Spatial distribution of phosphorus atoms surrounding spin centers of P-doped hydrogenated amorphous silicon elucidated by pulsed ESR

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Abstract

Local concentration of phosphorus ($C_{P\text{-loc}}$) in the vicinity of spin centers in P-doped a-Si:H has been determined for electron spin resonance components $g = 2.0043$, for $g = 2.0055$, and for a hyperfine structure (hf) with a splitting ~ 24 mT as a function of gaseous ratio of $C_{P\text{-gas}} = [PH_3]/[SiH_4]$. It has been observed, for both $g = 2.0043$ and 2.0055, that $C_{P\text{-loc}}$ increases with the increase of $C_{P\text{-gas}}$, however, that the ratio $C_{P\text{-loc}}/C_{P\text{-gas}}$ decreases with the increase of $C_{P\text{-gas}}$. In the films with small $C_{P\text{-gas}}$, $C_{P\text{-loc}}$ of $g = 2.0043$ and that of 2.0055 are significantly higher than the average P concentration in films.

1. Introduction

In phosphorus doped hydrogenated amorphous silicon (P-doped a-Si:H), three kinds of spin centers have been detected by electron spin resonance (ESR); $g = 2.0043$ in dark [1], $g = 2.0055$ under illumination [2], and a hyperfine (hf) structure of ^{31}P nucleus with splitting ~ 24 mT [3]. Their origins are crucially related to the doping mechanism in P-doped a-Si:H. Although these are assigned to be conduction band tail electrons, dangling bonds, and donor states, no clear experimental evidence to confirm their origins and microscopic structure has been reported for a long time [4].

In ESR spectra of amorphous semiconductors, weak hf interactions that give information of distribution of magnetic nuclei (^1H, ^{29}Si, ^{31}P, etc.) nearby paramagnetic spin centers are hidden underneath the line broadening due to random orientations and structural fluctuation. By applying the electron spin echo envelope modulation (ESEEM) method of pulsed ESR, the weak hf interaction can be extracted [5,6]. In the present work, the local P concentrations in the vicinity of the three spin centers in P-doped a-Si:H have been determined as a function of gaseous ratio of $[PH_3]/[SiH_4]$, $C_{P\text{-gas}}$.

2. Experimental

The samples of P-doped a-Si:H used here were deposited from SiH_4 and PH_3 mixtures with the

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ratio of $C_{P\text{-gas}} = 0.1$, 0.3, and 1% by a rf glow discharge method at a substrate temperature of 250°C. ESEEM spectra were recorded at 50 K using a two-pulse sequence. The detailed experimental conditions are similar to those described in Ref. [5].

ESEEM is a periodic variation of the echo intensity due to weak hf interaction between electron and nuclear spins which appears superimposed on the slow echo decays produced by a pulse sequence of a two-pulse Hahn echo (90°–τ–180°–τ echo, τ is scanned) or three-pulse stimulated echo (90°–τ–90°–T–90°–τ echo, T is scanned and τ is fixed) [5,7]. In two pulse ESEEM employed in this study, the modulation contains ENDOR frequencies $\nu_\alpha(\nu_\beta) = \nu_n + (-)1/2\nu_A$, as well as the sum frequency $(\nu_\alpha + \nu_\beta) = 2\nu_n$ and the difference frequency $(\nu_\alpha - \nu_\beta) = \nu_A$, where ν_A is the hf splitting, and ν_n the NMR frequency. In amorphous materials, an ESEEM spectrum in the frequency domain usually shows featureless peaks centered at ν_n and $2\nu_n$, since an ESEEM spectrum is a superposition of spectra at many different orientations. The detection of ν_n (^{31}P) was rather difficult in this experiment, since the modulation of ν_n (^{31}P) in time domain damps out rapidly due to a distribution of ν_A in the frequency domain which is likely to be caused by the small extent of the wave function of the unpaired electron onto the P atoms. Therefore, we have utilized, in this study, the sum frequency $2\nu_n$ (^{31}P) peak which is, at the first order, free from broadening due to the distribution of ν_A.

The local concentration of P in the vicinity of spin centers ($C_{P\text{-loc}}$) is estimated, at first approximation, from the intensity ratio of the $2\nu_n$ peak of ^{31}P ($I = 1/2$, natural abundance: 100%) to that of ^{29}Si ($1/2$, 4.7%) in the frequency domain spectra. The ^{29}Si at the first-nearest neighbors, i.e., back-bonded silicon in the case of dangling bond, does not contribute to ESEEM since the hf interaction is large [5,8]. The ^{29}Si modulation arises from ^{29}Si nuclei occupying the silicon sites which are the second nearest neighbors and furthest neighbors. Since the modulation depth depends on the distance r between electron spin and nucleus (proportional to r^{-6} for nuclei with $r > 0.36$ nm), main contributions to the ^{29}Si modulation are from the second and the third nearest neighbors. It is likely that the ^{31}P occupying these silicon sites contributes mainly to the ^{31}P modulation. The ^{31}P modulation arises from P atoms

which are located nearby spin centers and which do not have unpaired electrons such as P_4^+ and P_3^0.

3. Results

The frequency domain spectrum of two-pulse ESEEM at the center position of $g = 2.0043$ in dark and $g = 2.0055$ under illumination for $C_{P\text{-gas}} = 1\%$ is shown in Fig. 13(a) and (b), respectively. One can see the ν_n and $2\nu_n$ peaks from ^{29}Si ($\nu_n = 2.478$ MHz at 293 mT), the $2\nu_n$ peak from ^{31}P ($\nu_n = 5.050$ MHz at 293 mT), as well as the ν_n peak from ^{1}H ($I = 1/2$, 100%, $\nu_n = 12.46$ MHz at 293 mT). Table 1 shows $C_{P\text{-loc}}$ for different gaseous ratios, $C_{P\text{-gas}}$. As seen from Table 1, in the sample of $C_{P\text{-gas}} = 1\%$, $C_{P\text{-loc}}$ in dark ($g = 2.0043$) and that under illumination ($g = 2.0055$) are higher than $C_{P\text{-gas}}$. However, the average
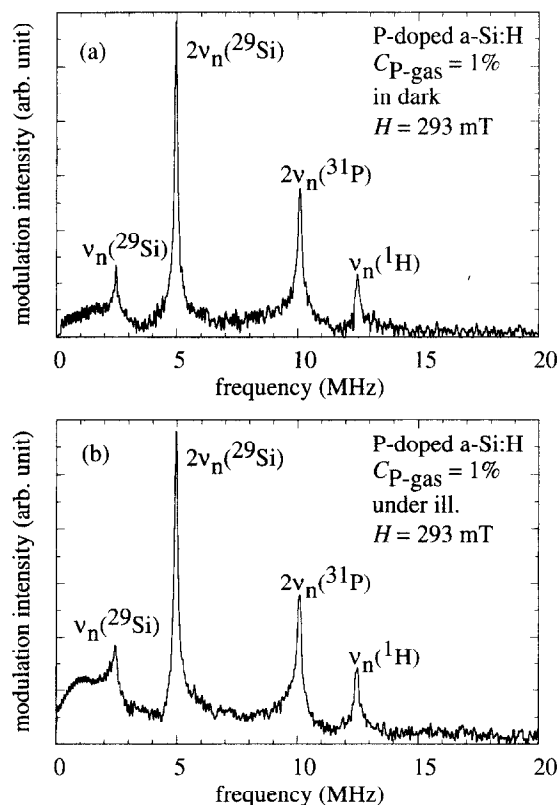

Fig. 1. The frequency domain spectra of 2-pulse echo ESEEM in dark (a) and under illumination (b) at the center position of $g = 2.0043$ and 2.0055 for $C_{P\text{-gas}} = 1\%$, respectively.

Table 1
Local concentration of P atom surrounding spin centers ($C_{\text{P-loc}}$) (%)

$[PH_3]/[SiH_3]$	1.0	0.3	0.1
$g = 2.0043$	2.2	1.1	0.51
$g = 2.0055$	2.3	1.0	0.44
hf	< 1.6		

P concentration in the film ($C_{\text{P-film}}$) measured by EPMA is almost twice of $C_{\text{P-gas}}$ and proportional to $C_{\text{P-gas}}$. Therefore, in the sample of $C_{\text{P-gas}} = 1\%$, $C_{\text{P-loc}}$ is almost equal to the $C_{\text{P-film}}$. When P atoms are spatially distributed randomly like ^{29}Si, $C_{\text{P-loc}}$ should vary in proportion to $C_{\text{P-gas}}$. However, $C_{\text{P-loc}}$ for $C_{\text{P-gas}} = 0.1\%$ is almost twice (2.3 for $g = 2.0043$ and 1.9 for $g = 2.0043$) of that expected from the value of $C_{\text{P-loc}}$ for $C_{\text{P-gas}} = 1\%$. In the films with low $C_{\text{P-loc}}$ is significantly higher than $C_{\text{P-film}}$.

4. Discussion

The above experimental result can be tentatively explained by an inhomogeneous distribution of P atoms, although the additional measurements, especially, for samples with $C_{\text{P-gas}}$ lower than 0.1% are needed for confirmation. One possibility is that, in the films with low $C_{\text{P-gas}}$, the spin centers might be preferentially formed in the region with higher P concentration. The other possibility for $C_{\text{P-loc}}$ higher than $C_{\text{P-film}}$ is that the spin centers in P-doped a-Si:H might accompany specific P atom(s) nearby in addition to P neighbors which are randomly distributed in the P-doped a-Si:H network. The distance to the specific P atom(s) is not closer than the second nearest neighbors since the intensity of $2\nu_n(^{31}\text{P})$ peak is comparable to the $2\nu_n(^{29}\text{Si})$ peak coming from ^{29}Si nuclei statistically distributed in the silicon sites of the network in its natural abundance of 4.7%. The contribution from the ^{31}P nuclei randomly distributed in the network is dominant for higher $C_{\text{P-film}}$, while the modulation arises mainly from the specific P atoms for low $C_{\text{P-film}}$. The existence of P atoms nearby dangling bonds with $g = 2.0055$ in P-doped a-Si:H was suggested by Okushi et al. on the basis of

their experimental results using isothermal capacitance transient spectroscopy [9]. They proposed a P-related charged dangling bond ($g = 2.0055$) in P-doped a-Si:H, in which P_4^+ is located proximate to a negatively charged dangling bond (D^-) due to the reduction of Coulombic energy. The ESR signals with $g = 2.0043$ which is observed in dark in P-doped a-Si:H is observed under illumination in undoped a-Si:H. The role of P atoms in P-doped a-Si:H might be assumed by impurities or charged defects in the case of undoped a-Si:H.

The values of $C_{\text{P-loc}}$ are listed (Table 1) for different spin centers of $g = 2.0043$ in dark, $g = 2.0055$ under illumination, and a hf structure with a splitting ~ 24 mT under illumination (measured at the low magnetic field component). As seen in Table 1, the spin centers of $g = 2.0043$ show a similar trend of $C_{\text{P-loc}}$ to that of $g = 2.0055$. This similarity might suggest that the origin of the $g = 2.0043$ signal is close to dangling bonds with $g = 2.0055$, and not like the band tail electrons with spreading wave functions. For $g = 2.0043$ in undoped a-Si:H, we reported that the wave function is localized like dangling bonds [4].

For spin center with a hf splitting ~ 24 mT, $C_{\text{P-loc}}$ was measured only for $C_{\text{P-gas}} = 1\%$, since the ESR signal intensity was weak for the films with lower $C_{\text{P-gas}}$. The ^{31}P nucleus with such a large hf splitting does not give rise modulation [5,8]. Therefore, $C_{\text{P-loc}}$ for the spin center with a large hf splitting does not count a P atom which is among the atoms constituting the spin centers and contains only the contribution from the outside P atoms in the network. As seen from the table, the $C_{\text{P-loc}}$ of the hf structure is smaller than that of other spin centers. This might suggests that, if we include the P atom exhibiting hf splitting ~ 24 mT into $C_{\text{P-loc}}$, the local concentration of P for the spin center with a large hf splitting might be close to those of other centers.

In this paper we did not touch upon the coordination number of P atoms, which is assumed to be three-fold and four-fold coordinated. This assumption is crucially related with the doping as well as defect creation mechanism and will be clarified by the ESEEM measurements using As ($I = 3/2$, natural abundance: 100%) doped a-Si:H through the information on the quadrapole coupling constant with As atoms surrounding electrons spins.

5. Summary

Local P concentrations in the vicinity of the spin centers in P-doped a-Si:H have been estimated by the ESEEM technique of pulsed ESR. The following experimental results have been obtained: (1) There was no linear relationship between $C_{P\text{-loc}}$ and $C_{P\text{-gas}}$, and $C_{P\text{-loc}}$ for $C_{P\text{-gas}} = 0.1\%$ was almost twice that expected from the value of $C_{P\text{-loc}}$ for $C_{P\text{-gas}} = 1\%$ in the spin centers with $g = 2.0043$ and 2.0055. (2) Local P concentrations in the vicinity of the spin centers for $g = 2.0043$ and 2.0055 were higher than the average P concentration of the films for low $C_{P\text{-gas}}$ films. (3) The value of $C_{P\text{-loc}}$ of the hf structure was smaller than that of other spin centers. To explain these experimental results the tentative model related with the spatial inhomogeneity of P atoms has been suggested.

Acknowledgements

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