Energy location of light-induced ESR centers in undoped a-Si:H

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Abstract

We report the light intensity dependence of ^{29}Si hyperfine (hf) structures of light-induced electron spin resonance (LESR) in undoped a-Si:H in order to detect changes of electronic structures of the $g = 2.004$ center against the shift of energy locations of $g = 2.004$ electrons. Within the light intensity range from 0.004 to 450 mW/cm^2, ^{29}Si hf structures of $g = 2.004$ were almost unchanged, which indicates that a magnitude of the spatial localization of $g = 2.004$ electrons is almost constant. Based on the experimental results, we discuss the energetic distribution of $g = 2.004$ electrons. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

In hydrogenated amorphous silicon (a-Si:H), light-induced electron-spin-resonance (LESR) signals of g [1] $= 2.004$ and 2.01 are observed under illumination at low temperatures, in addition to the dangling bond signal of $g = 2.0055$. On the basis of doping and photoluminescence experiments, the two LESR signals were tentatively attributed to conduction-band-tail electrons ($g = 2.004$) and valence-band-tail holes ($g = 2.01$) [1]. Therefore, the 2.004 and 2.01 centers directly correlate with band-tail states in the gap which play an important role in the transport properties.

In our recent paper [2], overlapped LESR signals of $g = 2.004$ and 2.01 were experimentally deconvoluted into two signals, by making use of the difference in their spin-lattice relaxation times. The deconvolution clearly showed that the high field side hyperfine (hf) structure of ^{29}Si (natural abundance of 4.7 at.%, nuclear spin of 1/2) belongs mainly to the $g = 2.004$ signal. Furthermore, the fraction of the deconvoluted hf structure of $g = 2.004$ in the total 2.004 signal was found to be about twice the ^{29}Si concentration in the film. It was therefore concluded that the wave function of the 2.004 center extends mainly over two Si atoms with an approximately uniform distribution. Accordingly, we suggested that the origin of the 2.004 center is electrons trapped at

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anti-bonding states of weak Si–Si bonds rather than those trapped at positively charged dangling bonds.

On the basis of the above results, an interesting question arises; where are these electrons energetically distributed in the band-tail states? In general, the extent of the wave function of localized electrons (or holes) depends on their energy positions in the energy gap, which should be directly reflected in [29]Si hf interactions such as splittings and/or intensities of hf signals. In this paper, we present experimental results of the light-intensity dependence of LESR spectra, especially focusing on changes of the [29]Si hf structures in the LESR spectrum, which is obtained through echo-detected ESR measurements of pulsed ESR on a [29]Si enriched sample. Based on the results, we discuss the energy position of $g = 2.004$ center and electron trapping process.

2. Experimental

We prepared a powdered a-Si:H sample (30 mg) with a [29]Si concentration of 9.1 at.% by using the standard rf-glow discharge technique at a substrate temperature of 250°C. The flakes with more than 1 μm in thickness were collected into a high-purity vitreous-silica tube (2.5 mm in inner diameter) for ESR measurements. The ESR spectra were measured using the two-pulse Hahn echo-detected ESR technique (90° pulse-τ-180° pulse-τ-echo, $\tau = 240$ ns). Details of our pulsed ESR spectrometer have been described previously [3]. LESR measurements were carried out at 30 K using a laser diode (685 nm). The sample temperature was monitored by a thermocouple placed in the sample during ESR measurements. With increasing light intensity, the measurement time was shortened to prevent the effect of photo-created dangling bonds. The repetition time for accumulating the echo signals was 150 ms to ensure complete recovery of the spin system.

3. Results

Fig. 1 shows the light-intensity dependence of the LESR intensity at 30 K. Solid and open circles represent the LESR spin density before and after subtracting the dangling bond density in the dark,
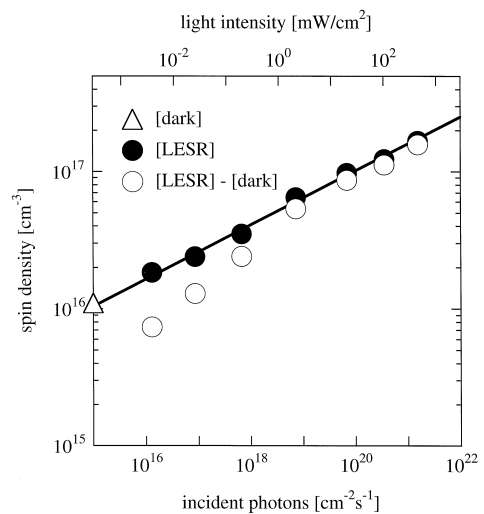

Fig. 1. Light-intensity dependence of LESR spin densities at 30 K.

respectively. The dangling bond density in the dark is also shown by an open triangle. It is noted that the above LESR spin densities are nominal, because in our experiments there are small unilluminated regions in the powder sample. The solid line in the figure represents the dependence of (light intensity)$^{0.2}$.

LESR spectra at various light intensities and the dangling bond signal are shown in Fig. 2. Light intensities of 0.004 and 450 mW/cm^2 were the smallest and largest, respectively, in our LESR measurements. The highest light intensity was limited by

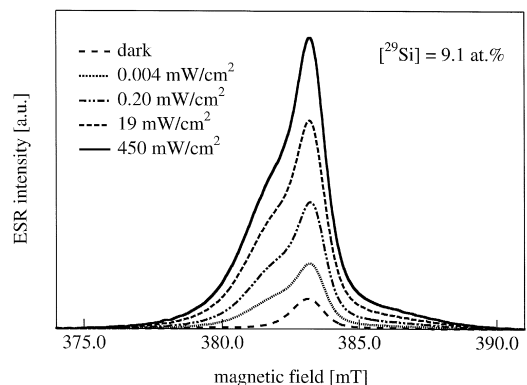Fig. 2. LESR spectra of the [29]Si-enriched (9.1 at.%) sample at light intensities of 0.004, 0.20, 19, and 450 mW/cm^2, which were obtained by the echo-detected ESR technique. A dangling bond spectrum is also shown.

a non-negligible increase of the sample temperature above 30 K. As shown in the figure, even for 0.004 mW/cm^2, the high-field-side ^{29}Si hf structure could be clearly detected, owing to the very flat baseline of the echo-detected ESR spectrum and large ^{29}Si concentration.

4. Discussion

According to the exponential band-tails model [4], the amount of shift of the quasi Fermi energy for electrons was roughly estimated to be about 50 meV for a change in the LESR spin density by a factor of 10–20, as is the case of Fig. 1. The estimation was made on the assumption that the Urbach energy for conduction band-tail is 20 meV [4,5] and the occupation of the tail states is given by a step function. Under this assumption, the maximum energy of band-tail electrons with a density of 7×10^{16} cm^{-3}, which corresponds to the maximum density of $g = 2.004$ signal of Fig. 1, was estimated to be 160 meV below the mobility edge, assuming 10^{19} cm^{-3} [6] for the effective density of states at the mobility edge. The estimated 160 meV agrees with the thermal activation energy of the dark conductivity of the heavily phosphorous doped a-Si:H having a comparable density of $g = 2.004$ spins [7].

Generally speaking, with decreasing energy of a trapped electron below the conduction band edge, the extent of its wave function should monotonically decrease. By applying a simple bounded-electron picture [7] to electrons at the shallowest and deepest levels in our experiments, which has been calculated to be 160 and 210 meV below the mobility edge, respectively, the ratio of their effective Bohr radii, a_{210}/a_{160}, was calculated to be 0.87. This reduction in the extent of electron wave function should result in an appreciable increase in the isotropic hf interactions which is determined by electron densities just on Si atoms. In the present case, an increase of the isotropic hf splitting of $g = 2.004$ can be roughly estimated to be 13% of itself, i.e., 7 mT (from Ref. [2]) $\times 13\% = 0.9$ mT.

To detect the changes of ^{29}Si hf structures in the LESR spectrum against the energy shift of electrons, LESR spectra at various light intensities were normalized to their peak heights, which are shown in

Fig. 3. In the figure, the heights of the high-field-side hf structures gradually decrease with decreasing light intensity, i.e., decreasing LESR intensity. This decrease is assumed, first of all, to originate from superposition of ^{29}Si hf structures of the dangling bond whose area fraction in the $g = 2.0055$ signal is approximately equivalent to the content of ^{29}Si, which is around one half of the case of $g = 2.004$ signal [2].

The number of dangling bonds under illumination has not been well estimated so far. However, as is seen in Fig. 2, the LESR spectra for light intensities of 450 and 19 mW/cm^2 are almost identical, which indicates no apparent contribution of the dangling bond signal to the LESR for high light intensities. Thus, we have to consider the contribution of the dangling bond signal on the LESR spectra only for the cases of illumination with low light intensities. To clarify the contribution of the dangling bond signal to the whole LESR for the lowest light intensity, we carried out a fitting analysis. We subtracted the dangling bond spectrum from the LESR spectrum for the lowest light intensity so that the resultant spectrum can fit to the LESR spectrum for the highest light intensity (450 mW/cm^2). The dangling bond signal intensity in the LESR for the lowest light intensity was estimated to be about 40% of the intensity in the dark.

Fig. 4 shows the original LESR spectrum for the highest light intensity (solid line) and the best fitted spectrum for the lowest light intensity (dashed line).
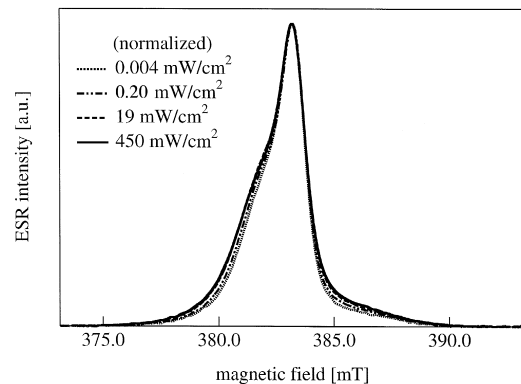

Fig. 3. LESR spectra of the ^{29}Si-enriched (9.1 at.%) sample at various light intensities (Fig. 2), which are normalized to their peak values.
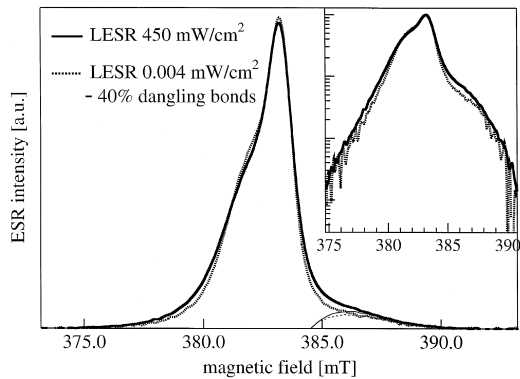
Fig. 4. The LESR spectra for the highest (450 mW/cm^2) and lowest (0.004 mW/cm^2) light intensities, which are indicated by solid and dashed lines, respectively. The LESR spectrum for the lowest light intensity was calculated by subtracting 40% dangling bond signal in the dark from the original spectrum. Thin lines show estimated high-field-side ^{29}Si hf structures which were obtained by a procedure described in the text (See Ref. 9 of Ref. [2]).

Thin lines show the high-field-side hf structures of both spectra which were obtained on the assumption that the tail region of the main peak of $g = 2.004$ decays exponentially (See Ref. 9 of Ref. [2]). The high-field-side hf structures of both spectra are almost identical, although the height of the high-field-side hf structure in the LESR for the lowest light intensity appeared to be still a little bit less than that for the highest light intensity. As is clearly seen on a logarithmic plot in the inset of Fig. 4, the isotropic hf splitting was found to remain unchanged within errors of ± 0.2 mT.

Our experimental result indicates that densities of $g = 2.004$ electrons just on two Si atoms are almost constant even for an increase in the spin density by more than a factor of 10, i.e., a shift of their energy position by about 50 meV. We speculate the reason why we could not detect the changes of electronic structures of the 2.004 electrons in two ways.

The first one is that $g = 2.004$ electrons distribute in a relatively narrow energy range compared to their original empty states, resulting in almost constant localization of every $g = 2.004$ electrons. We suggest that such distribution will be generated by some structural relaxation just after excited electrons are trapped at initial empty states. The structural relaxation of the weak Si–Si bonds has been speculated in

an ab initio theoretical calculation of charged weak Si–Si bonds [8]. Although the energy location of $g = 2.004$ electrons has not been determined quantitatively, we speculate that it is relatively deep by an energy gain of the structural relaxation compared to the empty states.

Another possibility is given by weaker dependence of the spatial localization of $g = 2.004$ electrons on their energy positions. In the above discussion, we expected about 0.9 mT change in the isotropic hf splittings on the basis of the simple model for electrons bound by a Coulomb force. However, if the extent of the wave function of $g = 2.004$ had much weaker dependence on a binding energy than that we have expected, it would be difficult to detect the changes in the isotropic hf interactions due to the 50 meV shift in the energy positions of $g = 2.004$.

5. Summary

We have measured the ^{29}Si hf structures of LESR spectra in the light intensity range from 0.004 and 450 mW/cm^2. However, no discernible change in the high-field-side ^{29}Si hf structure of $g = 2.004$ was observed. Based on the results, we suggest two possibilities. One is that the energy position of $g = 2.004$ electrons will be lowered towards the mid-gap and located in a relatively narrow range of energy, which may be caused by some structural relaxation just after excited electrons are captured in the band-tail states. The other proposal is that $g = 2.004$ electrons have weaker dependence of their spatial localization on their energy positions than that expected from the simple model for such as electrons bound by the Coulomb force.

Acknowledgements

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