

Electron Spin Resonance of Deuterium-Related Dangling Bonds in Deuterated Amorphous Silicon

by

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Abstract

Electron spin resonance (ESR) measurements in deuterated amorphous silicon (a-Si:D) have been carried out to elucidate the existence of deuterium-related dangling bonds, using two types of a-Si:D samples, i.e., samples prepared by reactive sputtering and glow-discharge (plasma-enhanced chemical vapour deposition) methods. The existence of deuterium-related dangling bonds is confirmed by deconvoluting the ESR spectrum into two components due to normal dangling bonds and deuterium-related dangling bonds and by obtaining the results consistent with those obtained from electron-nuclear double resonance (ENDOR) measurements in a-Si:D. Further, hyperfine structure due to ²⁹Si nucleus in a-Si:D has been resolved for normal dangling bonds, whose nature is also elucidated.

Keywords: ESR; Defect; Amorphous silicon; Light-induced effect; Amorphous network.

1 Introduction

In hydrogenated amorphous silicon (a-Si:H), the existence of two-types of silicon-dangling bonds, i.e., normal dangling bonds and hydrogen-related dangling bonds (dangling bonds having hydrogen at a nearby site, as shown in Fig. 1), has been suggested from electron-nuclear double resonance

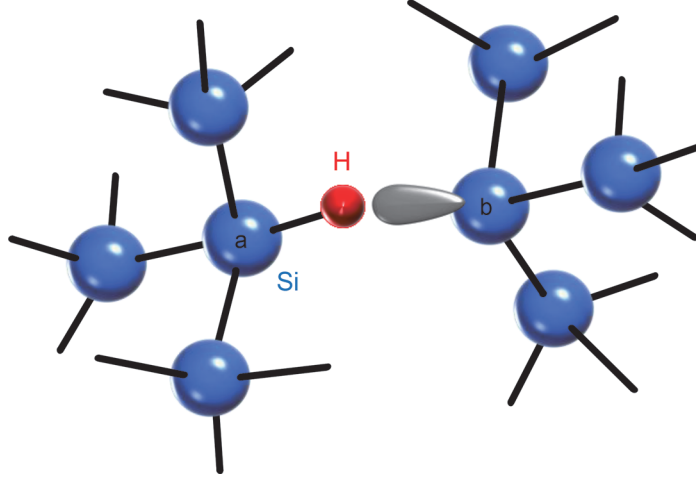


Figure 1: Schematic illustration of the hydrogen-related dangling bond in a-Si:H.

(ENDOR) measurements [1, 2]. In the electron spin resonance (ESR) spectrum of hydrogen-related dangling bonds, hyperfine splitting due to hydrogen nuclear spin (proton) has not been resolved so far, except for hydrogen atom incorporated on the interface between substrate and film or near the surface of a-Si:H film [3]. Thus, it is difficult to identify directly such a dangling bond by ESR spectra, but deconvolution of the ESR spectrum into two components due to normal dangling bonds and hydrogen-related dangling bonds may lead us to estimate the isotropic and anisotropic hyperfine interaction constants in the ESR spectrum of hydrogen-related dangling bonds [4, 5]. Furthermore, the ENDOR technique is an excellent tool for identification of such a dangling bond from the observation of the ENDOR signal due to hydrogen nucleus, from which hyperfine interaction constants may be estimated. When hydrogen is substituted by deuterium, the ESR line shape of hydrogen-related dangling bonds should be changed somehow, because the isotropic and anisotropic hyperfine interactions with hydrogen nuclei contributing to the line shape would be changed.

The presence of the hydrogen-related dangling bond was first suggested from a model of light-induced defect creation in a-Si:H [6]. After then, the light-induced creation of the hydrogen-related dangling bond has been observed in ESR measurements of a-Si:H [4, 7, 8] and hydrogenated polycrystalline silicon (pm-Si:H) [9, 10]. The light-induced annealing of the hydrogen-related dangling bond has been observed in ESR measurements of a-Si:H [11–13]. Furthermore, the thermal annealing of the light- and thermally-induced dangling bond has also been observed in ESR measurements of a-Si:H [14, 15] and pm-Si:H [16]. The results of the ESR spectrum into two components due to normal dangling bonds and hydrogen-related dangling bonds have been reviewed by Morigaki and Hikita [17].

In this paper, we present the results of the ESR measurements in a-Si:D and compare them with those obtained for a-Si:H. Further, we discuss the nature of dangling bond electrons in a-Si:H and a-Si:D.

2 Experimental

The sample of SP a-Si:D used in this study was prepared on a water-cooled substrate by reactive sputtering (SP) of Si of 120 W in a mixture gas of Ar and D₂ whose ratio $[D_2] / ([Ar] + [D_2])$ was 0.30. The samples of GD a-Si:D and GD a-Si:H were prepared, using glow-discharge (GD) technique with pure SiD₄ and pure SiH₄ gas, respectively. The former sample was prepared at 70°C and annealed at 150°C, while the latter sample was prepared at 100°C.

The ESR measurements were carried out at room temperature, using a conventional X-band ESR spectrometer (JEOL JES-FE3X) operating at 9.4 GHz. The observed ESR spectra were deconvoluted into two components, as will be mentioned in Section 3, using the FESRSDS (Fitting of ESR Spectrum for Disordered System) program [4].

3 Results and Discussion

ESR spectra observed for two samples, i.e., SP a-Si:D and GD a-Si:D are shown in Figs. 2 and 3, respectively. The observed ESR spectra are deconvoluted into two components a and b due

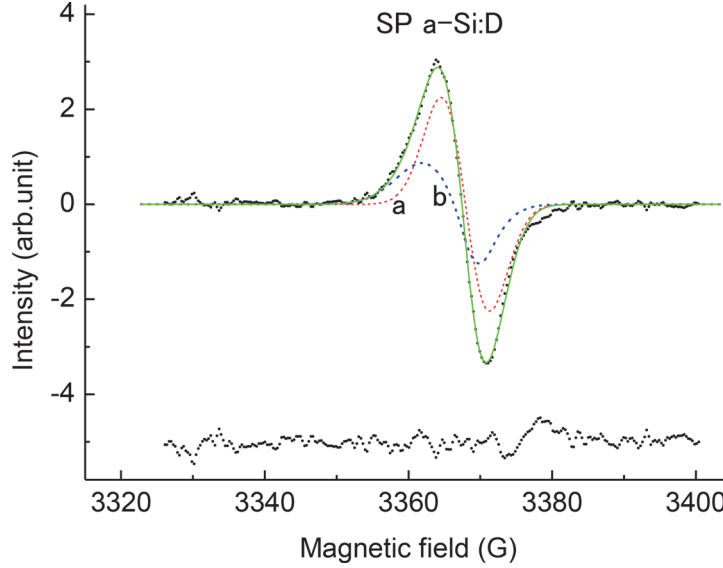


Figure 2: The ESR spectrum observed for a-Si:D sample prepared by reactive sputtering method and deconvolution of the ESR spectrum into two components due to normal dangling bonds, a, and hydrogen-related dangling bonds, b. The values of ESR parameters used for the curves a and b are shown in Table 1. The residual between the calculated curve a + b and the observed spectrum is shown in the lower part of the figure with a scale twice extended compared with other curves.

to normal dangling bonds and deuterium-related dangling bonds, respectively, using the values of ESR parameters listed in Table 1. For normal dangling bonds, isotropic g -value is assumed for simplicity, while for deuterium-related dangling bonds, anisotropic g -values of axial symmetry,

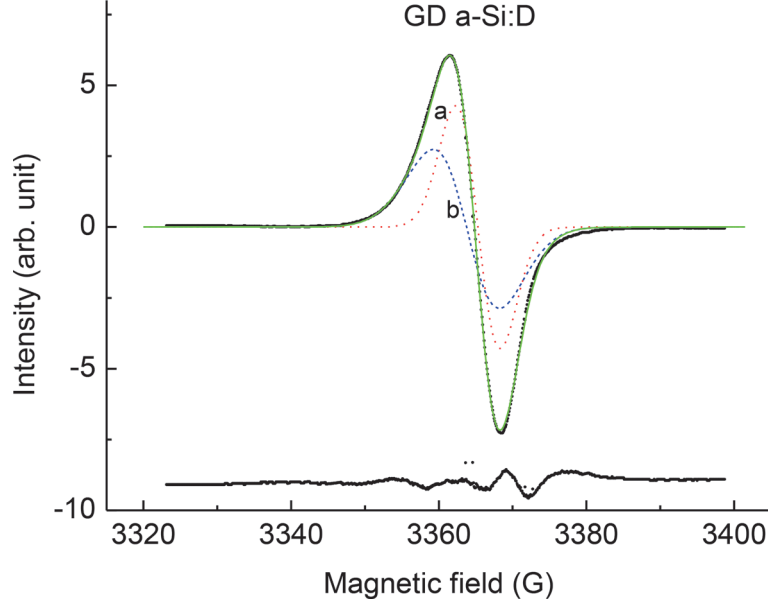


Figure 3: The ESR spectrum observed for a-Si:D sample prepared by glow-discharge (plasma-enhanced chemical vapour deposition) method and deconvolution of the ESR spectrum into two components due to normal dangling bonds, a, and hydrogen-related dangling bonds, b. The values of ESR parameters used for the curves a and b are shown in Table 1. The residual between the calculated curve $a + b$ and the observed spectrum is shown in the lower part of the figure with a scale twice extended compared with other curves.

Table 1: The values of parameters used in the calculation

	Normal DB (a)			H-related DB (b)							N_s (cm^{-3})
	g_a	σ_a (G)	N_a (%)	$g_{//}$	$g_{\perp}$	$A_{//}$ (G)	$A_{\perp}$ (G)	$\sigma_{//}$ (G)	$\sigma_{\perp}$ (G)	N_b (%)	
a-Si:H	2.0051	3.5	60	2.0038	2.0068	15	2	2.0	5.3	40	4.9×10^{17}
a-Si:D (SP)	2.0039	3.4	39.3	2.0036	2.0060	1.55	0.3	1.2	4.5	60.7	4.2×10^{18}
a-Si:D (GD)	2.0048	3.0	38.9	2.0053	2.0060	2.97	0.3	2.7	5.3	61.1	$\sim 10^{17}$

DB represents the dangling bond.

σ is the standard deviation of the Gaussian spin-packet.

N_a and N_b represent the ratio of the intensities of the components (a) and (b) to the total intensity corresponding to the spin density N_s , respectively.

N_s is the measured spin density.

$g_{//}$ and $g_{\perp}$ and anisotropic hyperfine interaction constants, $A_{//}$ and $A_{\perp}$, are assumed, where $//$ and $\perp$ designate the direction parallel and perpendicular to the symmetric axis, respectively. The spin packet is assumed for both dangling bonds to be Gaussian-shape, whose standard deviation is given by σ . For comparison, the result of deconvolution of ESR spectra in GD a-Si:H sample prepared at 100°C [4] is also shown in Table 1. If the wave function of dangling bond electrons in a-Si:D is the same as that in a-Si:H and atomic configuration around the dangling bond in a-Si:D is also the same as that in a-Si:H, differences in isotropic and anisotropic hyperfine interaction constants between a-Si:H and a-Si:D are determined by difference in the nuclear g -values, g_D and

g_H , of deuterium and hydrogen nuclei. This can be checked by comparing the ratios of $A_{iso}(D)$ to $A_{iso}(H)$ and of $A_{aniso}(D)$ to $A_{aniso}(H)$ with the ratio of g_D and g_H .

From the values of the parameters shown in Table 1, the values of the ratio of $A_{iso}(D)$ to $A_{iso}(H)$ and of the ratio of $A_{aniso}(D)$ to $A_{aniso}(H)$ are 0.191 and 0.203, respectively. These ratios are in principle given by the ratio of the nuclear moments of D and H, i.e., the ratio of g_D to g_H , that is 0.154. This value is close to those of the above two values, but there still remains some difference. This means that the atomic configurations of D- and H-related dangling bonds around the dangling bond site are somehow different owing to the network relaxation, and that there is also a slight difference in the nature of wave function of dangling bond electrons between in a-Si:D and in a-Si:H.

Further, we can compare the value of $A_{\perp}(D)$ ($= 0.3$ gauss (G)) with its value estimated from ENDOR measurements in a-Si:D, that is $A_{\perp}(D) = 0.33 \text{ G}^1$ [2]. There is a good agreement between the above two values, so that this shows that the result deduced from deconvolution of ESR spectra is consistent with that deduced from ENDOR measurements.

Furthermore, we have carried out ESR measurements in various kinds of GD a-Si:H samples prepared at 120°C , using gas-dilution ratio of γ ($\equiv [\text{SiH}_4] / ([\text{SiH}_4] + [\text{H}_2])$) [5]. From the deconvolution of the observed ESR spectra and the calculation of anisotropic hyperfine interaction constant, the distance between dangling bond site and hydrogen, R , has been estimated to be $2.1\text{--}2.9 \text{ \AA}$, depending on γ , that is, depending on optical gap energy.

Recently, pulse-ENDOR measurements on ^1H nuclei in a-Si:H have been carried out by Fehr et al.[18]. From their results, we have pointed out that the ENDOR spectrum has a shoulder around $\nu_{\text{RF}} - \nu_0 = -5 \text{ MHz}$, where ν_{RF} and ν_0 are the RF frequency and the proton natural resonance frequency, respectively, and that this frequency corresponds to $R = 2.2 \text{ \AA}$ [19]. Thus, this may be further evidence for the existence of the hydrogen-related dangling bonds. Further, it is worth noting that a similar hydrogen-related dangling bond, so called vacancy-hydrogen complex (see Fig. 4), has been identified from hyperfine structure due to a nearby hydrogen nucleus in ESR

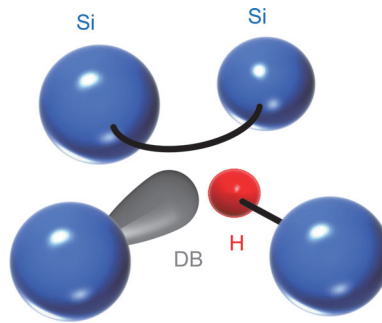


Figure 4: Atomic configuration of the vacancy-hydrogen complex in crystalline silicon: Model adapted from Ref. (20). DB represents the dangling bond.

spectra observed in crystalline silicon implanted with hydrogen at low temperatures ($\leq 100 \text{ K}$) [20]. The distance between dangling bond site and hydrogen is estimated to be $2.7 \text{ \AA}$ from the

¹In Ref. [2], it is written that a_D ($= A_{\perp}(D)$) is estimated to be 1.8 MHz . This is incorrect. a_D should be read 0.92 MHz ($= 0.33 \text{ G}$).

observed hyperfine interaction constant. Assuming that the Si–H bond length is 1.5 Å and that the structure is diamond type, the distance of 2.8 Å is estimated [20]. These distances lie in the range of 2.1–2.9 Å estimated from various kinds of a-Si:H samples prepared at 120°C with different γ values, as has already been mentioned.

In the following, we present the observed ESR spectra exhibiting hyperfine structure due to ^{29}Si nucleus at the dangling bond site of the normal dangling bond (the natural abundance of ^{29}Si is 4.67%) in GD a-Si:D, as shown in Fig. 5. For a-Si:H, Biegelsen and Stutzmann [21, 22]

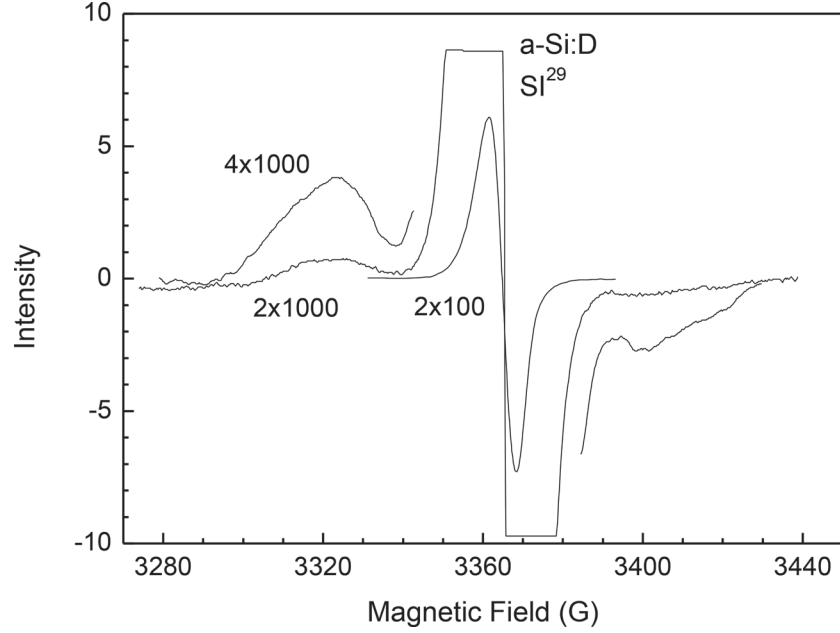


Figure 5: The ESR spectrum and hyperfine components due to ^{29}Si nucleus at the dangling bond site of the normal dangling bond observed for a-Si:D sample prepared by glow-discharge method. The three curves are shown with different scales. The scale numbers are shown along with each curve.

reported the observation of hyperfine structure due to ^{29}Si nuclei in natural and enriched a-Si:H samples. For comparison between hyperfine structures observed in a-Si:D and a-Si:H, we take the separation between two inflection points, i.e., a valley at the low magnetic field side and a peak at the high magnetic field side from the central magnetic field of differential ESR curves. For a-Si:D and a-Si:H, 56.7 G and 50.9 G [21,22] are given, respectively. Thus, the difference between the above two values is not so large.

The nature of wave function of dangling bond electrons of normal dangling bonds can be evaluated in terms of tight-binding approximation: The wave function is given by

$$\psi = \sum_j \eta_j \psi_j, \quad (1)$$

$$\psi_j = \alpha_j (\psi_{3s})_j + \beta_j (\psi_{3p})_j, \quad (2)$$

where the wave function at the j th site is composed of atomic 3s and 3p orbitals, ψ_{3s} and ψ_{3p} at the j th site whose percentage 3s and 3p characters are designated by α_j^2 and β_j^2 , respectively.

The isotropic and anisotropic hyperfine interaction constants of the unpaired electron with ^{29}Si nucleus at the j th site, A_{iso} and A_{aniso} are given by

$$A_{iso,j} = (8\pi/3)g_e g_n \mu_B \mu_n \alpha_j^2 \eta_j^2 |\psi_{3s}(0)_j|^2, \quad (3)$$

$$A_{aniso,j} = (2/5)g_e g_n \mu_B \mu_n \beta_j^2 \eta_j^2 \langle r_{3p}^{-3} \rangle_j, \quad (4)$$

respectively, where g_e , g_n , μ_B and μ_n are the electronic and nuclear g -values, the Bohr magneton and the nuclear magneton, respectively, and $\langle r_{3p}^{-3} \rangle_j$ is the average value of $\langle r^{-3} \rangle$ of the $3p$ state on the j th site. $A_{//}$ and $A_{\perp}$ are given by

$$A_{//} = A_{iso} + 2A_{aniso}, \quad (5)$$

$$A_{\perp} = A_{iso} - A_{aniso}. \quad (6)$$

The computer-simulated hyperfine structure with ^{29}Si nucleus is shown in Fig. 6 (see the figure

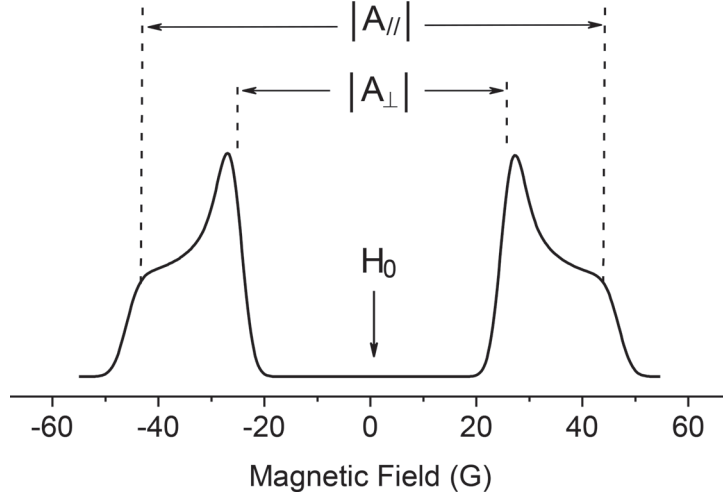


Figure 6: The computer-simulated hyperfine structure with the values of ESR parameters shown below: $g_{iso} = 2.004$, $A_{//} = 93$ G, $A_{\perp} = 51$ G and $\sigma_{iso} = 2$ G. The isotropic g -value and the isotropic σ value are assumed for simplicity.

caption for the used values of ESR parameters). The wave function can be estimated from an analysis of hyperfine structure in ESR spectra. For a-Si:H, the nature of wave function of dangling bond electrons of normal dangling bonds has been given from the ENDOR-detected ESR spectra, as follows [23]: $\eta_0^2 = 0.54$, $\alpha_0^2 = 0.10$, and $\beta_0^2 = 0.90$, where η_0^2 , α_0^2 , and β_0^2 are the normalized electron density, the percentage $3s$ character, and the percentage $3p$ character at the dangling bond site, respectively. These values of parameters have been deduced from hyperfine splitting of $|A_{//}|$ ($= 120$ G) and $|A_{\perp}|$ ($= 67$ G). For a-Si:D, we obtain $|A_{//}| = 93$ G and $|A_{\perp}| = 51$ G from computer simulation, as shown in Fig. 6, from which we obtain $\eta_0^2 = 0.43$, $\alpha_0^2 = 0.10$, and $\beta_0^2 = 0.90$. Thus, the dangling bond electron of normal dangling bonds in a-Si:D is more delocalized than that in a-Si:H. This difference may arise from the difference in network relaxation arising from those in the vibration frequencies of the Si–H and Si–D bonds and their spatial distribution in the network. However, the reason is not obvious at present. It is worth noting that the wave function shown above in a-Si:H and a-Si:D deviates from tetrahedrally-hybridized orbital of sp^3

and exhibits more p -like character.

The atomic configuration of normal dangling bonds in a-Si:H has been discussed in more detail by Biegelsen and Stutzmann [22]. A detailed experimental and theoretical study of normal dangling bonds has been performed by Fehr et al.[24].

Finally, we note from Table 1 that the ratio of N_b/N_a in a-Si:D is opposite to that in a-Si:H. In a-Si:D, two types of samples, i.e., SP a-Si:D and GD a-Si:D are similar to each other in this ratio. The difference between a-Si:H and a-Si:D may be related to the incorporation process of hydrogen and deuterium into amorphous network of silicon. At present, however, the exact origin of this difference is not known.

4 Conclusion

From the deconvolution of ESR spectra in a-Si:D, we obtain the results consistent with those obtained from ENDOR measurements in a-Si:D, and we also obtain a consistent result from their comparison with the isotropic and anisotropic hyperfine interaction constants in a-Si:H. Such an overall comparison between a-Si:D and a-Si:H leads us to conclude that the hydrogen-related dangling bonds exist in a-Si:H.

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