H,O,N).

Although the electrostatic mechanism seems most reasonable the possibility of trapping via van der Waals forces cannot be excluded. In crystalline quartz the atomic hydrogen sites[37] are thought to be interstitially located in the *c*-axis channels between silicon atoms. The nearest neighbors in these sites are four oxygen atoms in a nearly tetrahedral configuration. In this case the oxygen cage is so small that the hyperfine constant actually increases[72] over the free atom value, but for glassy SiO_2 the *A* value is reduced. It is commonly presumed[37] that the increased cage diameters in the less dense vitreous phase allow the van der Waals interaction to decrease the *s* density on the hydrogen atom. One cannot exclude this possibility as an explanation for the trapping of atomic hydrogen in SiO_x regions of *a*-Si:H.

Because there is considerable oxygen contamination even in nominally undoped films, the concentration of atomic hydrogen generated by x irradiation at 77 K could be on the order of 10^{14} cm^{-3} even in these films. Unfortunately, this density is below our level of detection with current experimental techniques.

Although we can infer from the bimolecular decay of the ESR signal that the atomic hydrogen forms molecular hydrogen on thermal annealing, the ESR results provide no information concerning the parentage of atomic hydrogen in *a*-Si(H,O,N). We speculate that the relatively small number of atomic hydrogen centers ($\sim 10^{15}$ cm^{-3}) results from a radiation-induced breaking of weak Si-H bonds. This bond breaking should increase the dangling-bond ESR signal and may be responsible for some of the increased dangling-bond ESR signal seen after x irradiation. Because most of the increase in the dangling-bond ESR response can be annealed by heating to $\sim 200-250\,^{\circ}$C, the production of atomic hydrogen by breaking $Si-H$ bonds cannot account for most of the increase in the Si dangling-bond line after x irradiation. The majority of this line probably results from breaking weak $Si-Si$ bonds which can reform on annealing.

Because there are two distinct environments for both the atomic hydrogen ESR sites and the ^{1}H NMR sites,[60,61] we examine whether there is any correspondence between the two measurements. As described in Sec. III the broadening of the ESR lines, which results from the same dipolar mechanism responsible for the linewidths in the NMR experiments,[60,61] yields two distinct ESR sites whose linewidths are 3.4 G (Lorentzian) and ~50 G (Gaussian). In comparison, the NMR linewidths are ~1 G (Lorentzian) and ~5 G (Gaussian) for the two distinct hydrogen clustered environments which are always observed.[60,61] In addition, the intensity ratios of broad-to-narrow components obtained from NMR and ESR are ~2:1 and ~10:1, respectively. It is not possible to calculate precisely the dipolar contributions to the linewidth in either the NMR or ESR situations, but they must both be on the order of

$$\Delta\omega \sim \gamma_i H_{\text{loc}} \ , \tag{6}$$

where

$$H_{\text{loc}} \sim \frac{\gamma_n h}{r^3} \ .$$

In Eq. (6) γ_i is the gyromagnetic ratio of the resonant spin (nuclear or electronic; γ_n or γ_e, respectively), r is a measure of the average nearest-neighbor hydrogen separation. Thus, H_{loc} is an estimate of the local field generated at the resonant site by the surrounding hydrogen atoms.

Since the ESR and NMR linewidths are within a factor of 10 of one another in spite of the fact that $\gamma_e \sim 10^3 \gamma_n$, the atomic hydrogen exists in an environment which is very different from that of the majority of bonded hydrogen atoms in a-Si:H. This fact is not surprising because the atomic hydrogen requires oxygen for stability. If the atomic hydrogen is trapped in an oxygen cage, then this defect will be considerably more isolated from bonded hydrogen atoms than these atoms are from one another.

Thus, we should not expect correspondence between the NMR environments and the environments of the atomic hydrogen defects created by x irradiation. However, the appearance of two distinct sites for the atomic hydrogen defects with parameters *similar* to those occurring for all of the bonded hydrogen atoms indicates that these defects may be trapped with roughly similar efficiencies in either environment.

It is clear from the preceding discussion that both of the atomic hydrogen sites in a-Si:H yield inhomogeneously broadened ESR lines. In the absence of spin diffusion,[73] the saturation curve of Fig. 8 at high microwave powers should become independent of power,[74,75] and the falloff at high power in this figure could be indicative of the breakdown of the Lorentzian spin packet approach[76,77] of Portis[74] and Hyde.[75] If we ignore this possible complexity, the saturation curve at 110 K yields an order of magnitude estimate for T_1 of 10^{-5} sec for the narrow component of the atomic hydrogen centers. Although not measured, the T_1 for the broad component at this temperature is at least an order of magnitude faster.

V. SUMMARY

Samples of nominally undoped and O- and N-doped a-Si:H have been x irradiated at 77 K, and several metastable, paramagnetic responses have been observed. In all samples after x irradiation, the intensities of the Si dangling-bond line increased by factors of between 2 and 10, and no discernible differences were observed in either the g values or the linewidths. Some undoped samples of a-Si:H display an ESR spectrum attributable to NO_2 molecules trapped in the a-Si:H matrix ($\sim 10^{16}$ cm^{-3}). Attempts to enhance the NO_2 response by doping films with O_2 and N_2 [a-Si:(H,O,N)] did not succeed because of the occurrence of an oxygen-associated hole center (OHC) which masked any possible increase in the NO_2 signal.

Four ESR responses have been positively identified in x-irradiated a-Si:(H,O,N). These include (1) neutral atomic hydrogen trapped in the a-Si:(H,O, N) matrix ($\sim 10^{15}$ cm^{-3}), (2) a Si dangling bond in the a-Si network, (3) an oxygen-associated hole center which is probably a singly coordinated oxygen bonded either to a silicon or to another oxygen ($\sim 10^{16}$ cm^{-3}), and (3) an sp^3-hybridized dangling bond on a silicon which is bonded to three oxygen atoms (E' center; $\sim 10^5$ cm^{-3}).

Oxygen is required to stabilize the atomic hydrogen centers in a-Si:H, and we have suggested that the atomic hydrogen is held electrostatistically near surface oxygen atoms. These centers decay thermally above about 300 K, and the decay mechanism probably involves two hydrogen atoms combining to form H_2 which diffuses out of the sample. There are at least two distinct sites for the metastable atomic hydrogen in a-Si:H.

The g tensor provides firm evidence that the oxygen-associated hole center is partially localized on a singly-coordinated oxygen atom, but it is not possible to determine whether the oxygen is bonded to a silicon or to another oxygen because the g tensors are relatively insensitive to the details of the oxygen bonding. These centers anneal above ~200 °C.

The metastable decrease in both the dark conductivity and the photoconductivity in undoped *a*-Si:H after prolonged exposure to light (Staebler-Wronski effect) has previously been attributed to an increase in the number of Si dangling bonds. Although this explanation may still be viable, it is also possible that the light-induced conductivity changes of Staebler and Wronski may be due to the presence of deep hole traps associated with oxygen atoms. In general, the present results have uncovered a number of defects, which are not due to Si or H atoms bonded in the *a*-Si:H network, but which may be important in controlling both the optical and the electronic properties. For example, the traps which limit minority carrier diffusion lengths in *a*-Si:H devices may be impurity species rather than Si dangling bonds.

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