

Model of Light-Induced Defects in Hydrogenated Amorphous Silicon — Electron-Spin Echo Measurements —

by

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(Received on Jul. 8, 2016; accepted on Aug. 13, 2016)

Abstract

The results of electron-spin echo measurements in hydrogenated amorphous silicon (a-Si:H) by Fehr et al. (Phys. Rev. Lett. **112** (2014), 066403) are interpreted in terms of our model of light-induced defects in a-Si:H, i.e., normal dangling bonds and hydrogen-related dangling bonds. We obtain good agreements between calculation and observation by Fehr et al. on ESR spectra associated with electron-spin echo decay components in light-soaked a-Si:H.

Keywords: ESR; Electron-spin echo; Defect; Amorphous silicon; Light-induced effect.

1 Introduction

Prolonged illumination on hydrogenated amorphous silicon (a-Si:H) creates defects, i.e., so-called light-induced defects which causes degradation of amorphous silicon solar cells such as a decrease in their conversion efficiency [1]. Therefore, it is important to elucidate the mechanism of light-induced defect creation and the nature of light-induced defects in order to prevent the light-induced degradation of a-Si:H. We have already proposed a model of the mechanism of light-induced defect creation and of the nature of light-induced defects [2–4], in which normal dangling bonds, as

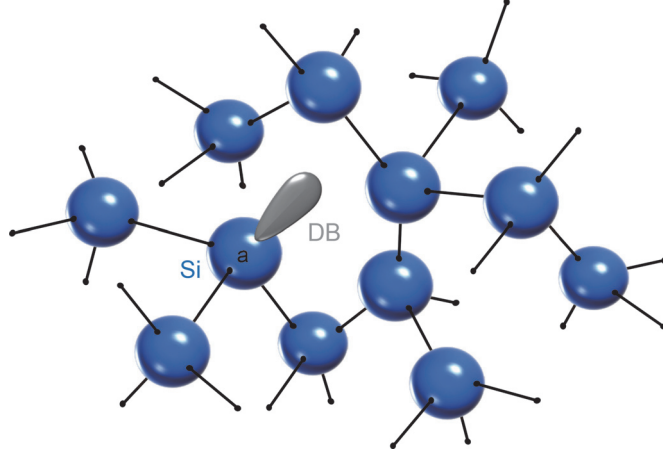


Figure 1(a): Schematic illustration of the normal dangling bond in a-Si:H.

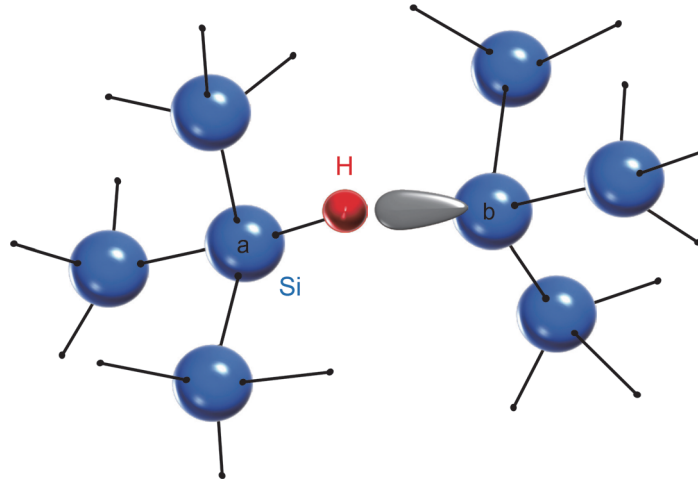


Figure 1(b): Schematic illustration of the hydrogen-related dangling bond in a-Si:H [5].

shown in Fig. 1(a), and hydrogen-related dangling bonds (dangling bonds having hydrogen at a nearby site), as shown in Fig. 1(b), are created under prolonged illumination through the following processes: A hole is self-trapped in a specific weak Si-Si bond that is a weak Si-Si bond adjacent to a Si-H bond (Fig. 2(a)) and then is recombined with an electron most nonradiatively (Fig. 2(b)) and eventually the weak bond is broken. Using the recombination energy associated with nonradiative recombination between the electron and the hole, the Si-H bond is switched towards the weak Si-Si bond (Fig. 2(c)). After switching of the Si-H bond (Fig. 2(c)) and breaking of the weak Si-Si bond, the two close dangling bonds created under illumination are separated by movement of hydrogen due to hopping and/or tunneling (Fig. 2(d)) and eventually two separate dangling bonds (Fig. 2(d)), i.e., a normal dangling bond and a hydrogen-related dangling bond are created under illumination, as shown in Fig. 2(d). Some of such two separate dangling bonds become more separate so as to be isolated normal dangling bonds and isolated hydrogen-related dangling bonds, as have been shown by calculations based on the above light-induced creation processes [4]. Detailed accounts on the light-induced defect creation mentioned above have been presented

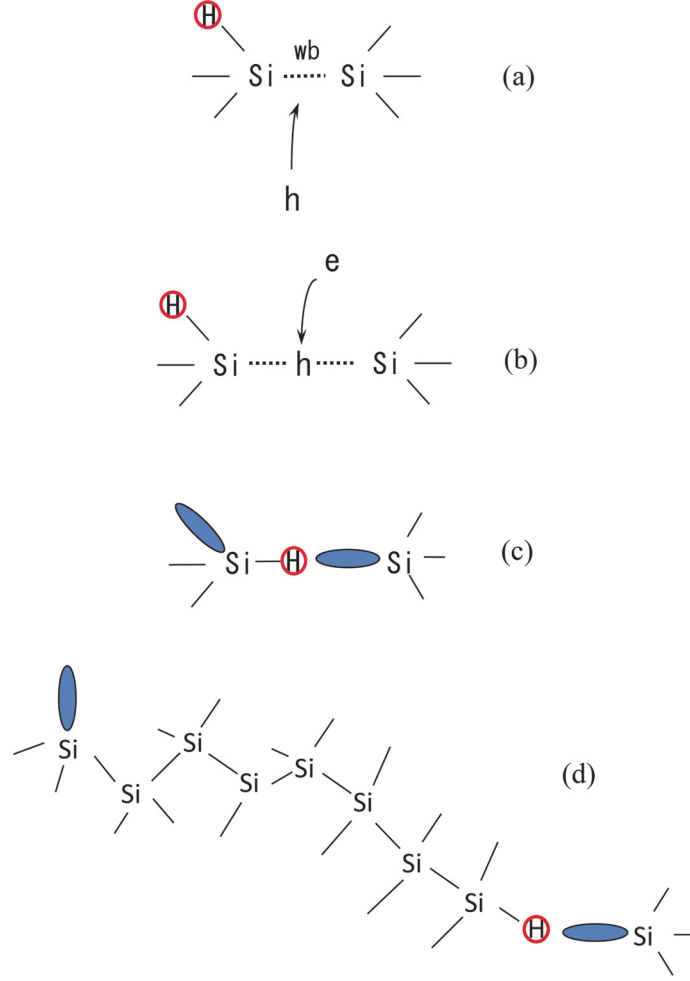


Figure 2: Atomic configurations involved in the formation of two types of dangling bonds, i.e., normal dangling bonds and hydrogen-related dangling bonds, under illumination: (a) self-trapping of a hole in a weak Si-Si bond (wb) adjacent to a Si-H bond, (b) electron-hole recombination at a weak Si-Si bond, (c) switching of a Si-H bond towards the weak Si-Si bond, leaving a dangling bond behind, (d) formation of two separate dangling bonds through hydrogen movement after repeating the processes shown in (a)–(c).

in Refs. [3, 4].

Recently, the electron-spin echo measurements on light-soaked and annealed a-Si:H have been performed by Fehr et al. [6], in which the amplitude of the electron-spin echo (ESE) signal has been measured as a function of period between the first $\pi/2$ pulsed and the second π pulse. From the results, it has been found that the ESE decay has two components, i.e., fast and slow ones. The lineshapes of the first decay component and the slow decay component against magnetic field have also been measured [6]. In this paper, we interpret the results in terms of our model mentioned above. From our interpretation, we conclude that there are present two types of dangling bonds such as mentioned above in a-Si:H.

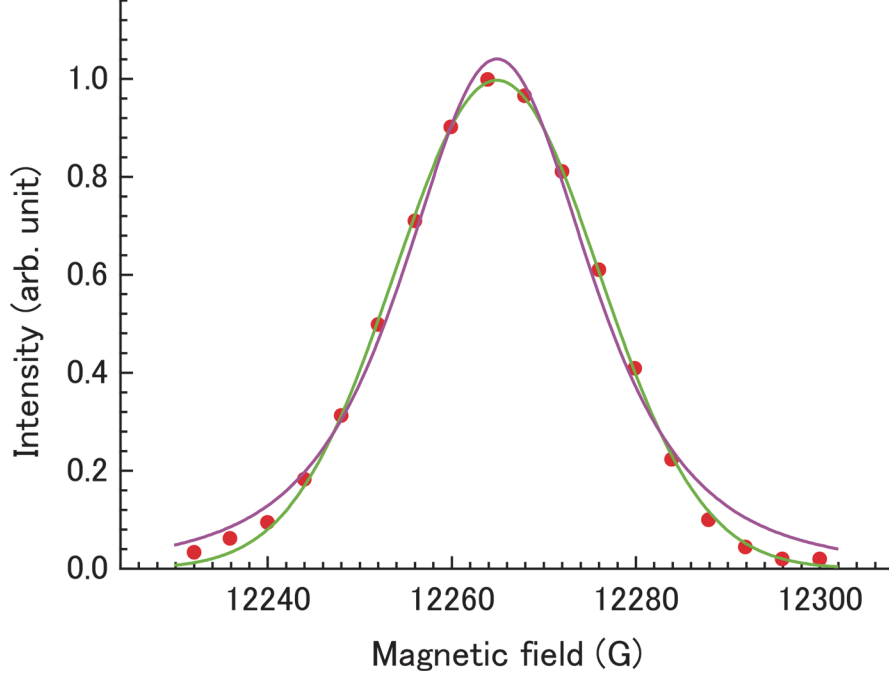


Figure 3(a): Experimental points: The normalized ESR spectrum obtained from the fast decay component of the ESE signal (cited from Ref. [6]). The green curve: It is the Gaussian curve given by eq. (1) with the σ value of 11.11 ± 0.89 . The g -value is 2.005387 ± 0.00014 . The red curve: It is the Lorentzian curve given by eq. (3) with the Γ value of 18.37 ± 0.54 . The g -value is 2.005387 ± 0.00043 .

2 Electron-spin echo (ESE) measurements and interpretation

As mentioned in Section 1, two ESE decay curves have been observed at 60 K and 34 GHz with characteristic times of $2.4 \mu\text{s}$ and $11.4 \mu\text{s}$ [6], in which the defects responsible for respective ESE decay components are called type I and type II. The normalized ESR spectra for defects type I and defects type II have been extracted from fitting of ESE decays, as shown in Figs. 3(a) and (b). The experimental points shown in Fig. 3(a) are fitted by Gaussian and Lorentzian curves with the following functions:

$$f_G(H) = \exp\{-(H - H_0)^2/2\sigma^2\}, \quad (1)$$

$$h\nu = g\mu_B H_0, \quad (2)$$

where H_0 , σ , h , ν , g , and μ_B are the central magnetic field, the standard deviation of Gaussian, the Planck constant, microwave frequency, g -value, and the Bohr magneton, respectively, and

$$f_L(H) = \frac{\Gamma_L^2}{4(H - H_0)^2 + \Gamma_L^2}, \quad (3)$$

where Γ_L is the full width at half maximum (FWHM) of Lorentzian.

First, we consider the result of Fig. 3(a), that is, defects type I. Figure 3(a) shows that the ESR spectrum is more fitted by the Gaussian curve than by the Lorentzian curve with the following

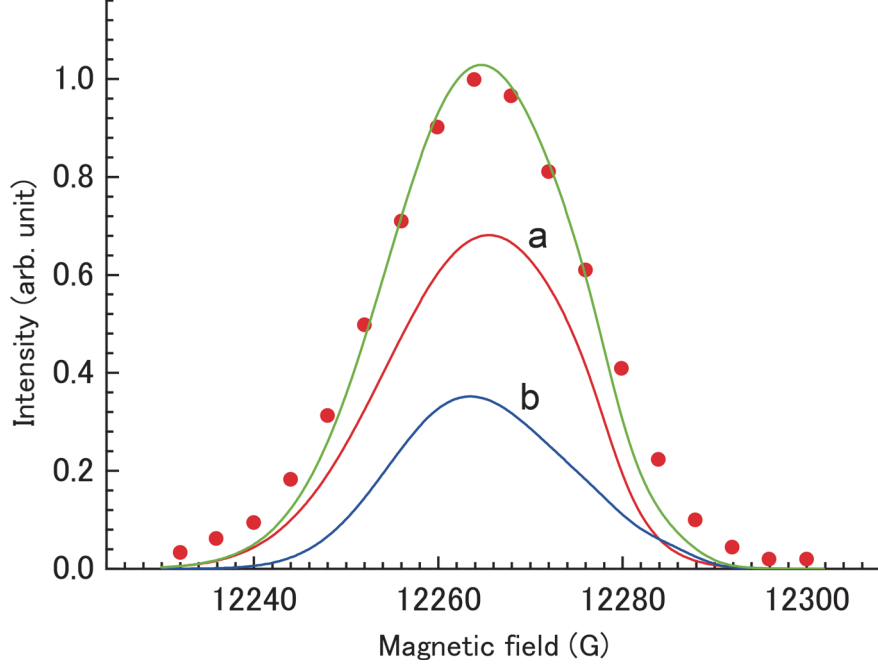


Figure 3(b): Experimental points: The normalized ESR spectrum obtained from the fast decay component of the ESE signal (the same points as those in Fig. 3(a), cited from Ref. [6]). The red curve *a* is the ESR spectrum of the normal dangling bond with the following values of the parameters: $g_{//} = 2.00341$ and $g_{\perp} = 2.00627$, $\sigma_{//} = 2$ G and $\sigma_{\perp} = 10$ G, where $//$ and $\perp$ are parallel and perpendicular to the principal axis, respectively, and σ is the spin packet width. The blue curve *b* is the ESR spectrum of the hydrogen-related dangling bond with the following values of the parameters: $g_{//} = 2.00246$ and $g_{\perp} = 2.00642$, $A_{//} = 8.3$ G and $A_{\perp} = 3.5$ G, $\sigma_{//} = 2.5$ G and $\sigma_{\perp} = 7.2$ G, where A is the hyperfine interaction constant with hydrogen nucleus. The green curve is the sum of the curves *a* and *b*.

values of the parameters: For Gaussian, $g = 2.005387 \pm 0.00014$, $\sigma = 11.11 \pm 0.89$. For Lorentzian, $g = 2.005387 \pm 0.00043$, $\Gamma = 18.37 \pm 0.54$. Further, Fehr et al. [6] conclude that the spin relaxation suggests from the ESE decay to be due to exchange interaction between neighboring spins separated with $16 \text{ \AA}$. Thus, the above result indicates that exchange broadening occurs between unpaired spins, i.e., normal dangling bonds and/or hydrogen-related dangling bonds in our model. Exchange interaction between different types of spins leads us to exchange broadening, while exchange narrowing occurs between identical spins that leads us to Lorentzian shape [7]. The unpaired spins in the present case are obviously not identical species. However, the above exchange interaction is too weak for spins separated by $16 \text{ \AA}$, because dipolar interaction between two spins separated by $16 \text{ \AA}$ is very weak, that is, less than 0.1 G. Thus, the above interpretation is not appropriate. In our model, a normal dangling bond and a hydrogen-related dangling bond form a separate pair, as shown in Fig. 2(d). The distance between these two dangling bonds is estimated to be $13 \text{ \AA}$ [3]. This value is close to $16 \text{ \AA}$ that is the value estimated by Fehr et al. [6] from the ESE decay. Thus, such a pair gives rise to spin relaxation of two spins.

ESR spectra due to normal dangling bonds and hydrogen-related dangling bonds are calculated

[8], using the following values of parameters: (1) normal dangling bonds: $g_{//} = 2.00341$ and $g_{\perp} = 2.00627$, $\sigma_{//} = 2$ G and $\sigma_{\perp} = 10$ G, where $//$ and $\perp$ are parallel and perpendicular to the principal axis, respectively, and (2) hydrogen-related dangling bonds: $g_{//} = 2.00246$ and $g_{\perp} = 2.00642$, $A_{//} = 8.3$ G and $A_{\perp} = 3.5$ G, $\sigma_{//} = 2.5$ G and $\sigma_{\perp} = 7.2$ G, where A is the hyperfine interaction constant with hydrogen nucleus. In Fig. 3(b), the experimental points obtained by Fehr et al. [6] are fitted by a curve made up from the above two calculated curves a and b with ratio of 2.07 in intensity (area). Fitting of the total calculated curve to the experimental points obtained by Fehr et al. [6] is good except for the tails of both sides. Two types of normal dangling bonds and hydrogen-related dangling bonds should contribute equally to the ESR spectrum, because they are coupled with each other. However, as mentioned above, they do not contribute equally to the ESR spectrum, so that this reason remains as an open question. This is related to the intensity of the ESE signal. Thus, as one of the reasons, difference in the spin-lattice relaxation time between normal dangling bonds and hydrogen-related dangling bonds should be taken into account. The spin-lattice relaxation time of hydrogen-related dangling bonds may be shorter than that of normal dangling bonds, because the stretching vibration of the Si-H bond in the hydrogen-related dangling bond assists the spin energy transfer from the spin system of the dangling bond to the lattice. Thus, the intensity of the ESE signal for hydrogen-related dangling bonds becomes smaller than that for normal dangling bonds, as seen in Fig. 3(b), where the respective intensities (area) are 8.46 and 17.48 in the scales of Fig. 3(b). Concerning the spin-lattice relaxation time, T_1 , as shown in Ref. [9], it is longer than the phase relaxation time, T_2 , e.g., at 60 K, $T_1 = 4.72 \times 10^2 \mu\text{s}$ and $T_2 = 1.57 \times 10^2 \mu\text{s}$. Thus, concerning the ESE decay, as shown in Ref. [6], contribution of T_1 to it is smaller than that of T_2 . However, inequality of the calculated curves a and b arise from relative importance of T_1 for normal dangling bonds and hydrogen-related dangling bonds against the ESE signal intensity. As shown above, difference in the value between T_1 and T_2 is small, so that the spin-lattice relaxation contributes slightly to the ESE signal intensity compared to the phase relaxation.

On the other hand, Fehr et al. [6] suggest that the spins are located on the inner surface of microvoids, because the distance of 16 Å may be explained in terms of a spin cluster on the inner surface of microvoids.

Secondly, we consider Fig. 3(c), that is defects types II. Fehr et al. [6] conclude that the slow decay component of defects type II is due to hyperfine interaction with hydrogen nuclei. In our model, defects type II seem to be hydrogen-related dangling bonds, as shown in Fig. 1(b). The ESR spectrum is due to hydrogen-related dangling bonds with anisotropic g -values, $g_{//}$ and $g_{\perp}$, and anisotropic hyperfine interaction constants, $A_{//}$ and $A_{\perp}$. The ESR spectrum is fitted by two calculated curves with the following values of parameters:

- (1) $g_{//} = 2.0038$ and $g_{\perp} = 2.0069$, $A_{//} = 8.3$ G and $A_{\perp} = 3.5$ G, $\sigma_{//} = 5$ G and $\sigma_{\perp} = 14.5$ G, where $\sigma_{//}$ and $\sigma_{\perp}$ are the spin packet width being parallel and perpendicular to the principal axis, respectively.
- (2) $g_{//} = 2.0038$ and $g_{\perp} = 2.0069$, $\sigma_{//} = 5$ G and $\sigma_{\perp} = 14.5$ G.

The values of the parameters of (1) correspond to those for hydrogen-related dangling bonds

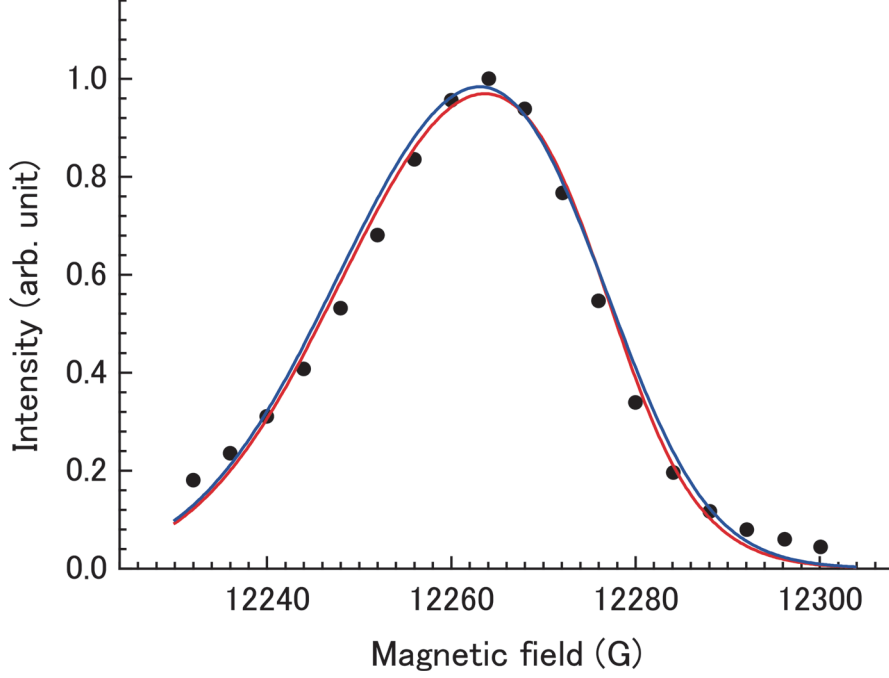


Figure 3(c): Experimental points: The normalized ESR spectrum obtained from the slow decay component of the ESE signal (cited from Ref. [6]). The red and blue curves: They are the ESR spectra of the hydrogen-related dangling bond with the following values of the parameters: Red curve: $g_{//} = 2.0038$ and $g_{\perp} = 2.0069$, $A_{//} = 8.3$ G and $A_{\perp} = 3.5$ G, $\sigma_{//} = 5$ G and $\sigma_{\perp} = 14.5$ G. Blue curve: $g_{//} = 2.0038$ and $g_{\perp} = 2.0069$, $\sigma_{//} = 5$ G and $\sigma_{\perp} = 14.5$ G. The blue curve is drawn for showing how the hyperfine interaction parameters affect the ESR spectrum for ESR measurements at 34 GHz (see the text).

with $r = 2.7$ Å (r : the distance between the dangling bond site and the hydrogen nucleus) [10, 11]. The values of the parameters of (2) are taken for showing how the hyperfine interaction parameters affect the ESR spectrum for ESR measurements at 34 GHz. Since the values of $A_{//}$ and $A_{\perp}$ are small compared to the Zeeman energy, two curves are quite similar to each other. However, this result is consistent with Fehr et al.'s conclusion [6] that defects type II affect the spin relaxation through hyperfine interaction with hydrogen nucleus.

In the following, we discuss two types of hydrogen-related dangling bonds. We take hydrogen-related dangling bonds coupled with normal dangling bonds for Fig. 3(b), i.e., type I, while we take isolated hydrogen-related dangling bonds for Fig. 3(c), i.e., type II. Thus, the values of $g_{//}$, $g_{\perp}$, $\sigma_{//}$, and $\sigma_{\perp}$ are different between two types. This is due to difference in environment around the dangling bond, so that it affects the g -shift and the σ value, because the σ value reflects spatial variation of atomic structure of each dangling bonds. The g -shift is smaller for Fig. 3(b) than that for Fig. 3(c), so that the σ value is smaller for Fig. 3(b) than that for Fig. 3(c). A quantitative consideration is required on the reason of difference in g -shift for isolated hydrogen-related dangling bonds and hydrogen-related dangling bonds coupled to normal dangling bonds. This is related to difference in environment around the dangling bonds, that is, a structural problem to be considered

in future.

Fehr et al. [6] have observed that thermal annealing of samples results in decrease of the average g -value, that is, defects of type II change to those of type I. In our model, defects of type II are isolated hydrogen-related dangling bonds whose g -values are $g_{//} = 2.0038$ and $g_{\perp} = 2.0069$ in Fig. 3(b) and those of type I are pairs of two types of dangling bonds, that is, g -values of normal dangling bonds are $g_{//} = 2.00341$ and $g_{\perp} = 2.00627$, while those of hydrogen-related dangling bonds are $g_{//} = 2.00246$ and $g_{\perp} = 2.00642$. The g -values of both dangling bonds are smaller than those of isolated hydrogen-related dangling bonds. Thus, these results are consistent with Fehr et al.'s observation [6] mentioned above.

3 Conclusion

In Section 2, we have interpreted the origins of the ESE fast and slow decay components observed by Fehr et al. [6] in terms of our model of light-induced defects in a-Si:H. From good agreements in the ESR spectra associated with both components between calculation and observation, it is concluded that there are present two types of dangling bonds, i.e., normal dangling bonds and hydrogen-related dangling bonds as their coupled pairs separated by 13 Å and their isolated ones in light-soaked and as-deposited a-Si:H, as have been shown in Ref. [4].

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