

Origin of Optically Induced Electron-Spin Resonance in Hydrogenated Amorphous Silicon

S. Yamasaki, H. Okushi, A. Matsuda, and K. Tanaka

Electrotechnical Laboratory, 1-1-4, Umezono, Tsukuba-City, Ibaraki 305, Japan

J. Isoya

University of Library and Information Science, 1-2, Kasuga, Tsukuba-City, Ibaraki 305, Japan

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^{29}Si hyperfine structure in an optically induced electron-spin-resonance spectrum has been detected in hydrogenated amorphous silicon using a pulsed technique. The optically induced ESR signal is accompanied by an increase in the subbandgap optical absorption. These observations suggest that the optically induced ESR signals originate from a localized state similar to the singly occupied dangling-bond state observed in dark, which is phenomenologically similar to the defect properties in chalcogenide glasses.

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Amorphous semiconductors can be classified roughly into two broad categories, namely, chalcogenide glasses and tetrahedrally bonded amorphous materials. Concerning defect properties, different views are adopted for the two kinds of materials at the present time.

In chalcogenide glasses, although the dangling-bond signal in dark is hardly observable, an optically induced dangling-bond signal has been detected at low temperatures using electron-spin-resonance (ESR) and optical-absorption spectroscopy.^{1,2} In order to explain the origin of the optically induced signal, a charged defect state with negative effective correlation energy U was proposed.^{3,4}

On the other hand, in hydrogenated amorphous silicon ($\alpha\text{-Si:H}$), the dangling-bond signal in dark has been observed by ESR ($g=2.005$) and optical-absorption measurements.^{5,6} In addition to the dark ESR signal, two kinds of optically induced ESR signals, with $g=2.004$ and 2.01 , have also been detected at low temperatures.⁷ However, on the basis of the study of doped materials and comparison with photoluminescence, the origin of the optically induced ESR signal in undoped $\alpha\text{-Si:H}$ has been indirectly identified with conduction-band-tail electrons ($g=2.004$) and valence-band-tail holes ($g=2.01$),⁸ which is different from the case in chalcogenide glasses. Unlike chalcogenide glasses, no direct evidence for the origin of the optically induced ESR signal in $\alpha\text{-Si:H}$ has been reported so far.

In this Letter, we report the optically induced ESR spectrum along with the ^{29}Si hyperfine structure measured at low temperatures, which is similar to that of the dangling-bond signal in dark, and also a simultaneous increase in the subbandgap optical absorption. The phenomenological similarity between experimental results in $\alpha\text{-Si:H}$ and chalcogenide glasses is pointed out.

Undoped $\alpha\text{-Si:H}$ and $\alpha\text{-Si:D}$ samples were deposited by the rf-glow-discharge technique from undiluted SiH_4 and SiD_4 on a metal foil at a temperature of 200–

250°C, respectively. The flakes, weighing 10 mg, were collected in a silica-glass tube for ESR measurements. The spin densities were between 3×10^{15} and 1×10^{16} cm^{-3} .

In order to obtain a wide-dynamic-range ESR spectrum, required for quantitative analysis of ^{29}Si hyperfine lines with small intensities, the technique of electron-spin echo of pulsed ESR was employed. Field-swept mode spectra were obtained by recording the amplitude of the Hahn echo (90° pulse– τ – 180° pulse– τ –echo) as a function of magnetic-field strength. The optically induced ESR spectrum was obtained by subtracting the dark ESR spectrum from that obtained under illumination from a krypton laser ($\lambda=676$ nm) of 4-mW output. In order to measure subbandgap optical-absorption spectra at low temperatures, photoacoustic spectroscopy was employed.⁹ The amplitude of subbandgap absorption includes errors at most around 30%, originating from the unknown dependence of the quantum efficiency of a non-radiative recombination process on photon energy. The laser (bias light) used for the optically induced ESR measurements was also used for this experiment.

Figure 1 shows the dark and optically induced ESR spectra with a logarithmic vertical scale, obtained in the form of magnetic-field-swept electron-spin-echo spectra at 56 K. The actual peak height of the optically induced ESR signal was 3 times as large as that in dark. As shown in Fig. 1, the dark ESR spectrum exhibits clear shoulders on both sides of the main peak ($g=2.005$) which originate from the hyperfine interaction between the nuclear spin of ^{29}Si , amounting to 4.7 at.% of natural abundance, and the electron spin of a singly occupied dangling bond.^{10–12}

On the other hand, the high-intensity region of the optically induced signal reveals a two-component structure consisting of a broad line at $g=2.01$ and a narrow line at $g=2.004$, which is essentially the same as reported so far. The important feature of the spectrum is that it is

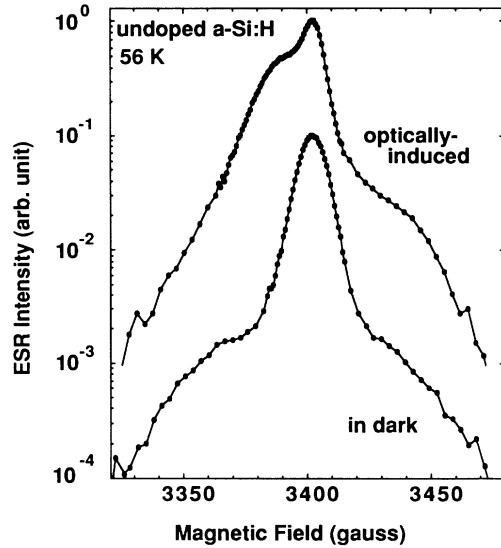


FIG. 1. Optically induced and dark ESR spectra, obtained as electron-spin-echo spectra at 56 K.

accompanied by shoulders on both sides, although the lower-magnetic-field-side shoulder is not clear. This structure can be analyzed as the convolution of narrow and broad components with their hyperfine structures, which has been confirmed as follows.

(1) The microwave-frequency dependence of the linewidth of the main peaks and their shoulders was measured using 9.4- and 11.3-GHz cavities in dark and under illumination, as summarized in Table I. The linewidths are expressed, in this study, as the full width at one-fifth of each peak height. In the case of the main peaks, the linewidth increases considerably (10%–20%) with an increase of microwave frequency, implying that the linewidth is predominantly determined by the distribution of the g value. In the case of the shoulders for both dark and optically induced signals, the increase of the linewidth amounts to only a small fraction of the linewidth. This can be reasonably explained if the contribution from the broadening of each main peak is taken into account. At these microwave frequencies, the linewidth of the shoulders is determined mainly by the dis-

TABLE I. Linewidths of main peaks and shoulders of dark and optically induced ESR spectra. [(11.3 GHz)/(9.4 GHz) = 1.20.]

	Main ^a (dark)	Shoulder (dark)	Main ^b (light)	Shoulder (light)
(a) 9.4 GHz	19.7 G	120.5 G	38.9 G	111.6 G
(b) 11.3 GHz	22.3 G	123.3 G	46.2 G	117.6 G
(b) – (a)	2.6 G	2.8 G	7.3 G	6.0 G
(b)/(a)	1.13	1.02	1.19	1.05

^a $g = 2.005$.

^b $g = 2.01$.

tribution of the spin Hamiltonian parameters other than the g value. This means that the two shoulders come from the hyperfine structure or fine structure and not from two independent spin centers.

(2) The turning angle through which the microwave magnetic field rotates the electron spins has been varied by the duration of the microwave pulse. The maximum amplitude of the two-pulse echo is obtained when the turning angles of the first and the second pulses are set to be 90° and 180° , respectively. The pulse durations for 90° and 180° pulses when one of $\Delta M_S = \pm 1$ transitions of an $S = 1$ system is excited are $1/\sqrt{2}$ times those for an $S = \frac{1}{2}$ system.¹³ The microwave pulse durations which maximize the echo amplitude of the shoulders were the same as those for the main peaks. Therefore, the shoulders do not come from fine structure of a spin system with $S = 1$ but arise from hyperfine structure of an $S = \frac{1}{2}$ system.

(3) Generally, in undoped a -Si:H there are nuclear spins of ^{29}Si ($I = \frac{1}{2}$, natural abundance of 4.7%), ^1H ($\frac{1}{2}$, 99.98%), and a small amount of undesirable impurities of ^{17}O ($\frac{5}{2}$, 0.037%), ^{13}C ($\frac{1}{2}$, 1.1%), and ^{14}N (1, 99.6%). However, the present spectrum did not show any essential change in either a deuterated sample (a -Si:D) or in samples having different impurity levels. Therefore, we can rule out the possibility of ^1H , ^{17}O , ^{13}C , or ^{14}N being the origin of the hyperfine structure.

Although more detailed information is needed for the deconvolution of the optically induced ESR spectrum in Fig. 1, the following information has been obtained from the higher-magnetic-field-side shoulder of the spectrum. The hyperfine structure due to both the narrow ($g = 2.004$) and broad ($g = 2.01$) components should contribute to the shoulders, and, actually, the integrated area of the higher-magnetic-field-side shoulder was estimated to be around 2.3% of the area of the whole spectrum, which corresponds to one-half of 4.7% (the natural abundance of ^{29}Si) of the total spectrum. This fact also means that the wave function of the spin center is localized mainly on one Si atom. When the wave function is spread over two Si atoms, the area of the hyperfine structure must be as large as 9.0% ($2 \times 0.047 \times 0.953$) of the total area of the ESR spectrum because its hyperfine structure is due mainly to pairs of ^{29}Si and ^{28}Si . Furthermore, the hyperfine splitting widths are estimated to be 70 ± 20 G which is almost the same as that of dangling-bond centers observed in dark (70 G). These results show that the ESR signals with $g = 2.004$ and 2.01 originate from spin centers localized mainly on one Si atom, with splitting width similar to dangling bonds observed in dark.

From the above evidence, the origin of the localized spin centers with $g = 2.004$ and 2.01 is straightforwardly suggested as the different kinds of singly occupied dangling-bond states or dangling-bond-like localized states.

From a doping study and correlation with photoluminescence, the origin of the optically induced ESR signal has been attributed to conduction-band-tail electrons and valence-band-tail holes,⁸ although the detailed structure of the tail state has not been clear so far. When the wave function of a carrier trapped at the tail state is spread over several Si atoms, the ratio of the area of hyperfine structure to the total ESR spectrum should be several times the natural abundance and its splitting width should be small. Therefore, we can rule out this possibility. A weak bond with a bond length longer than that of a normal Si-Si bond might be another candidate for the tail state. From the above discussion, a carrier localized on two Si atoms at both ends of a weak bond cannot be the origin of the optically induced ESR centers. However, on the assumption that a carrier trapped at a weak bond has a dangling-bond-like localized wave function, it can be the origin of the optically induced ESR centers. Namely, the wave function should have an asymmetric structure with lattice relaxation by the trapping of a carrier, and be localized mainly on one Si atom with a hyperfine splitting width similar to that of the dangling-bond center observed in dark.

The optically induced signal is also detected by optical-absorption measurements, as in chalcogenide glasses.^{1,2} Figure 2 shows the low optical-absorption spectra measured by photoacoustic spectroscopy at 56 K with and without bias light. The absorption spectrum without bias light is the usual one for undoped *a*-Si:H. With bias light, excess absorption, spreading towards lower photon energy, appears in the spectra.¹⁴ Figure 3 shows the temperature dependence of the optically induced ESR signal as well as of the excess optical absorption induced by the bias light. The temperature dependences of both quantities are quite similar, suggesting that the origin of the optically induced ESR signal and optically induced optical absorption is identical. The characteristic absorption feature extending down to

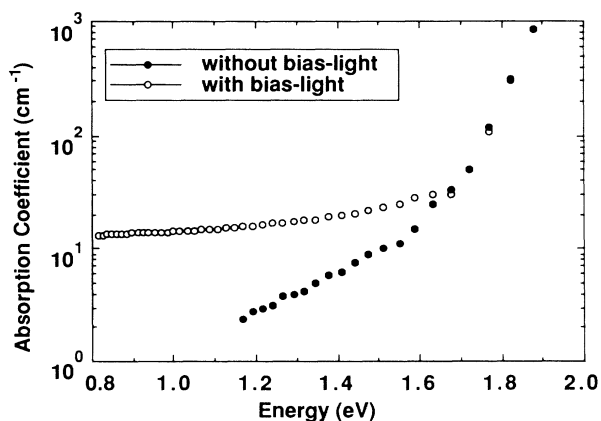


FIG. 2. Optical-absorption spectra with and without bias light at 56 K. Additional absorption extending toward lower photon energies is clearly observed.

much lower photon energy suggests that the optically induced centers should be energetically located closer to the band edge.

It is well known that phosphorus- (P-) and boron- (B-) doped *a*-Si:H also show $g=2.004$ and 2.01 ESR signals in dark, respectively.¹⁵ The coincidence of the g values and shapes of those spectra with the present data leads to the speculation that the ESR signals in doped samples also originate from the same spin centers as the optically induced ESR signals. In an earlier work, it was pointed out from results of electron-nuclear-double-resonance (ENDOR) measurements that the spin center with $g=2.004$ in P-doped *a*-Si:H has the same spread of wave function as that of a singly occupied dangling-bond state in undoped *a*-Si:H.¹⁶

The position of the Fermi level in doped *a*-Si:H gives us more information on the energetic positions of spin centers with $g=2.004$ and 2.01 . For the case of P- (B-) doped *a*-Si:H, where the Fermi level is close to the conduction- (valence-) band edge, the appearance of $g=2.004$ (2.01) in dark suggests that the spin center of $g=2.004$ (2.01) is located close to the conduction- (valence-) band edge. Generally, the g value varies as a function of the energetic position of the spin center as well as its spin-orbit coupling constant and the nature of its wave function. The difference in the g value among the $g=2.005$, 2.004 , and 2.01 signals is at least a result of a difference in their energetic positions in the quasi-band-gap, considering the discussion about the energetic position. The reason why three centers occur at different energy positions is not clear at the present stage. A detailed study of the hyperfine structure is needed.

On the basis of optically detected magnetic-resonance (ODMR) measurements, Morigaki suggested that the origin of the optically induced ESR signals having $g=2.004$ and 2.01 was the different kinds of dangling-

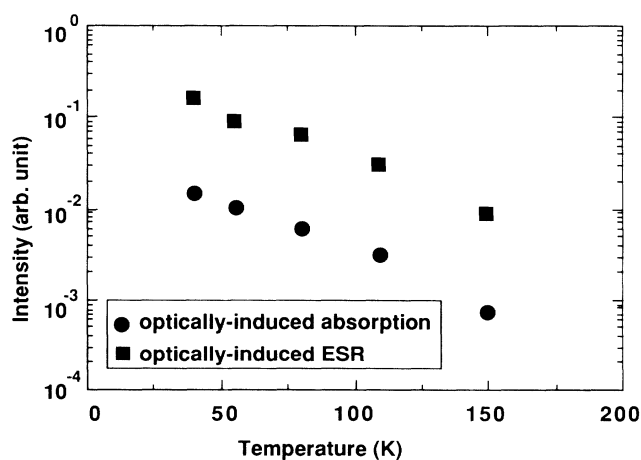


FIG. 3. Temperature dependences of the additional optical absorption at a low photon energy (0.8 eV) and of the optically induced ESR intensity.

bond states since they act as quenching centers to photoluminescence.¹⁷ The ODMR results are, therefore, consistent with the present work.

The behaviors of optically induced ESR and optical-absorption spectra in undoped *a*-Si:H are quite similar to those in the chalcogenide glasses, although some quantitative difference exists in their thermal relaxation times. In chalcogenide glasses, most of the optically induced ESR signal remains even after cutting off the light at around 56 K. On the other hand, for *a*-Si:H, the signal almost disappears within several 100 ms after cessation of illumination at 56 K. However, for lower temperatures, a larger amount of the optically induced signal remains stable after cutting off the light. For example, in the case of illumination at 33 K, one-half of the optically induced ESR signal remains observable even 3 h after cessation of illumination. This signal is completely annealed out at room temperature, as also observed in chalcogenide glasses. The difference in the thermal relaxation time of optically induced centers between the two categories of materials is partly due to the difference in the network flexibility arising from the different average coordination numbers in the two materials.

In order to explain an optically induced ESR signal, charged defect states have been proposed in chalcogenide glasses.^{3,4} A similar concept might be applicable to *a*-Si:H. At the initial stage of the research in *a*-Si:H, several authors proposed the possibility of a charged state in tetrahedrally bonded amorphous semiconductors. Adler¹⁸ and Elliott¹⁹ independently calculated the energies of various bonding states in tetrahedrally bonded amorphous semiconductors and suggested that charged states are preferable to neutral dangling bonds.

In conclusion, the origin of the optically induced ESR signal in undoped *a*-Si:H has been identified to be a localized state with structure similar to a singly occupied dangling-bond state from a ²⁹Si hyperfine study. The additional optical absorption due to the optically induced localized states has also been detected. The phenomenological similarity of experimental results between *a*-Si:H

and chalcogenide glasses has been pointed out.

¹S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. Lett. **34**, 1346 (1975).

²S. G. Bishop, U. Strom, and P. C. Taylor, Phys. Rev. Lett. **36**, 543 (1976).

³R. A. Street and N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).

⁴M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).

⁵S. Yamasaki, K. Nakagawa, H. Yamamoto, A. Matsuda, H. Okushi, and K. Tanaka, in *Proceedings of the Topical Conference on Tetrahedrally Bonded Amorphous Semiconductors, Carefree, Arizona, 1981*, edited by R. A. Street, D. K. Biegelsen, and J. C. Knights, AIP Conference Proceedings No. 73 (American Institute of Physics, New York, 1981), p. 258.

⁶W. B. Jackson and N. M. Amer, in *Proceedings of the Topical Conference on Tetrahedrally Bonded Amorphous Semiconductors, Carefree, Arizona, 1981* (Ref. 5), p. 263.

⁷J. C. Knights and D. K. Biegelsen, Solid State Commun. **22**, 133 (1977).

⁸R. A. Street and D. K. Biegelsen, J. Non-Cryst. Solids **35 & 36**, 651 (1980).

⁹S. Yamasaki, Philos. Mag. **56**, 79 (1987).

¹⁰D. K. Biegelsen and M. Stutzmann, Phys. Rev. B **33**, 3006 (1986).

¹¹S. Yamasaki, M. Kaneiwa, S. Kuroda, H. Okushi, and K. Tanaka, Phys. Rev. B **35**, 6471 (1987).

¹²M. Stutzmann and D. K. Biegelsen, Phys. Rev. B **40**, 9834 (1989).

¹³D. J. Sloop, H. Yu, T. Lin, and S. I. Weissman, J. Chem. Phys. **75**, 3746 (1981).

¹⁴H. Sano, S. Nonomura, and S. Nitta, Solid State Commun. (to be published).

¹⁵R. A. Street and D. K. Biegelsen, in *The Physics of Hydrogenated Amorphous Silicon*, edited by J. D. Joannopoulos and G. Lucovsky (Springer-Verlag, Berlin, 1984).

¹⁶S. Yamasaki, S. Kuroda, J. Isoya, H. Okushi, and K. Tanaka, J. Non-Cryst. Solids **77 & 78**, 727 (1985).

¹⁷K. Morigaki, Jpn. J. Appl. Phys. **22**, 375 (1983).

¹⁸D. Adler, Phys. Rev. Lett. **41**, 1755 (1978).

¹⁹S. R. Elliott, Philos. Mag. B **38**, 325 (1978).