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Hydrogen states probed by electron-spin resonance of phosphorus donors in silicon

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Hydrogen in phosphorus-doped silicon has been investigated by monitoring shallow donor P by electron-spin resonance (ESR). Significant broadening in motionally narrowed ESR lines is first observed in Si samples treated with hydrogen plasma. It is found from the donor-concentration dependence that the broadening is caused by the Fermi-contact hyperfine interaction between hydrogen nuclear spins and donor or conduction electrons. Results of annealing hydrogen-passivated Si indicate that an intermediate state of hydrogen with a P donor neighbor is formed via dissociation of P-H complexes at 150–350 °C, and that hydrogen diffuses in *n*-type Si above 350 °C.

Hydrogen in crystalline semiconductors has presented fundamental problems to be challenged and is of technical importance because of its passivation effect.[1] Many experimental and theoretical works have been performed on hydrogen stable configurations,[2–5] diffusion,[4,6,7] local motion,[8] charge states,[1,4,5] metastability and bistability,[9] and formation and dissociation of hydrogen-associated complexes[7,8,10–12] in silicon. No direct electron-spin resonance (ESR) measurements giving detailed information of microstructures, however, have been reported for hydrogen and hydrogen-associated complexes except a few examples of H ion implantation[13] which has the problem of introducing point defects. One of the open questions remaining is hydrogen behavior and stable configurations in *n*-type Si. We have utilized ion-implanted phosphorus donors with average concentrations ranging from 1×10^{18} to $2\times10^{19}/cm^3$ as an ESR probe for a study of the processes of hydrogen passivation and dissociation of P-H complexes. In these concentrations, the impurity band is formed below about $4\times10^{18}/cm^3$ at which the insulator-metal transition takes place.[14,15] It is expected that the linewidth of the motionally narrowed ESR is increased due to the Fermi-contact hyperfine interaction, because hydrogen has a nuclear spin of $\frac{1}{2}$ and a nuclear magneton 2.47 times larger than that of P nucleus.

In this paper, we demonstrate the ESR line broadening induced by the introduction of hydrogen and suggest formation of an intermediate state of hydrogen with a P donor neighbor in *n*-type Si. The latter result is obtained through an ESR study on recovery of shallow-donor P by thermal annealing of hydrogen-passivated Si.

For hydrogen passivation floating-zone (FZ) Si wafers were implanted with P at doses of 5×10^{13}–$1\times10^{15}/cm^2$ at an energy of 70 or 90 keV. The implanted wafers were activated with a furnance annealing of 950 °C for periods of 30 min to 2 h. Hydrogen passivation was done with a high-frequency (13.56 MHz) glow discharge apparatus. Samples were exposed to an H_2 plasma produced by glow discharge between a parallel plate reactor at a power density of 1.3 W/cm^2 and a pressure of 0.3 Torr. Exposure times were varied from 5 to 180 min. The surface temperature of the Si samples was measured by an optical reflectivity method[16] and estimated to be less than 140 °C. For comparison, H passivation was done for the off-center nitrogen center in Si that has a deep-donor level (E_c -0.33 eV).[17,18] Thermal annealing of passivated samples were also done in flowing pure nitrogen gas at temperatures from 100 to 900 °C to investigate the dissociation process of the P-H complexes formed with H passivation.

The ESR measurements of shallow-donor P and deep-donor off-center N in Si were made at temperatures ranging from 4 to 100 K with an *X*-band spectrometer, using continuous-flow liquid-helium cryostats. The ESR spectrum of P donors becomes a single Lorenzian line due to the motional narrowing,[14,15] while the ESR spectrum of the deep-donor off-center N shows hyperfine structure caused by nuclear spin of N because of localization of donor electrons.[17,18]

Significant broadening was observed in the motionally narrowed ESR line, as shown in Fig. 1, after hydrogen plasma treatment. Figure 2 shows the broadening for various Si samples as functions of the treatment or passivation time. The ESR linewidth is found to increase with the passivation time. If this change is due to decrease in electrically active P donors caused by hydrogen passivation, the ESR linewidth should inversely decrease in the range of the donor concentration used in this study, considering the donor concentration dependence[14,15] of the linewidth. The results suggest that high-concentration hydrogen introduced in Si changes the spin relaxation of P donor or conduction electrons. It is also noted that the increment of the ESR linewidth is larger for Si with higher P concentration than with lower concentration. Delocalization of donor electrons is enhanced for higher donor concentration.[15] For Si samples with donor concentrations above $4\times10^{18}/cm^3$, delocalized electrons in the conduction band can interact with much more hydrogen nuclear spins as compared to donor electrons in the impurity band. The line gets narrower again after annealing at temperatures above 400 °C, which will be mentioned later. These results indicate that the broadening is due to the Fermi-contact hyperfine interaction of donor (for 1–4 $\times10^{18}/cm^3$) or conduction (for above $4\times10^{18}/cm^3$) electrons with nuclear spins of high-density ($10^{19}/cm^3$ order) hydrogen atoms introduced in Si.

Figure 3 shows a decrease in the amount of the shal-

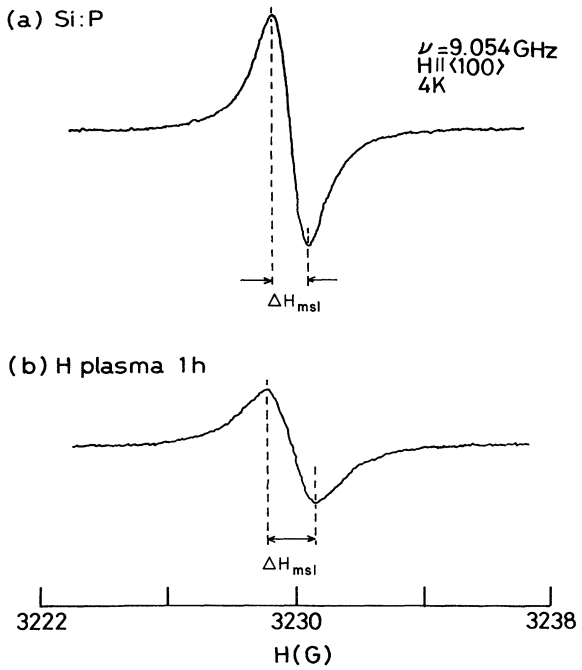

FIG. 1. Typical ESR signals of P donor and/or conduction electrons in Si (950 °C, 30 min) implanted at 70 keV with a dose of 2×10^{14} P^+/cm^2 (a) before and (b) after hydrogen passivation for 1 h.

low-donor P and deep-donor off-center N, obtained from ESR measurements at 100 K, with increasing passivation time. The P donors are partially passivated even at exposure times longer than 60 min, when the decrement is 35%, i.e., $1.75\times10^{13}/cm^2$. On the other hand, the off-center N is completely passivated at a time of 30 min. It is clear that for comparable hydrogenation conditions,

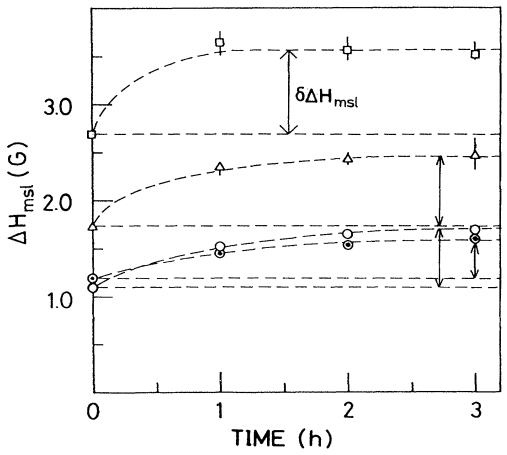

FIG. 2. ESR linewidth ΔH_{msl} (where msl denotes maximum slope) at 4 K for various Si samples (950 °C, 30 min) implanted at 70 keV with doses of (⊙) 5×10^{13}, (○) 2×10^{14}, (△) 5×10^{14}, and (□) 1×10^{15} P^+/cm^2 as functions of passivation time. These doses correspond to the average concentration of 1.0×10^{18}, 4.0×10^{18}, 1.0×10^{19}, and 2.0×10^{19} cm^3, respectively.

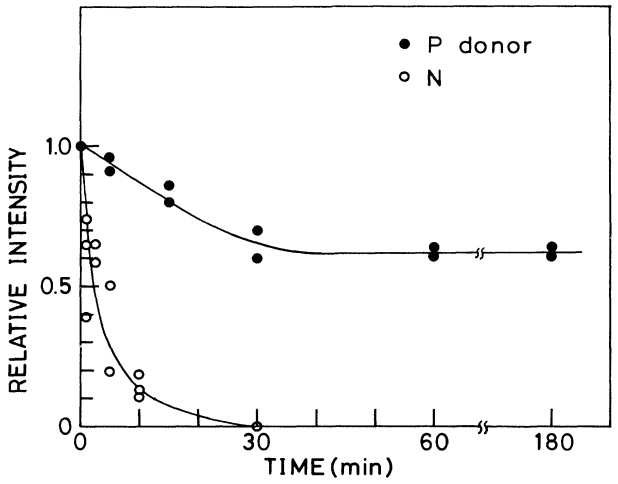

FIG. 3. Relative amount of shallow P donors (90 keV, 5×10^{13} P^+/cm^2, 950 °C, 30 min Si) and off-center N as functions of passivation time.

passivation of shallow donors is less pronounced than for the deep-donor off-center N. The off-center N is trigonally distorted with C_{3v} symmetry about the ⟨111⟩ axis,[17] so H is presumably located on the largely distorted bond between N and Si, i.e., bond centered (BC), as for shallow acceptors.[8,19]

The resistivity and Hall voltage were also measured for comparison at room temperature with a van der Pauw method for variously treated Si samples which were implanted at 90 keV at a dose of 2×10^{14} P/cm^2. The results of the electron concentration in Table I clearly indicate consistency with the ESR results in Fig. 3. As indicated by Johnson, Herring, and Chadi,[10] the increase in Hall mobility was observed after hydrogen passivation. This is due to a decrease in ionized-donor scattering as the P donor concentration decreases.[10]

In order to investigate the dissociation process of the P-H complexes and diffusion of hydrogen in *n*-type Si, we have performed annealing experiments for partially passivated donors. The ESR intensity and linewidth were measured at 4 and 100 K to monitor electrical recovery of donors through dissociation. The results of a series of 60-

TABLE I. Effects of hydrogen passivation on electron concentration and Hall mobility, and relative ESR intensity proportional to the amount of P donors and ESR linewidth ΔH_{msl} in phosphorus-doped silicon (90-keV P, $2\times10^{14}/cm^2$).

	Hall measurements		ESR measurements	
Treatment	n_s (cm^{-2})	μ_n (cm^2/Vs)	P donors (relative)	ΔH_{msl} (G)
Starting Si:P	2.1×10^{14}	212	1.0	2.34 ± 0.1
H passivation	1.5×10^{14}	251	0.75	2.38
200 °C annealing	2.0×10^{14}	225	0.99	2.62
400 °C annealing	2.0×10^{14}	217	1.0	2.39

min isochronal annealings are shown in Fig. 4. The recovery stage for the amount of P donors is seen at 150 °C in Fig. 4(a). The activation energy for dissociation of the P-H complex is estimated to be 1.4 eV by assuming the first-order reaction and a pre-exponential frequency factor of 10^{13} s^{-1}. This activation energy and the recovery temperature are in good agreement with the results obtained by Bergman *et al.*[11] from the infrared absorption measurements. After the P-H complexes have fully dissolved at 200 °C, up to 900 °C there is no significant change in the ESR intensity, within an experimental error, proportional to the amount of electrically activated P donors [see Fig. 4(a)]. This is also consistent with the results of the Hall measurements in Table I.

On the other hand, in Fig. 4(b) the ESR linewidth ΔH_{msl} (where msl denotes maximum slope) obtained at 4 and 100 K broadens at a limited annealing temperature range between 150 and 350 °C. The onset (150 °C) of the broadening is coincident with that of the recovery of P donors. This indicates that the additional broadening is partly due to an increase in donor concentration.[15] Since the average donor concentrations for the Si samples used here are 2.1×10^{18} and $4.0\times10^{18}/cm^3$, most of the donor electrons are in the impurity band,[15] therefore, they are not so delocalized compared with the conduction electrons originated from P donors with concentrations higher than $4\times10^{18}/cm^3$. This broadening is probably caused by hyperfine interaction between donor electrons in the impurity band and hydrogen nuclear spin ($I=\frac{1}{2}$). These considerations suggest that hydrogen atoms do not diffuse away, but continue to stay near P donors at temperatures below 300 °C after dissociation of the P-H complexes.

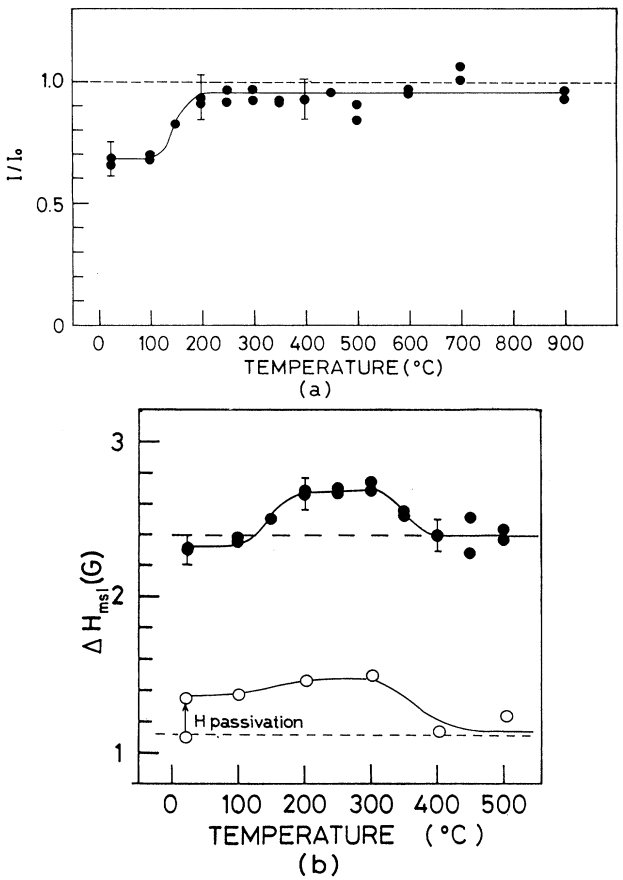

FIG. 4. Annealing behaviors of P donors in the H-passivated Si; (a) relative amount of shallow donors measured at 100 K for Si (950 °C, 2 h) implanted at 90 keV with a dose of 2×10^{14} P^+/cm^2 and (b) ESR linewidths (●) measured at 100 K for the same sample as (a) and (○) measured at 4 K for 70 keV, $2\times10^{14}/cm^2$ implanted Si (950 °C, 30 min).

There is, however, another possibility for ESR broadening that some scattering centers for conduction electrons are produced through dissociation of the P-H complexes or hydrogen introduction.[20] From the results in Table I, it is obvious that there is no decrease in Hall mobility after annealing of H-passivated samples at 200 °C and there is increase after *H* passivation, as compared with that for the initial Si wafer. Consequently, the possibility of the introduction of electron-scattering centers can be ruled out for both the cases of ESR broadening.

Thus, an intermediate state yielding the ESR line broadening is formed in the process of dissociation of the P-H complexes, and is likely to consist of a P donor and hydrogen atom(s) staying just near the P atom. As the intermediate state in *n*-type Si, one possible configuration is a BC hydrogen and a tetrahedral-interstitial (T_d) hydrogen near the P atom, forming a metastable molecule-like hydrogen, H_2^*. This is stable according to the model of Chang and Chadi.[7] In this case the P-H complex encounters a neutral hydrogen atom that is mobile in *n*-type Si at temperatures around 150 °C, resulting in the formation of the molecule-like hydrogen. If so, the H_2^* is immobile at moderate temperatures lower than 300 °C, as deduced from the result of the ESR linewidth in Fig. 4(b). Johnson and Herring[21] also reported a nonmonatomic center associated with hydrogen that forms during hydrogen diffusion in *n*-type Si. It is noted in Fig. 4(b) that the ESR linewidth begins to decrease at 350 °C and reaches the initial value above 400 °C. This suggests that the H_2^* or H atom(s) become mobile above 350 °C and diffuses away out of or into a Si wafer. This temperature is consistent with the experiment of out diffusion of a hydrogen atom on the Si surface[22] and a hydrogen molecule from crystalline Si.[23]

In conclusion we have first observed line broadening of ESR of P donor and/or conduction electrons after the introduction of hydrogen in Si. Furthermore, additional line broadening and recovery to the initial value are observed after annealing of H-passivated Si at temperatures of 150 to 350 °C and above 350 °C, respectively. These broadening are caused by the Fermi-contact hyperfine interaction between hydrogen nuclear spins and donor and/or conduction electrons. The ESR method using donor impurity probe is demonstrated to be useful for study on hydrogen state in Si. Analysis of detail hydrogen states will be performed from the hyperfine interaction, measuring H concentration by secondary-ion-mass spectrometry. Direct detection of super-hyperfine structure is also anticipated for the possible configuration of H atom(s) staying just near P in Si with a much lower P concentration. These studies are in progress.

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[1]S. J. Pearton, M. Stavola, and J. W. Corbett, Mater. Sci. Forum **38-41**, 25 (1989).

[2]B. B. Nielsen, J. U. Andersen, and S. J. Pearton, Phys. Rev. Lett. **60**, 321 (1988).

[3]R. F. Kiefl, M. Celio, T. L. Estle, S. R. Kreitzman, G. M. Luke, T. M. Riseman, and E. J. Ansaldo, Phys. Rev. Lett. **60**, 224 (1988).

[4]C. G. van de Walle, Y. Bai-Yam, and S. T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988).

[5]K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **60**, 1422 (1988).

[6]F. Buda, G. L. Chiarotti, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 294 (1989).

[7]K. J. Chang and D. J. Chadi, Phys. Rev. Lett. **62**, 937 (1989).

[8]M. Stavola, K. Bergman, S. J. Pearton, and J. Lopta, Phys. Rev. Lett. **61**, 2786 (1988).

[9]G. D. Watkins, in *Proceedings of the 15th International Conference on Defects in Semiconductors* (Trans. Tech. Publ., Aedermannsdorf, Switzerland, 1989), p. 39.

[10]N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 769 (1986).

[11]K. Bergman, M. Stavola, S. J. Pearton, and J. Lopta, Phys. Rev. B **37**, 2770 (1988).

[12]P. Deak and L. C. Snyder, Radiat. Eff. Def. Solids, **111 & 112**, 77 (1989).

[13]Yu. V. Gorelkinskii and N. N. Nevinnyi, Pis'ma Zh. Tekh. Fiz. **13**, 105 (1987) [Sov. Tech. Phys. Lett. **13**, 45 (1987)].

[14]K. Murakami, K. Masuda, and S. Namba, Solid State Commun. **18**, 663 (1976).

[15]J. D. Quirt and J. R. Marko, Phys. Rev. B **7**, 3842 (1973).

[16]K. Murakami, Y. Tohmiya, K. Takita, and K. Masuda, Appl. Phys. Lett. **45**, 659 (1984).

[17]K. Murakami, H. Kuribayashi, and K. Masuda, Phys. Rev. B **38**, 1589 (1988).

[18]K. Murakami, H. Kuribayashi, and K. Masuda, Jpn. J. Appl. Phys. **27**, L1414 (1988).

[19]M. Stavola, S. J. Pearton, J. Lopta, and W. C. Dantremont-Smith, Phys. Rev. B **37**, 8313 (1988).

[20]R. J. Eliott, Phys. Rev. **96**, 266 (1954).

[21]N. M. Johnson and C. Herring, Phys. Rev. B **38**, 1581 (1988).

[22]N. Yabumoto, K. Saito, M. Morita, and T. Ohmi, Jpn. J. Appl. Phys. **30**, L419 (1991).

[23]C. Kisielowski-Kemmerich and W. Beyer, J. Appl. Phys. **66**, 552 (1989).