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Passivation of shallow impurities in Si by annealing in H₂ at high temperature

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We have found by infrared absorption that shallow acceptors in Si can be passivated throughout the bulk of a semiconductor sample several mm thick by annealing in H₂ at high temperature (>900 °C) and quenching to room temperature. The total number of shallow centers passivated in such samples is comparable to the number in highly doped surface layers passivated in a hydrogen plasma at lower temperature (typically <400 °C). The importance of bulk passivation techniques is discussed.

The interest in hydrogen in semiconductors has increased dramatically since the discovery that shallow impurities can be passivated by complexing with H which has been introduced from a H-containing plasma.¹⁻⁴ The earlier studies of H in semiconductors in which the H was introduced during growth in an H₂ ambient⁵⁻⁸ have been eclipsed by the many recent studies of plasma-passivated samples. Here, we report new results on the introduction of H into semiconductors by annealing in H₂ at high temperature followed by rapid quenching. The surprising result is that acceptor-H complexes can be formed throughout the bulk of an Si sample by such a treatment⁹ even though acceptor-H complexes are only stable up to a few hundred °C.

Several groups have examined bulk semiconductors that had been grown in an H₂ ambient⁵⁻⁸ or had H indiffused at elevated temperature from an H₂ ambient.^{10,11} For example, Hall⁷ and Haller and co-workers^{5,6} have discovered several H-related species in Ge that had been grown in H₂. In contrast, most recent activity on the hydrogen passivation of shallow impurities has focused on thin layers (typically 1 μm);¹⁻⁴ the hydrogen is often indiffused at low temperature (150-400 °C) from an H-containing plasma. The possibility that shallow acceptors and donors might be passivated by the indiffusion of H at high temperatures has not been explored, presumably because these complexes dissociate^{12,13} at a few hundred °C.

In our experiments, Si samples were sealed in quartz ampoules that had been evacuated and then filled with 0.6 atm of H₂ gas at room temperature. The sealed ampoules were annealed at temperatures between 900 and 1280 °C and then quenched to room temperature by withdrawing the ampoule from the furnace and dropping it into ethylene glycol at room temperature. Infrared (IR) absorption spectra were measured at a resolution of 2 cm⁻¹ with a Bomem DA3.16 Fourier transform spectrometer.

IR spectra of bulk, acceptor-doped Si samples (with N_A of the order of 10¹⁶ cm⁻³) that had been annealed in H₂ are shown in Fig. 1. The H-stretching features that are observed have frequencies and absorption strengths similar to those reported^{12,14,15} for acceptor-H complexes in samples that were doped with concentrations greater than 10¹⁸ cm⁻³ by ion implantation and then passivated by exposure to an H₂ plasma at 200 °C. Sample characteristics and the

strengths of H-stretching IR absorption are compared in Table I for plasma-passivated layers and H₂-annealed samples. The quantity $xA = x \int \alpha(\sigma) d\sigma$, where x is the sample thickness and A is the integrated absorption coefficient for the H-stretching band, is proportional to the number of acceptor-H centers per cm², i.e., throughout the thickness of the sample. The values of xA show that the number/cm² of passivated centers in both types of samples is comparable.

The data in Fig. 1 and Table I demonstrate that H-acceptor complexes are formed and that they must be present throughout the bulk of the samples annealed at 1280 °C in H₂ to give rise to absorption bands with strengths comparable to the thin layers of acceptor-H complexes with much higher concentrations that were studied previously. It was further confirmed that the passivation is uniform throughout the sample thickness by remeasuring the IR absorption after grinding 1 mm from the surfaces of an H₂ treated, B-doped sample that was initially 3 mm thick. Vibrational absorption due to B-H centers was observed with a strength consistent with the 1 mm thickness of the thinned sample and a uniform distribution of centers through the sample.

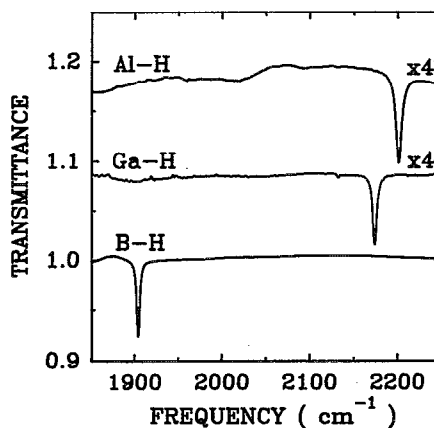


FIG. 1. IR spectra measured near liquid He temperature for acceptor-doped, Si samples that had been annealed in H₂ gas at 1280 °C for 30 min and then quenched to room temperature. The acceptor concentrations are 6 × 10¹⁶, 1 × 10¹⁶, and 0.7 × 10¹⁶ cm⁻³ for the B, Al, and Ga doped samples, respectively.

TABLE I. Sample characteristics and the areas of the H-stretching IR absorption bands for acceptor-H complexes. Characteristics of thin, heavily doped layers that were passivated in an H₂ plasma are shown on the left-hand side. Characteristics of bulk-doped samples that were passivated by annealing in H₂ are shown on the right-hand side. The quantity xA is the product of the sample thickness, x , and the integrated absorption coefficient, A , for the H-stretching band. (Data were published previously in Ref. 12 for the heavily doped layers that were passivated in an H₂ plasma.)

Acceptor	H ₂ -plasma (< 220 °C)			H ₂ -anneal (1280 °C)		
	N_A (cm ⁻³)	x (μm)	xA (cm ⁻¹)	N_A (cm ⁻³)	x (cm)	xA (cm ⁻¹)
B	3×10^{19}	1.4	1.2	1.7×10^{17}	0.28	0.52
B				1.5×10^{16}	0.24	0.05
Al	3×10^{18}	1.2	0.13	1.0×10^{16}	0.28	0.17
Ga	1×10^{19}	0.4	0.34	0.7×10^{16}	0.26	0.10

In order to determine [B-H] from the strength of the IR absorption, we have reexamined previous results¹⁴ for a B-implanted sample that had been passivated in an H₂ plasma. (This sample's characteristics are also given in Table I here.) The integrated absorption coefficient for the H-stretching band is $A = 8.6 \times 10^3$ cm⁻². The concentration of B-H centers for this sample, determined from the spreading resistance profiles shown in Fig. 2, leads to the calibration

$$[B-H]/A = (2.5 \times 10^{15} \text{ cm}^{-1}). \quad (1)$$

This calibration is close to that determined¹⁴ for Al-H complexes in Si. With this calibration we find that [B-H] = 4.6×10^{15} cm⁻³ and 5.0×10^{14} cm⁻³ for the samples with [B] = 1.7×10^{17} cm⁻³ and 1.6×10^{16} cm⁻³, respectively. Hence, roughly 3% of the B is passivated by the

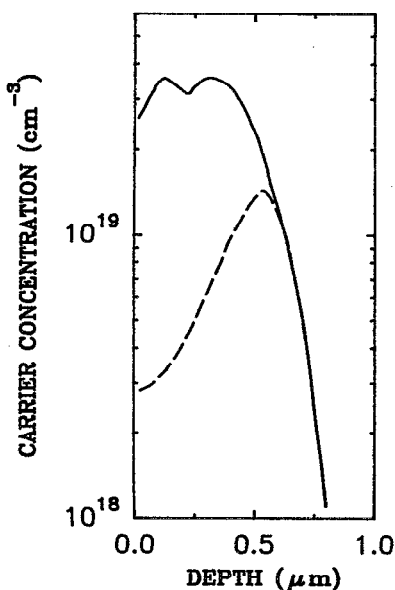


FIG. 2. Spreading resistance profiles of the free-carrier concentration before (solid line) and after (dashed line) H₂ plasma exposure for 3 h at 120 °C for the Si:B layer whose characteristics are given in Table I. The doped layer was formed by ion implantation with multiple energies (see Ref. 12). (Both sides of the Si sample were implanted with B to give the total layer thickness given in Table I.)

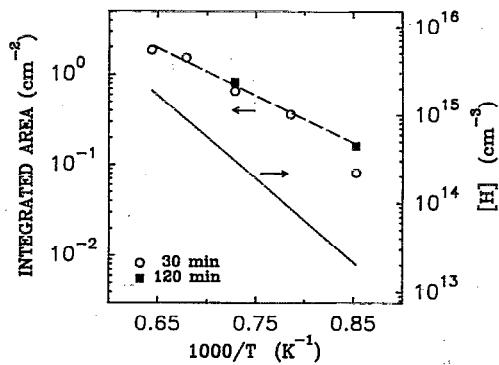


FIG. 3. The integrated absorption coefficient, A , for the H-stretching vibration of the B-H complex vs the reciprocal of the annealing temperature for Si samples with $[B] = 1.7 \times 10^{17}$ cm⁻³ that were annealed in H₂, and then quenched. The concentration scale on the right-hand side is related to A by Eq. (1) in the text. The solid line is the solubility of H in pure Si determined by Van Wieringen and Warmoltz (see Ref. 19).

anneal in H₂ at 1280 °C. For the Al-doped sample we find $[Al-H] = 1.3 \times 10^{15}$ cm⁻³ and that 8% of the Al is passivated. The more complete passivation of Al is consistent with this complex's greater binding energy.¹³

When H was introduced into n -type Si doped with P or As by annealing at 1280 °C in H₂ gas and quenching, IR bands at 1555 and 1561 cm⁻¹ that have been assigned to P-H and As-H complexes^{15,16} were not detected. We confirmed that H had diffused into our samples in the following experiments. A 2.5 MeV electron irradiation with a dose of 1×10^{17} e⁻/cm² produced IR features at 1839, 1987, 1990, and 2062 cm⁻¹ in our n -type samples. These features have been observed previously in Si that had been implanted with protons at room temperature¹⁷ and in Si that had been grown in an H₂ ambient and then irradiated with 1.5 MeV electrons.¹⁸ These absorption features have been assigned to lattice damage that is decorated with H; their presence in our samples following irradiation confirms the presence of H.

We have explored the role of the temperature and duration of the H₂-soaking treatment on the concentration of B-H complexes that are formed. In Fig. 3, [B-H] is plotted versus the reciprocal of the temperature of the H₂ anneal for the sample doped with $[B] = 1.7 \times 10^{17}$ cm⁻³. The open circles are for 30 min anneals and the closed squares are for 120 min anneals. At 1100 °C, increasing the duration of the anneal slightly increases the strength of B-H absorption. At 900 °C, increasing the duration of the anneal increases the B-H absorption by a factor of 2 indicating that H has not fully diffused through the sample during the 30 min anneal. The diffusion constant determined by Van Wieringen and Warmoltz¹⁹ (VWW) is 3.7×10^{15} cm²/s at 900 °C which gives a \sqrt{Dt} diffusion length of 0.26 cm for the 30 min anneal in H₂ which is comparable to the thickness of the sample.

The dashed line shown in Fig. 3 is the best fit to the data. (At 900 °C, the data for the 120 min anneal were used.) If we use the calibration of the B-H absorption given in Eq. (1), the temperature dependence of [B-H] for our samples is given by

$$[B-H] = 1.2 \times 10^{19} \exp(-1.04 \text{ eV}/kT) \text{ cm}^{-3}. \quad (2)$$

Also shown in Fig. 3 is the hydrogen solubility determined by VWW,¹⁹ $S_H = 2.4 \times 10^{21} \exp(-1.88 \text{ eV}/kT) \text{ cm}^{-3}$. At 1280 °C, the B-H concentration is greater than the VWW solubility by only a factor of 2.7. At 900 °C, the B-H concentration in our samples exceeds the VWW solubility by more than a factor of 20. Note that the activation energies in Eq. (2) and the solubility determined by VWW differ by nearly a factor of 2.

The dependence of the number of centers formed upon the temperature of the anneal is presumably due to the temperature dependence of the H solubility. While the H solubility should not depend on the hole concentration because the Fermi level is at mid-gap during the high-temperature anneal,²⁰ the strength of the B-H absorption does depend on the initial [B] in our experiments (see Table I). We conclude that during the quench, there are competing reactions that involve H and that an increased [B] favors the formation of [B-H]. The reactions that are usually considered are $H + H \rightleftharpoons H_2$ and $B + H \rightleftharpoons BH$. These reactions also depend upon the charge state of the reactants.²¹ Hence, the boron concentration also affects the reaction rates through the change in Fermi level position as the sample cools. At present, our results place a lower limit on the amount of hydrogen that can be incorporated into B-doped samples by annealing in H₂ at high temperature.

The study of hydrogen-passivated deep impurities has been hampered by their low solubility compared to typical dopants; the reduced concentration does not lead to a sufficient total number of hydrogen-passivated centers in thin layers for easy examination by structure sensitive techniques such as IR absorption or electron paramagnetic resonance. Hence, we expect that there will be renewed interest in H-introduction techniques in which H can be introduced throughout the bulk of a semiconductor sample; the total number of hydrogen passivated centers introduced in bulk samples should permit structure-sensitive studies of species with solubilities that are decades smaller than is typical of dopants.

In conclusion, we have shown that acceptor impurities in Si can be passivated by annealing bulk samples in H₂ at high temperature and quenching. H is incorporated at con-

centrations that are well above the solubility of H determined by Van Wieringen and Warmoltz.¹⁹ Similar treatments did not result in the passivation of shallow donors in *n*-type Si. It is expected that this bulk-passivation technique will prove useful in studies of H-passivated deep levels.

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