

Note on the Signal Intensity of Electron-Nuclear Double Resonance in Hydrogenated Amorphous Silicon

by

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Abstract

We have calculated the ENDOR (electron-nuclear double resonance) signal intensity in hydrogenated amorphous silicon, using the theory of distant ENDOR proposed by Lambe et al. (Phys. Rev. **122** (1961) 1161). Two sites of hydrogen located from a normal dangling bond with mutual distance of 4.80 Å and 5.12 Å are considered in this paper. The ENDOR signal intensity is related to a change in the nuclear spin polarization with ENDOR.

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

1 Introduction

Hydrogenated amorphous silicon (a-Si:H) has been extensively investigated from the following viewpoints, i.e., from fundamental physics in the disordered system, because this material forms amorphous network that is one of typical disordered systems, and also from applications such as solar cells, thin-film transistors, etc. [1]. In this material, hydrogen plays an important role in its electronic properties, because hydrogen atoms terminate those silicon-dangling bonds which prevent impurity doping in order to get n-type or p-type doped semiconductors. Further, knowledge of distribution of hydrogen in the amorphous network is so important as to understand electronic properties of this material. As described in a previous paper [2], measurements of electron-nuclear

double resonance (ENDOR) provide us with an important means for knowledge of distribution of hydrogen. In a previous paper [2], we present the results of computer-simulation of ENDOR spectra in comparison with experimental ones obtained by Fehr et al. [3], in which various sites of hydrogen are taken into accounts, i.e., a hydrogen site close to a normal dangling bond, so-called hydrogen-related dangling bond [4], and other hydrogen sites distributed around a normal dangling bond following to the result of neutron-scattering measurements by Bellisent et al. [5].

In a previous paper, we have not calculated the signal intensity of ENDOR spectra. Therefore, in this paper, we present the result of its calculation, using the theory of distant ENDOR by Lambe et al. [6] for two sites of hydrogen located from a normal dangling bond site at $r = 4.80$ Å and 5.12 Å (r : distance between hydrogen site and normal dangling bond site). This result is quite important for understanding the distribution of hydrogen atoms being distant from the dangling bond site.

2 Theory of distant ENDOR [6]

Distant ENDOR is defined as being ENDOR of nuclei located far from an unpaired electron. Lambe et al. [6] used a model of dynamical nuclear polarization [7, 8] in which forbidden transition, i.e., forbidden double spin-flip transition of electron and nuclear spins is excited (nuclear spin has $1/2$). When microwave power is applied at a resonance frequency of a normal dangling bond and RF power at an ENDOR frequency (nuclear magnetic resonance (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. They obtain the approximate result of m , as follows:

$$\frac{m}{m_0} = \frac{1 + (2T_N/T_1T_2) \left[\frac{1}{2}g'S / \left(1 + \frac{1}{2}g'S \right) \right] h(\omega - \omega_0) [1 + (4/\pi)(T_2^*)^2 \omega(\omega_0 - \omega)]}{1 + (2T_N/T_1T_2) \left[\frac{1}{2}g'S / \left(1 + \frac{1}{2}g'S \right) \right] h(\omega - \omega_0) \left(1 + \frac{1}{4}g'S \right)}, \quad (1)$$

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

where T_N , T_1 , T_2 , g' , T_2^* , γ , ω_0 , and H_1 are the nuclear spin-lattice relaxation time, 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 inverse of the line width of a local field distribution, the gyromagnetic ratio of electrons, the central electron spin resonance (ESR) frequency, and the magnitude of the microwave field. 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

$$\int_0^\infty h(\omega' - \omega_0) d\omega' = 1. \quad (3)$$

The ESR signal is detected as a change in dispersion part χ' and absorption part χ'' of microwave magnetic susceptibility with ESR, but it is detected mainly as χ' at the saturation condition, because χ' is much larger than χ'' at this condition. χ_0 is the static magnetic (spin) susceptibility. Thus, we are concerned with χ' for the ENDOR signal, as follows:

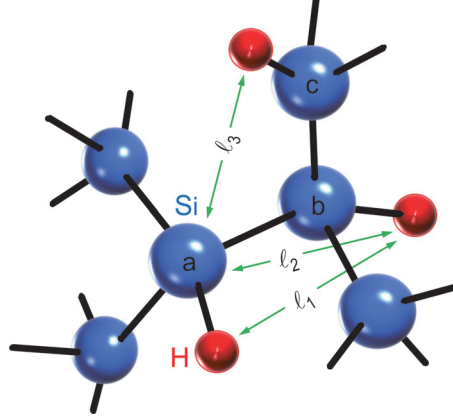


Figure 1: Schematic illustration of the local structure being composed of silicon atoms and hydrogen atoms. The distances ℓ_1 , ℓ_2 , and ℓ_3 are cited from Bellisent et al. [5] as follows: $\ell_1 = 3.3 - 4.3$ Å, $\ell_2 = 3.2$ Å, and $\ell_3 = 3.72 - 5.12$ Å. (Reproduced from [2]).

$$\chi'(\omega) = \frac{1}{2}\chi_0 \left\{ \int_0^\infty \frac{2\omega'^2 h(\omega' - \omega_0) d\omega'}{\omega'^2 - \omega^2} + \left(\frac{m}{m_0}\right) \frac{\frac{1}{2}g'S}{\left(1 - \frac{1}{2}g'S\right)} \left(\frac{2\pi}{T_2}\right) h(\omega - \omega_0) \right\}. \quad (4)$$

The ENDOR signal intensity is proportional to a change in χ' upon application of the RF power at the ENDOR frequency, i.e., change in χ' when m becomes zero. This change is expressed by $\Delta\chi'$.

3 Results and Discussion

Figure 1 shows the sites of hydrogen located around a normal dangling bond, in which the distances ℓ_1 , ℓ_2 , and ℓ_3 are shown. The values of distances given in the figure caption are taken from radial density function obtained from neutron-scattering measurements by Bellisent et al. [5]. For distant ENDOR, dipole-dipole interaction leads us to anisotropic hyperfine interaction [2]. By averaging out the hyperfine interaction, we obtain ENDOR spectra for $r = 4.80$ Å and 5.12 Å, as shown in Fig. 2. The distribution function of local field is reflected on the curves for $r = 4.80$ Å and 5.12 Å shown in Fig. 2. As an example, the intensity at the natural NMR frequency is derived from the curve in Fig. 3 for $r = 5.12$ Å. The values of parameters used in the calculation of the ENDOR signal intensity are listed in Table 1 for $r = 4.80$ Å and 5.12 Å. The number of hydrogen with $r = 4.80$ Å and 5.12 Å is evaluated from radial density function of hydrogen $g(r)$, i.e., $4\pi r^2 g(r)$, and is given in Table 1. The value of H_1 is taken to be 10 gauss for a pulsed ENDOR measurement [3]. The calculated results of $\Delta m/m_0$ and $\Delta\chi'/\chi_0$ at $\omega = \omega_0$, using eqs. (1) and (4), respectively, are given as follows:

$$\Delta m/m_0 = 6.99 \times 10^{-7} \text{ and } \Delta\chi'/\chi_0 = -0.434 \text{ for } r = 4.80 \text{ Å}, \quad (5)$$

$$\Delta m/m_0 = 6.99 \times 10^{-7} \text{ and } \Delta\chi'/\chi_0 = -0.456 \text{ for } r = 5.12 \text{ Å}. \quad (6)$$

In eq. (1), difference in the value of m between $r = 4.80$ Å and 5.12 Å comes from $h(0)$ and

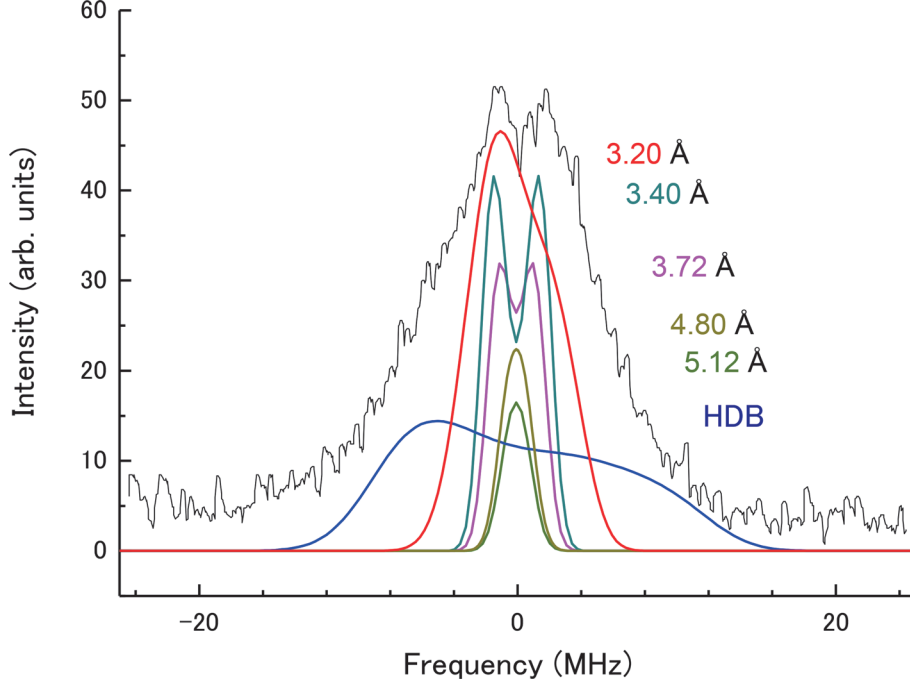


Figure 2: The computer-simulated ENDOR spectra in a-Si:H. HDB (blue): The values of the parameters are given below: $g_{//} = 2.0050$ and $g_{\perp} = 2.0056$, $A_{//} = 19.6$ MHz and $A_{\perp} = 2.80$ MHz, $\sigma_{//} = 2.24$ MHz and $\sigma_{\perp} = 3.36$ MHz. The matrix ENDOR spectra for various 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 [2]. The Fehr ENDOR spectrum [3] is also shown. For the notation of symbols, see [2]. (Reproduced from [2]).

T_2^* , i.e., the values of $h(0)$ and T_2^* become larger for $r = 5.12$ Å compared to $r = 4.80$ Å. In the above consideration, we assume that the other values of parameters are the same for both r . This assumption is not unreasonable, because the values of T_N , T_1 , T_2 , and g' are not so much affected by nuclei distant from a normal dangling bond site.

The ENDOR signal intensity corresponds to $\Delta\chi'$ with application of the RF power at the ENDOR frequency, i.e., change in χ' when m becomes zero.

For other values of r , ENDOR mechanism becomes different, i.e., these ENDORs are called matrix ENDOR ($r = 3.20$ Å to 3.72 Å) and local ENDOR (due to HDB in Fig. 2). Thus, further investigation is required to elucidate the signal intensity of ENDOR spectra shown in Fig. 2.

In this paper, calculation is done only for $\omega = \omega_0$. Thus, it should be extended over the whole range of ω . This will be reported in a later publication.

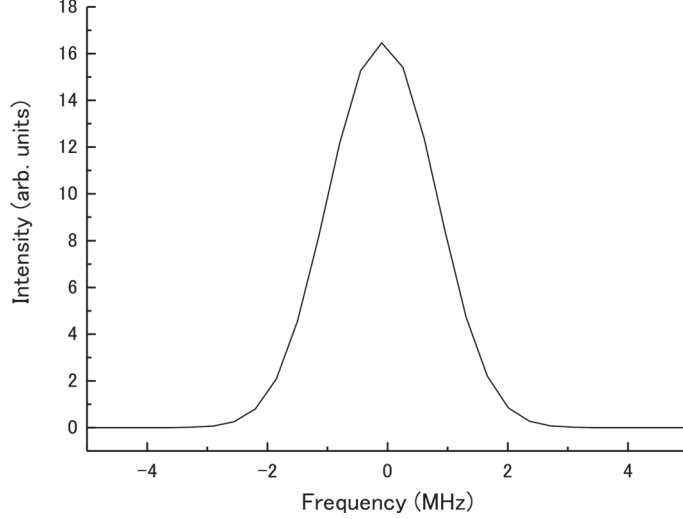


Figure 3: The computer-simulated ENDOR spectrum for $r = 5.12 \text{ \AA}$. An extended curve from that shown in Fig. 2.

Table 1: The values of parameters used in the calculation

$r(\text{\AA})$	$T_N(\text{ms})$	$T_1(\mu\text{s})^{1)}$	$T_2(\mu\text{s})^{1)}$	g'	$T_2^*(\mu\text{s})$	$h(0)^{2)}$	$4\pi r^2 g(r)$
4.80	100	4.72×10^2	1.57×10^2	0.01	0.14	15.5	273
5.12	100	4.72×10^2	1.57×10^2	0.01	0.15	16.3	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. [9], while a pulsed ENDOR measurement by Fehr et al. [3] was done at 80 K.
- 2) The value of $h(0)$ for $r = 5.12 \text{ \AA}$ is determined from the curve shown in Fig. 2, following to the scale of the coordinate in Fig. 2. The value of $h(0)$ for $r = 4.80 \text{ \AA}$ is determined, taking the area of the curve shown in Fig. 2 for $r = 4.80 \text{ \AA}$ to be the same as the area of the curve for $r = 5.12 \text{ \AA}$, because $h(\omega - \omega_0)$ is a normalized function.

4 Conclusion

In summary, we have considered the signal intensity of ENDOR spectra in a-Si:H, using the theory of distant ENDOR by Lambe et al. [6]. This theory is based on a model of dynamical nuclear polarization in which forbidden transition of the electronic levels interacting with nuclear spins located distant from the electron is taken into account. We have calculated the ENDOR signal intensity at $\omega = \omega_0$ for distant nuclei (hydrogen) with $r = 4.80 \text{ \AA}$ and $5.12 \text{ \AA}$. The signal intensity is proportional to $\Delta\chi'/\chi_0$ being related to a change in the difference in nuclear spin polarization with ENDOR. The value of $\Delta\chi'/\chi_0$ for $r = 4.80 \text{ \AA}$ is comparable with that for $r = 5.12 \text{ \AA}$. There are many hydrogen sites around a normal dangling bond, but relatively close sites are related to ENDOR spectra, in which we have considered only two sites. Concerning closer sites, further consideration is required to elucidate the ENDOR signal intensity for so called

matrix ENDOR and local ENDOR. This is a future problem.

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