

Electron-Nuclear Double Resonance Spectra of Dangling Bonds due to Distant Nuclei in Hydrogenated Amorphous Silicon

Kazuo MORIGAKI^{*1}, and Kosei TAKEDA^{*2}

^{*1} Department of Electrical-System Engineering, Hiroshima Institute of Technology,
Miyake, Saeki-ku, Hiroshima-shi, Hiroshima, 731-5193, Japan
Present address: C-305, Wakabadai 2-12, Inagi, Tokyo, 206-0824, Japan
E-mail: k.morigaki@yacht.ocn.ne.jp

^{*2} Department of Physics, School of Science, Tokai University,
Hiratsuka-shi, Kanagawa, 259-1292, Japan
Present address: 5-107, Fuchinobe-Honcho 1-22, Chuo-ku,
Sagamihara-shi, Kanagawa, 252-0202, Japan
E-mail: kmtakeda@athena.ocn.ne.jp

(Received on July 13, 2018; accepted on Dec. 10, 2018)

Abstract

We have calculated the ENDOR (electron-nuclear double resonance) spectrum of dangling bonds due to a distant hydrogen nucleus in hydrogenated amorphous silicon, using the theory of distant ENDOR proposed by Lambe et al. (Phys. Rev. **122** (1961), 1161). We are concerned with a site of hydrogen located from a dangling bond with mutual distance of 5.12 Å. The calculated ENDOR spectrum is compared with the observed ENDOR spectrum by Fehr et al. (Phys. Stat. Solidi A **207** (2010), 552).

Keywords: ESR; Electron-nuclear double resonance; Defect; Amorphous silicon; Amorphous network.

1 Introduction

In a previous paper [1], we have calculated the signal intensity of electron-nuclear double resonance (ENDOR) of dangling bonds due to distant hydrogen nuclei on the basis of Lambe et al.'s theory [2], particularly the intensity of dispersion part (χ') at the central electron spin resonance (ESR) frequency. In this paper, we deal with the ENDOR spectrum, which consists of a change in the z -component of magnetization with nuclear magnetic resonance (NMR), because the observed ENDOR signal is detected, using the pulsed ENDOR measurement [3, 4], particularly observing a change in the intensity of the electron spin echo (ESE) signal with NMR (so-called Davies method [5]). Thus, in this paper we calculate ENDOR spectra associated with a change in the z -component of magnetization with NMR due to distant hydrogen nuclei. For comparison, we also calculate ENDOR spectra associated with a change in the dispersion part χ' and absorption part χ'' with NMR. In Section 2, we present the formula of these quantities by Lambe et al. [2], and, in Section 3, we present the calculated ENDOR spectra associated with changes in those quantities with NMR. In Section 4, we discuss on the comparison between calculated ENDOR spectra and observed ENDOR spectra [4].

2 Theory of Distant ENDOR

We consider distant ENDOR observed in a-Si:H in terms of Lambe et al.'s theory [2] which is based on the dynamical nuclear polarization [6, 7]. In this theory, forbidden double spin-flip transition of electron and nuclear spins ($I = 1/2$) is excited. We summarize Lambe et al.'s theory, below: The difference in electron spin population is defined as follows:

$$n(\omega') = N^-(\omega') - N^+(\omega'), \quad N(\omega') = h(\omega' - \omega_0), \quad (1)$$

where $h(\omega' - \omega_0)$ is a local field distribution of microwave frequency ω' with a central ESR frequency ω_0 , and $N^-(\omega')$ and $N^+(\omega')$ are the part of electrons with spin down and the part of electrons with spin up, respectively.

$n(\omega')$ is given by

$$n(\omega') = \frac{n_0(\omega') + (\pi S / 2T_2)N(\omega')[g'(\omega + \Delta - \omega') - g'(\omega - \Delta - \omega')]m}{1 + (\pi S / 2T_2)[2g(\omega - \omega') + g'(\omega + \Delta - \omega') + g'(\omega - \Delta - \omega')]}, \quad (2)$$

$$S = \left(\frac{1}{2}\gamma H_1\right)^2 T_1 T_2, \quad (3)$$

where T_1 , T_2 , g' , γ , H_1 and $n_0(\omega')$ are the spin-lattice relaxation time of electrons, the spin-spin relaxation time of electrons (the inverse of the width of a spin-packet), the relative strength of forbidden and allowed transitions, the gyromagnetic ratio of electrons, the magnitude of the microwave field, and the equilibrium value of $n(\omega')$ in the absence of fields, respectively. $g'(\omega - \Delta - \omega')$ is the natural line shape function, in which Δ is the nuclear Zeeman splitting.

When microwave power is applied at a resonance frequency of a normal dangling bond and RF power at an ENDOR frequency (NMR frequency) is further applied, the difference in nuclear spin polarization is defined as $m = M^- - M^+$, in which M^+ and M^- are the fraction of nuclei with spin up and spin down, respectively. The approximate result of m is obtained, as follows:

$$\frac{m}{m_0} = \frac{1 + (2T_N/T_1 T_2) \left[\frac{1}{2} g' S / (1 + \frac{1}{2} g' S) \right] h(\omega - \omega_0) [1 + (4/\pi)(T_2^*)^2 \omega(\omega_0 - \omega)]}{1 + (2T_N/T_1 T_2) \left[\frac{1}{2} g' S / (1 + \frac{1}{2} g' S) \right] h(\omega - \omega_0) (1 + \frac{1}{4} g' S)}, \quad (4)$$

where T_N and T_2^* are the nuclear spin-lattice relaxation time and the inverse of the line width of a local field distribution, respectively. When the ESR line is inhomogeneously broadened about its center ω_0 with $1/T_2^*$, the line shape function is defined as $h(\omega - \omega_0)$ that is normalized with

$$\int_0^\infty h(\omega' - \omega_0) d\omega' = 1. \quad (5)$$

The pulsed ENDOR measurement [4] has been carried out with a pulse sequence [5]. Further, the ENDOR signal is detected as a change in the ESR signal associated with NMR, so that the change in the z -component of magnetization associated with NMR may be observed as the ENDOR signal. Thus, change in the z -component of magnetization is related to $\Delta n = n - n_0$.

Further, for comparison, $\Delta\chi'$ and $\Delta\chi''$ are given by

$$\chi'(\omega) = \frac{1}{2}\chi_0 \left\{ \int_0^\infty \frac{2\omega'^2 h(\omega' - \omega_0) d\omega'}{\omega'^2 - \omega^2} + \left(\frac{m}{m_0}\right) \frac{\frac{1}{2}g'S}{(1 - \frac{1}{2}g'S)} \left(\frac{2\pi}{T_2}\right) h(\omega - \omega_0) \right\}, \quad (6)$$

$$\Delta\chi'(\omega) = \chi'(\omega) - \chi_0, \quad (7)$$

$$\begin{aligned} \chi''(\omega) = \frac{1}{2}\chi_0\omega_0 h(\omega - \omega_0) & \left\{ \int_0^\infty \frac{\pi g(\omega - \omega') d\omega'}{1 + (\pi S / T_2) g(\omega - \omega')} + \text{constant term} - m(\omega_0 - \omega) \right. \\ & \left. \times [\text{positive definite term}] \right\}, \end{aligned} \quad (8)$$

$$\Delta\chi''(\omega) = \chi''(\omega) - \chi_0. \quad (9)$$

3 Results and Discussion

Fehr et al. [4] have carried out pulsed ENDOR measurements at 34 GHz and 80 K. In order to compare with their observed ENDOR spectrum (Fig. 1), we calculate Δn , using the values of parameters being listed in Table 1. For comparison, we also calculate $\Delta\chi'$ and $\Delta\chi''$. The calculated curves of the local field distribution curves, Δn , $\Delta\chi'$ and $\Delta\chi''$ are shown in Figs. 3(a), (b), (c), and (d) for $r = 5.12 \text{ \AA}$ (Fig. 2), respectively. The computer-simulated ENDOR spectra for $5.12 \text{ \AA}$ shown in Fig. 1 should be replaced by Fig. 3(b), because the spectrum shown in Fig. 1 is obtained from a transformation of the ESR spectrum involving hyperfine structure (dipolar interaction) with hydrogen nuclei, taking into account for distribution of hydrogen. This spectrum corresponds to the local field distribution curve, $h(\omega' - \omega_0)$, shown in Fig. 3(a). The spectrum shown in Fig. 3(b) is the ENDOR spectrum for $r = 5.12 \text{ \AA}$. A dip centered at the natural NMR frequency is seen in Fig. 3(b). This dip contributes partially to a dip seen in the observed ENDOR spectrum by Fehr et al. [4]. The actual dip to be compared with the observed dip should be determined from relative intensities at the central frequency for various values of r and also from the local ENDOR spectrum HDB (hydrogen-related dangling bond) in Fig. 1). The atomic configurations of normal dangling bond and hydrogen-related dangling bond are shown in Fig. 4.

The curve of χ'' is normally so-called absorption shape such as that shown for $r =$

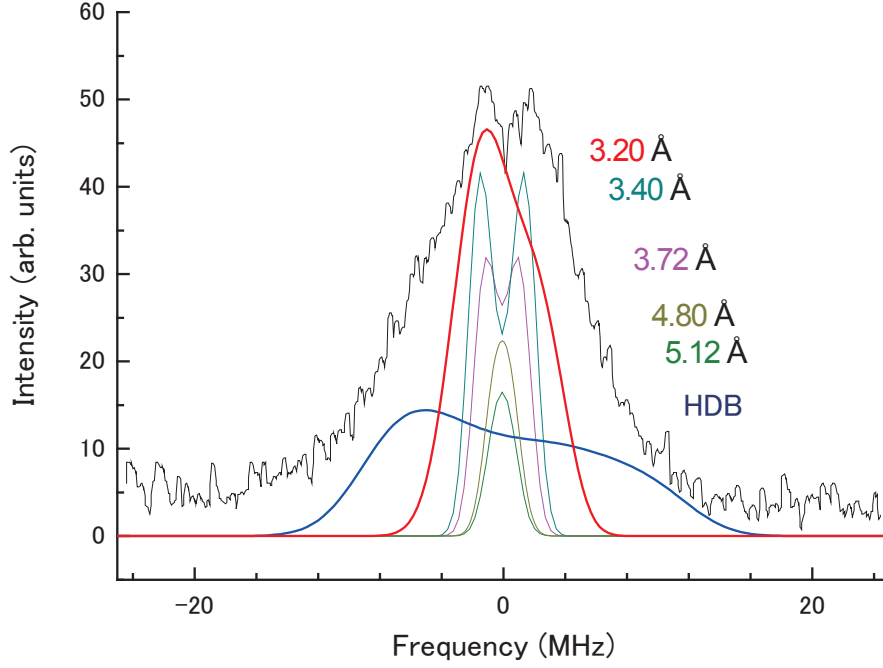


Figure 1: The computer-simulated ENDOR spectra in a-Si:H. HDB(blue): The values of the parameters are given below. $g_{//} = 2.0050$ and $g_{\perp} = 2.0056$, $A_{//} = 19.6$ MHz, $A_{\perp} = 2.80$ MHz, $\sigma_{//} = 2.24$ MHz, and $\sigma_{\perp} = 3.36$ MHz. The matrix ENDOR spectra for various distance between the dangling bond site and the hydrogen, r , are shown as follows: $r = 3.20$ Å (red). The values of the parameters are given below. $g_{//} = 2.0050$ and $g_{\perp} = 2.0056$, $A_{//} = 4.68$ MHz and $A_{\perp} = 2.34$ MHz, $\sigma_{//} = 1.12$ MHz, and $\sigma_{\perp} = 1.68$ MHz. $r = 3.40$ Å (sky blue), $r = 3.72$ Å (magenta), $r = 4.80$ Å (yellow brown), $r = 5.12$ Å (olive): The values of the parameters for these r are given in Table 1. The Fehr ENDOR spectrum [4] is also shown. For the notation of symbols, see [8]. (Reproduced from [8]).

Table 1 The values of parameters used in the calculation

r (Å)	T_N (ms)	T_1 (μ s) ¹⁾	T_2 (μ s) ¹⁾	g'	T_2^* (μ s)	$h(0)$ ²⁾	$4\pi r^2 g(r)$ ³⁾
5.12	100	4.72×10^2	1.57×10^2	0.01	0.15	16.4	245

1) The values of T_1 and T_2 are tentatively taken from those obtained by spin-echo measurements at 60 K by Fehr et al. [3], while a pulsed ENDOR measurement by Fehr et al. [4] was done at 80 K.

2) The value of $h(0)$ for $r = 5.12$ Å is determined from the curve shown in Fig. 3(a), following to the scale of the coordinate in Fig. 3(a).

3) $g(r)$ is a radial density function. The value of $4\pi r^2 g(r)$ corresponds to the number of hydrogen with the same r .

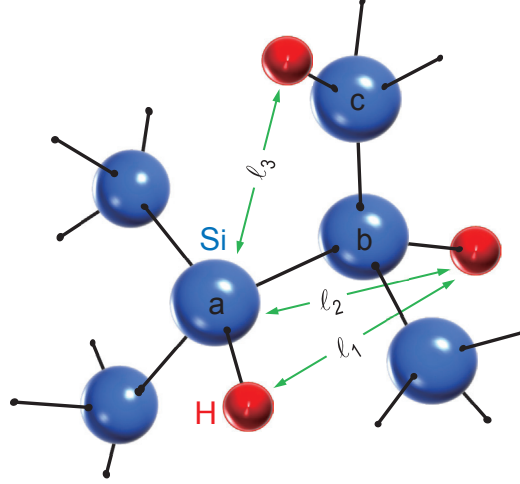


Figure 2: Schematic illustration of the local structure being composed of silicon atoms and hydrogen atoms. The distances ℓ_1 , ℓ_2 , and ℓ_3 are cited from Bellisent et al. [9] as follows: $\ell_1 = 3.3 - 4.3$ Å, $\ell_2 = 3.2$ Å, and $\ell_3 = 3.72 - 5.12$ Å. (Reproduced from [8]).

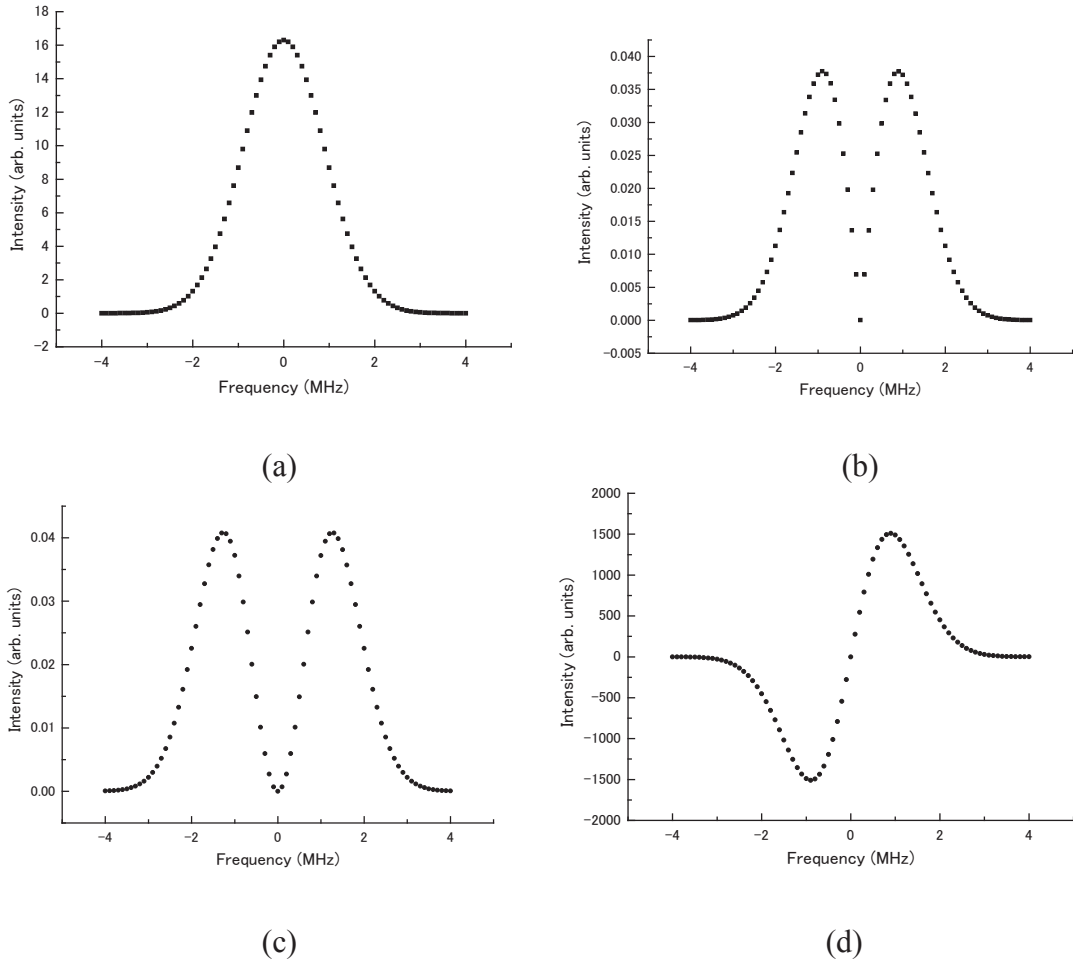


Figure 3: The calculated curves of the local field distribution curves (the central frequency = ω_0): (a), Δn : (b), $\Delta\chi'$: (c), and $\Delta\chi''$: (d) for $r = 5.12$ Å (Fig. 2).

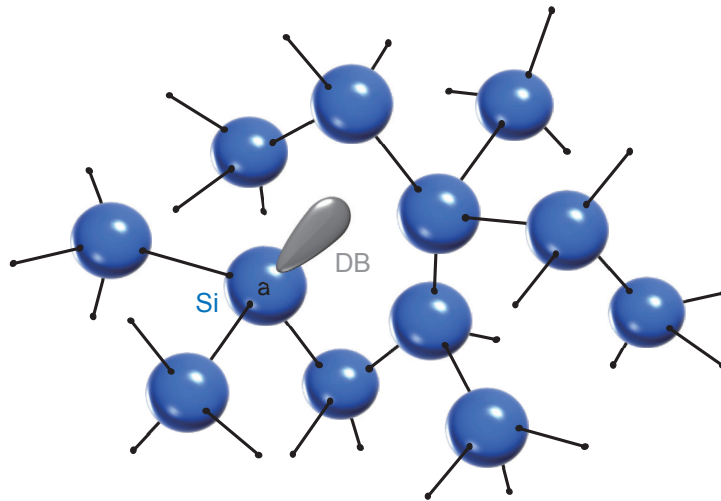


Figure 4(a): Schematic illustration of the normal dangling bond in a-Si:H [10].

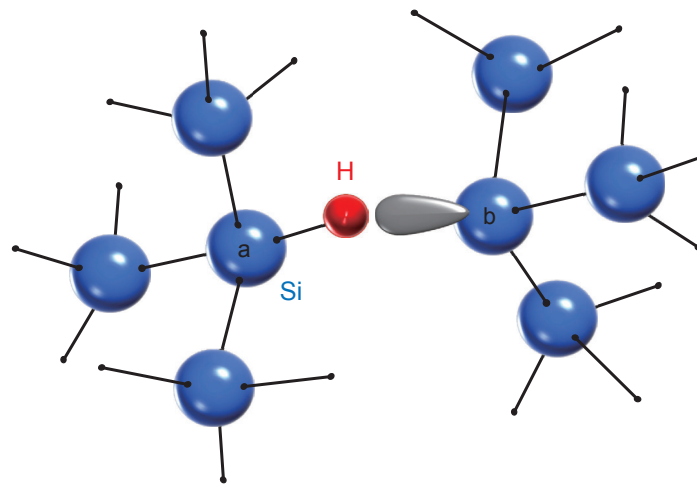


Figure 4(b): Schematic illustration of the hydrogen-related dangling bond in a-Si:H [10].

5.12 Å in Fig. 1, while the curve of χ' is normally so-called dispersion shape. However, the curve of $\Delta\chi''$ shown in Fig. 3(c) has a dip at the natural NMR frequency. This is related to the theory of distant ENDOR, but the physical meaning is not clear.

4 Conclusion

In this paper, we calculate the distant ENDOR spectrum of dangling bonds due to hydrogen nucleus with mutual distance of $r = 5.12$ Å, using the theory of distant ENDOR by Lambe et al. [2]. In the calculated ENDOR spectrum, a dip appears at the natural NMR frequency. This corresponds to a dip in the central region of the observed ENDOR spectrum by Fehr et al. [4]. The observed ENDOR spectrum should be compared with the composite ENDOR spectrum due to hydrogen nuclei being distributed around the dangling bond in such a way as shown in Fig. 2. The relative intensities of each calculated ENDOR spectra shown in Fig. 1 have not yet been determined, so that we have not yet obtained the composite ENDOR spectrum to be compared with the observed ENDOR spectrum by Fehr et al. [4]. This is a future problem.

References

- [1] K. Morigaki and K. Takeda, *Note on the signal intensity of electron-nuclear double resonance in hydrogenated amorphous silicon* Proc. Sch. Sci. TOKAI UNIV. **53** (2018) 1–6.
- [2] J. Lambe, N. Lurance, K. C. McIrvine, and R. W. Terhune, *Mechanisms of double resonance in solids*, Phys. Rev. **122** (1961) 1161–1170.
- [3] M. Fehr, A. Schnegg, B. Roch, O. Astakhov, F. Finger, R. Bittl, C. Teutloff, and K. Lips, *Metastable defect formation of microvoids identified as a source of light-induced degradation in a-Si:H*, Phys. Rev. Lett. **112** (2014) 066403-1–5. See also Supplemental Material for this reference cited in [9].
- [4] M. Fehr, A. Schnegg, C. Teutloff, R. Bittl, O. Astakhov, F. Finger, B. Roch, and K. Lips, *Hydrogen distribution in the vicinity of dangling bonds in hydrogenated amorphous silicon (a-Si:H)*, Phys. Stat. Solidi A **207** (2010), 552–555.
- [5] E. R. Davies, *A new pulse ENDOR technique*, Phys. Lett. **A47** (1974) 1–2.
- [6] A. Abragam and W. G. Proctor, *Polarisation dynamique des noyaux atomiques dans les solides*, Compt. Rend. **246** (1958) 2253–2256. See also A. Abragam, “The

- Principles of Nuclear Magnetism”, Oxford Univ. Press, Oxford, 1961, Chapter 9.
- [7] M. Abraham, M. A. H. MCAusand, and F. H. Robinson, *Dynamic nuclear polarization*, Phys. Rev. Lett. **2** (1959) 449–451.
 - [8] K. Morigaki, H. Hikita, and K. Takeda, *Computer-simulation of electron-nuclear double resonance spectra due to hydrogen-related dangling bonds in hydrogenated amorphous silicon –evidence for existence of hydrogen-related dangling bonds in hydrogenated amorphous silicon–*, Proc. Sch. Sci. TOKAI UNIV. **52** (2017) 27–35.
 - [9] R. Bellisent, A. Meunelle, W. S. Howells, A. C. Wright, T. M. Brunier, R. N. Sinclair, and F. Jansen, *The structure of amorphous Si:H using steady state and pulsed neutron sources*, Physica B **156 & 157** (1989), 217–219.
 - [10] K. Morigaki, H. Hikita, and K. Takeda, “*Model of Light-Induced Defects in hydrogenated amorphous silicon –electron-spin echo measurements–*”, Proc. Sch. Sci. TOKAI UNIV. **52** (2017) 37–45.