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Formation of hydrogen-boron complexes in boron-doped silicon treated with a high concentration of hydrogen atoms

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The formation of hydrogen (H) related complexes and their effect on boron (B) dopant were investigated in B-ion implanted and annealed silicon (Si) substrates treated with a high concentration of H. Isotope shifts by replacement of ^{10}B with ^{11}B were observed for some H-related Raman peaks, but not for other peaks. This shows proof of the formation of B-H complexes in which H directly bonds to B in Si. This is an experimental result concerning the formation of B-H complexes with H bonded primarily to B. Electrical resistivity measurements showed that the B acceptors are passivated via the formation of the observed B-H complexes, as well as the well-known passivation center in B-doped Si; namely, the H-B passivation center.

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I. INTRODUCTION

Hydrogen (H) was a hidden impurity in semiconductors until the 1980s due to the difficulty of detecting low concentrations of H atoms in semiconductors. Over the past two decades... however, many studies on hydrogen in semiconductors have been conducted and advances have been made in H-detection techniques such as infrared, Raman scattering, and secondary ion mass spectrometry (SIMS) measurements as well as in the development of hydrogen treatment methods. H exhibits technologically important behaviors in semiconductors.¹ Although H is now one of the most widely recognized impurities in semiconductors, many important problems remain to be solved.

Hydrogen passivation of shallow level impurities such as boron (B) in silicon (Si), one of the well-investigated phenomena in this field, is caused by the formation of a simple complex between H and B.¹ In this complex, an H atom is located at the bond-centered (BC) site between B and a neighboring host Si atom, and a so-called H-B passivation center is formed.²⁻⁵ In this passivation center, the hydrogen bonds primarily to the Si, while the B moves away from this Si almost into the plane of the other three Si neighbors.⁶ Hydrogen passivation of B in Si is very efficient because the Coulomb attraction between interstitial H^+ and B^- results in a very large capture radius.⁷ Thus, almost all B in Si can be passivated by H.^{8,9}

With increasing concentration of H, hydrogen molecules¹⁰⁻¹⁴ and extended planar defects called platelets^{9,15,16} are formed. Furthermore, additional H- [or deuterium (D)] related Raman peaks are observed in the range of 1900–2300 (1300–1700) cm^{-1} .^{17,18} The vibrational Raman peaks have been tentatively ascribed to H (D) decorated lattice defects with Si-H (Si-D) bonds. The formation of such H-related defects has been deduced from a theoretical calculation.¹⁹ The local structures and the effect on B

dopant, however, have not been experimentally clarified.

In the present study, we precisely investigated the isotope shift of H-related Raman peaks by the replacement of H with D and ^{10}B with ^{11}B , and obtained proof of the formation of B-H complexes in which H is bonded primarily to B in Si. Furthermore, in order to clarify the influence of the above-mentioned H-related complexes on B dopants, we measured the resistivity before and after hydrogenation and investigated the passivation of B acceptors due to the formation of B-H complexes.

II. EXPERIMENT

The specimens used in this study were *n*-type Cz-Si (1.4–2.3 Ωcm) implanted with 30–50 keV $^{11}\text{B}^+$ ions at doses of 1×10^{13} to $5 \times 10^{15} \text{cm}^{-2}$. To investigate the local structures of the B-related complexes, an isotope of $^{11}\text{B}^+$ ion, namely, $^{10}\text{B}^+$, was implanted at 30 keV at a dose of $1 \times 10^{15} \text{cm}^{-2}$. These implanted Si samples were annealed in a N_2 gas atmosphere at 900 °C for 30 min to electrically activate the B dopants. In order to check the effect of damage by implantation, a Si wafer with a B concentration of $1 \times 10^{19} \text{cm}^{-3}$ was also used. After the specimens were activated, they were placed in a quartz tube at a position 60 cm from the H plasma and hydrogenated by remote downstream treatments of high-flux H atoms at temperatures ranging from 120 to 330 °C. Damage by the H plasma is completely neglected in this remote method. The flow of H_2 gas was controlled at 95 SCCM (SCCM denotes cubic centimeter per minute at STP). In addition to the isotope experiments with B isotopes, D atoms were introduced using the same remote downstream system to distinguish whether the observed Raman peaks were H-related or not. The detailed hydrogenation procedures and their conditions have been reported elsewhere.²⁰

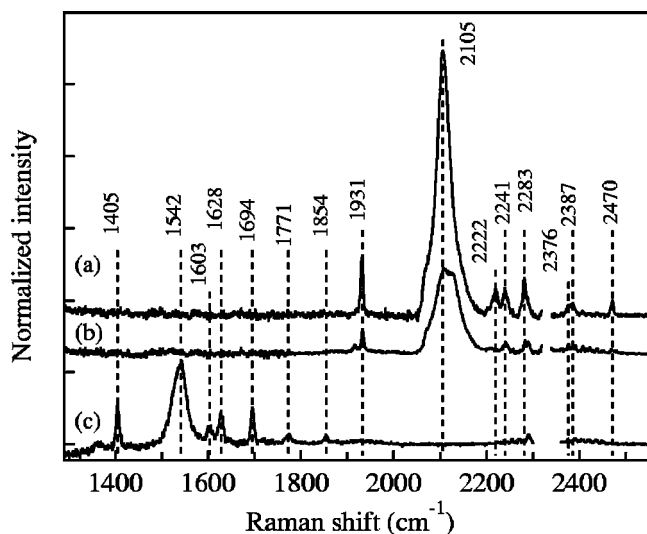


FIG. 1. Raman spectra observed for (a) Si implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ and (b) bulk Si, both of which were subjected to hydrogenation at 245 °C. The Raman spectrum shown in (c) was obtained for Si implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$, followed by deuteration at 245 °C.

Raman scattering measurements were performed at room temperature, with a 514.5 nm excitation light at a power of 100 mW. The Raman intensities were normalized by that of the optical phonon of Si measured for the same sample under the same conditions to compare the intensities among specimens. SIMS measurements were performed to investigate the depth profile of H introduced into the specimens. The primary ions were Cs^+ ions. The resistivities of the specimens were measured at room temperature by four-point probe measurements.

III. RESULTS

A. H and B related Raman peaks

The Raman peaks observed for specimens implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ followed by hydrogenation or deuteration at 245 °C are shown in Figs. 1(a) and 1(c), respectively. The result for the unimplanted Si wafer sample is also shown in Fig. 1(b). In the hydrogenated B-implanted specimen, several peaks were observed at 1931, 2105, 2222, 2241, 2283, 2376, 2387, and 2470 cm^{-1} . These peaks were also observed for the unimplanted Si wafer sample shown in Fig. 1(b), demonstrating that none of the peaks in Fig. 1(a) were related to defects caused by ion implantation.

In general, H-related localized vibrational modes (LVMs) are identified through the substitution of D, and the frequencies of the stretching vibration of X (any atom) -H bonds depend especially on the mass of atom X. In semiconductors, the frequencies of the stretching modes of X-H bonds can be estimated by using some simple molecule with a one-dimensional harmonic oscillator approximation, because the LVM frequencies are much higher than the host's vibrational frequencies, so the LVM does not propagate in the lattice. In this approximation, the ratio of $\gamma = \omega(\text{H})/\omega(\text{D})$ is given by

$$\gamma = (m_{\text{D}}/m_{\text{H}})^{1/2} [(m_{\text{H}} + m_{\text{X}})/(m_{\text{D}} + m_{\text{X}})]^{1/2}, \quad (1)$$

where m_{H} , m_{D} , and m_{X} are the mass of H, D, and X atoms, respectively. The value of γ is useful for distinguishing between the possible values of m_{X} that differ greatly, and for comparing a family of chemically related species in semiconductors, although this expression is seldom sufficiently valid to determine m_{X} accurately.

In the deuterated B-implanted specimen, isotope peaks were observed at 1405, 1542, 1603, and 1628 cm^{-1} , corresponding to those observed at 1931, 2105, 2222, and 2241 cm^{-1} , respectively, in the hydrogenated specimens. The frequency ratios are about 1.37–1.39. The square root of the reduced mass ratio for Si-D to Si-H estimated from Eq. (1) is about 1.390, which is in good agreement with the experimental values. This result shows that these peaks are due to the Si-H (Si-D) stretching mode. Here, the peak at 2105 cm^{-1} is the Si-H stretching mode of platelets.^{15,16} On the other hand, the frequency ratios of the remaining peaks at 2283, 2387, and 2470 cm^{-1} to those at 1694, 1771, and 1854 cm^{-1} , respectively, are about 1.33–1.35. These values are too low to be within the range of the values for the Si-H bonds. Rather, they are in good agreement with the square root of the reduced mass ratio for B-D to B-H estimated from Eq. (1); that is, about 1.359. This result suggests the formation of B-H (B-D) complexes in which H atoms directly bond with B atoms.

In order to confirm the formation of the new complexes with B-H bonds, Si wafer samples were implanted with an isotope of $^{11}\text{B}^+$ ion, namely, $^{10}\text{B}^+$ ion. The results are shown in Fig. 2. The peaks assigned to B-H complexes in Fig. 1 showed an isotope shift. The frequency ratios of the peaks observed for the specimen implanted with $^{11}\text{B}^+$ to that implanted with $^{10}\text{B}^+$ are about 1.003–1.005. These values are close to the ratio of the square root of the reduced mass for $^{10}\text{B-H}$ to $^{11}\text{B-H}$ estimated from Eq. (1); that is, about 1.004. Thus, the peaks observed at 2283, 2292, 2376, 2387, and 2470 cm^{-1} can be clearly identified as B-H complexes with B-H bonds. On the other hand, the peak at 1873 cm^{-1} , which is attributed to the H-B passivation center, did not shift. According to previous results by Pajot *et al.*²¹ and Watkins *et al.*,²² a small B-isotope-related shift has been observed for the peak due to the H-B passivation center. The reason why the isotope shift was not observed in this study is that it is very small, and would not be seen in room temperature Raman experiments. Moreover, no isotope shift was observed for the remaining peaks. These results also confirm the assignment of the peaks to the Si-H stretching mode. The peak at 2134 cm^{-1} is the Si-H stretching mode of the platelets. The peak frequency of the platelets in Fig. 2 differs from that in Fig. 1. This is due to the fact that the frequency of platelets strongly depends on the hydrogenation temperature.¹⁶ The results of the isotope shifts are summarized in Table I.

B. Dependence on concentration of B

Figure 3 shows the dependence of the Raman peaks related to B-H complexes on the concentration of B for specimens hydrogenated at two different temperatures: 165 °C and 245 °C. The peak intensities strongly depended on the

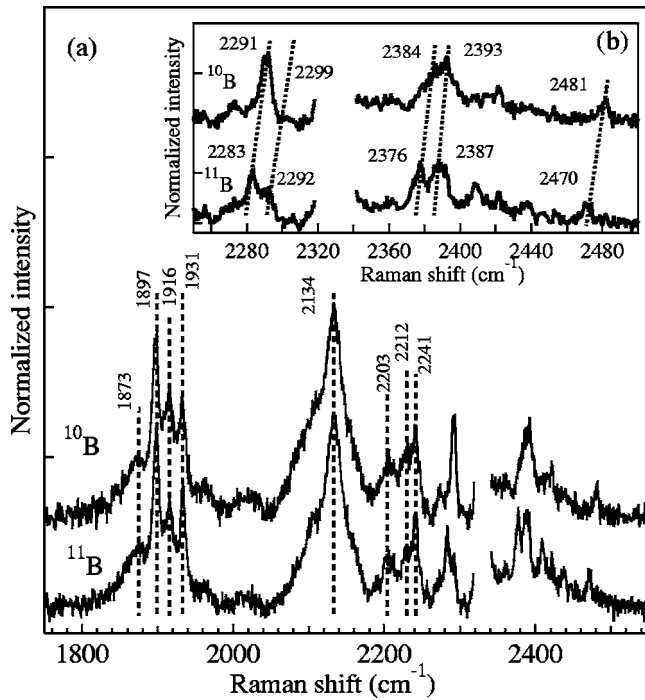


FIG. 2. (a) Raman spectra observed for Si implanted with $30 \text{ keV } ^{11}\text{B}^+$ ions or $^{10}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$, followed by hydrogenation at $220 \text{ }^\circ\text{C}$. The inset (b) shows a magnification of the peaks related to B-H complexes.

concentration of B and increased with the concentration of B. This result also provides evidence that these peaks are related to B. Furthermore, the peak intensities increased with the hydrogenation temperature; that is, the concentration of H introduced into the specimen. This result suggests that a high concentration of hydrogen is required to form B-H complexes. The intensities of the B-H and Si-H stretching peaks

TABLE I. Vibrational frequencies and isotopic ratios of H to D and ^{10}B to ^{11}B .

$\omega(^{11}\text{BH})$ $\times(\text{cm}^{-1})$	$\omega(^{11}\text{BD})$ $\times(\text{cm}^{-1})$	$\omega(^{11}\text{BH})/\omega$ (^{11}BD)	$\omega(^{10}\text{BH})$ $\times(\text{cm}^{-1})$	$\omega(^{10}\text{BH})/\omega(^{11}\text{BH})$
1873	1361	1.375	1873	1.000
1897	1381	1.375	1897	1.000
1916	1395	1.372	1916	1.000
1931	1405	1.374	1931	1.000
2105	1542	1.365	2105	1.000
2203			2203	1.000
2212			2212	1.000
2222	1603	1.386		
2228			2228	1.000
2241	1628	1.377	2241	1.000
2283	1694	1.348	2291	1.004
2292			2299	1.003
2376			2384	1.003
2387	1771	1.348	2393	1.003
2470	1854	1.333	2481	1.004

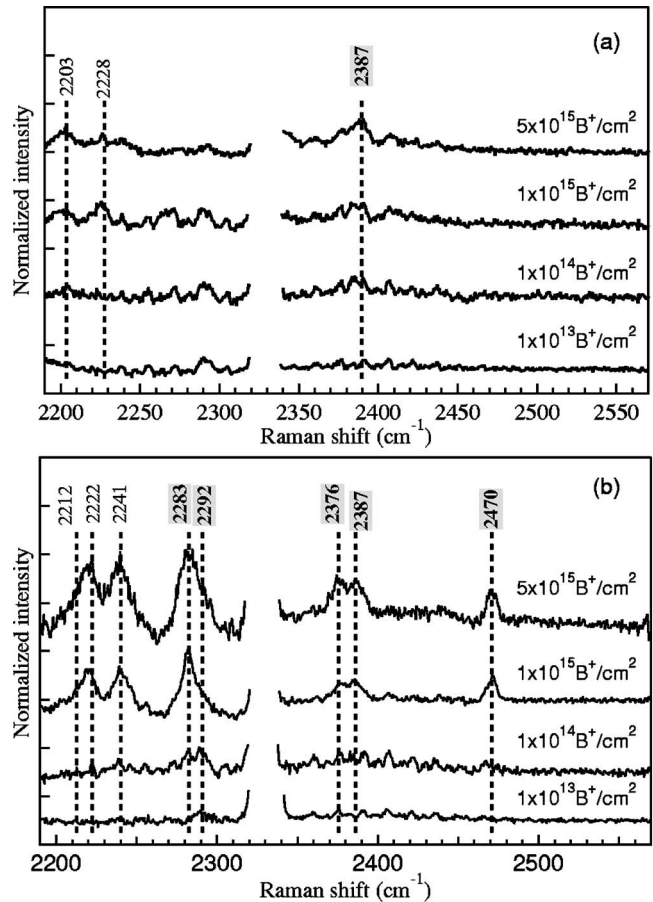


FIG. 3. Dependence of the Raman peaks related to B-H complexes on the concentration of B for specimens hydrogenated at two different temperatures: (a) $165 \text{ }^\circ\text{C}$ and (b) $245 \text{ }^\circ\text{C}$. The frequencies of the peaks related to B-H complexes are shadowed.

are summarized in Fig. 4. As well as the peak related to the B-H complexes, some of the peaks related to the Si-H stretching modes show an increase in intensity with an increasing concentration of B. The existence of such Si-H stretching modes suggests that Si-H bonds are also formed in the process of formation of B-H complexes.

C. Dependence on hydrogenation temperature and duration

The hydrogenation temperature and the concentration of hydrogen introduced into the specimen are important parameters for the formation of B-H complexes. Figure 5 shows the Raman peaks observed for specimens hydrogenated at different temperatures. The peak intensities of the B-H and Si-H stretching modes are summarized in Fig. 6. Here, the peak at about 2100 cm^{-1} is due to the Si-H stretching mode of the platelets. At the low hydrogenation temperature of $130 \text{ }^\circ\text{C}$, the main peak is due to the H-B passivation center. No H-B passivation centers were observed at temperatures of $245 \text{ }^\circ\text{C}$ or higher. After annihilation of the H-B passivation centers, various peaks appear with increasing hydrogenation temperature. The concentration of hydrogen introduced into specimens increases with increasing hydrogenation temperature,¹⁶ resulting in the formation of complicated

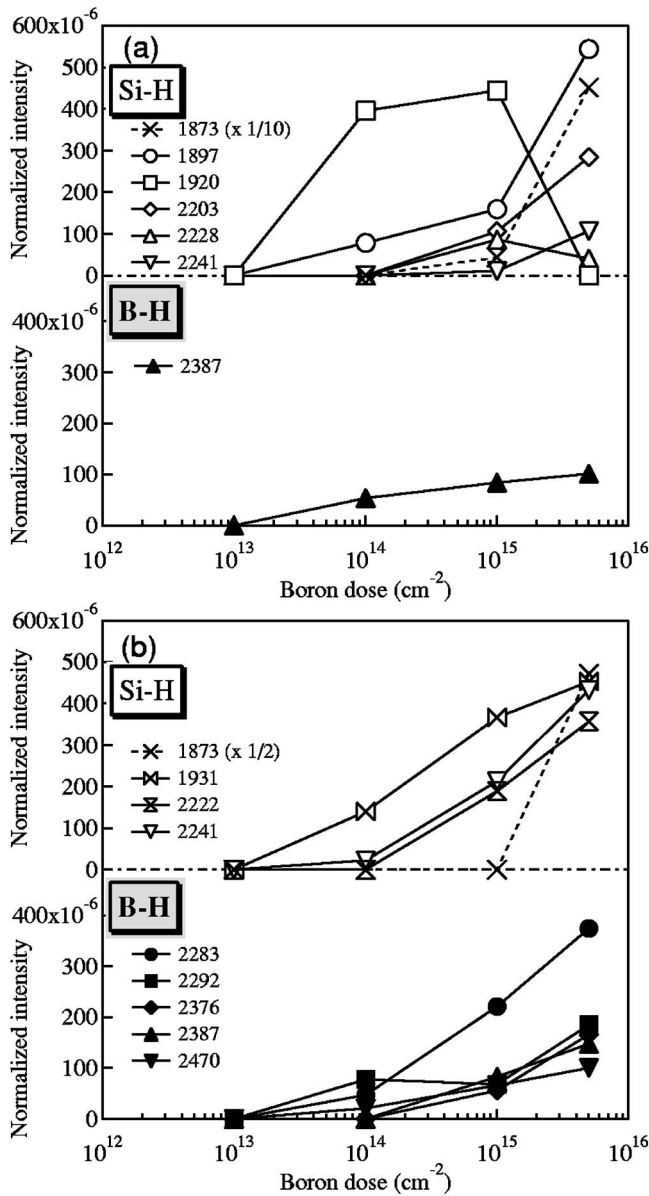


FIG. 4. Dependence of the intensities of H-related Raman peaks on the concentration of B for specimens hydrogenated at two different temperatures: (a) 165 °C and (b) 245 °C.

complexes with H such as B-H complexes and platelets. The intensities of the B-H stretching peaks at 2283 and 2470 cm^{-1} show a similar dependence on hydrogenation temperature to those of the Si-H stretching peaks observed at 1931, 2222, and 2241 cm^{-1} . The similar dependence suggests that both B-H and Si-H bonds are contained in the same complexes. The details will be discussed in Sec. IV.

Figures 7 and 8 show the dependence of the Raman peaks and their intensities on the hydrogenation duration. Hydrogenation was performed at a constant temperature of 190 °C. Peaks due to the B-H stretching modes were observed for the specimens treated for 10 min or longer. The intensities significantly increased up to 60 min and then remained almost constant for longer durations. The dependence of the B-H stretching peaks at 2283 and 2470 cm^{-1} on the hydrogenation duration is similar to that of the Si-H stretching peaks at

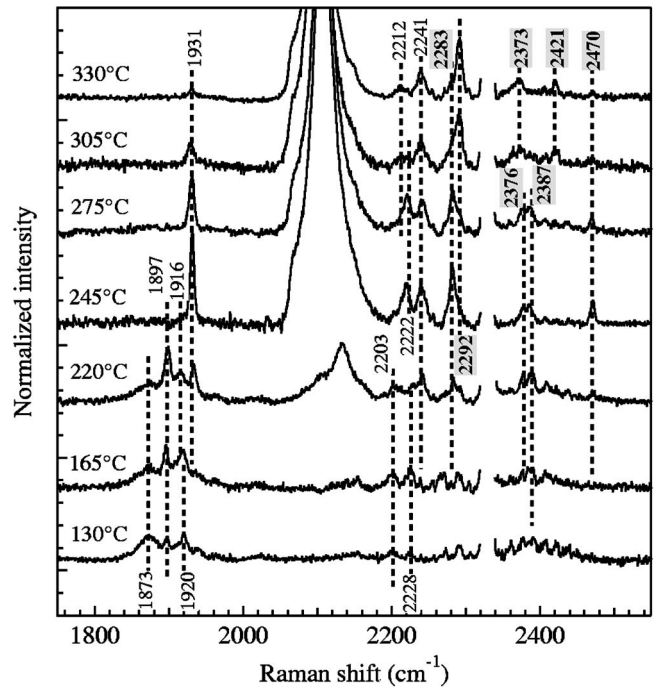


FIG. 5. Raman spectra observed for specimens hydrogenated at different temperatures. The specimens were implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$, followed by hydrogenation at each temperature shown for 30 min. The frequencies of the peaks related to B-H complexes are shadowed.

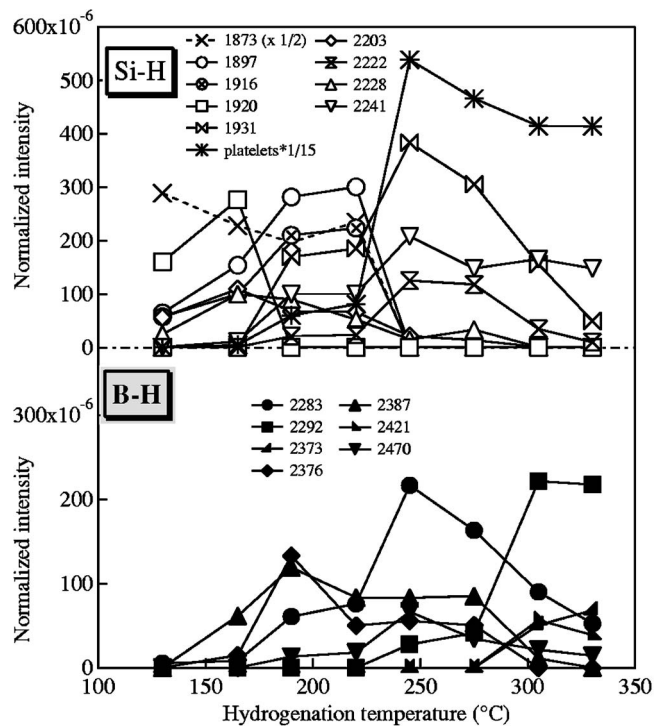


FIG. 6. Dependence of the peak intensities of H-related Raman peaks on the hydrogenation temperature. The specimens were implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$, followed by hydrogenation at each temperature shown for 30 min.

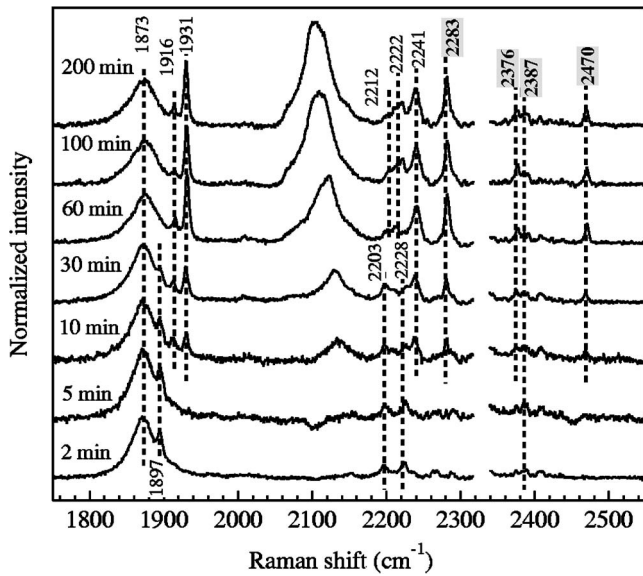


FIG. 7. Raman spectra observed for specimens hydrogenated for different durations. The specimens were implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $5 \times 10^{15} \text{ cm}^{-2}$, followed by hydrogenation at 190 °C. The frequencies of the peaks related to B-H complexes are shadowed.

1931, 2222, and 2241 cm^{-1} , as well as the case for the dependence on hydrogenation temperature shown in Fig. 6. On the other hand, the peak intensity of the H-B passivation center was almost constant.

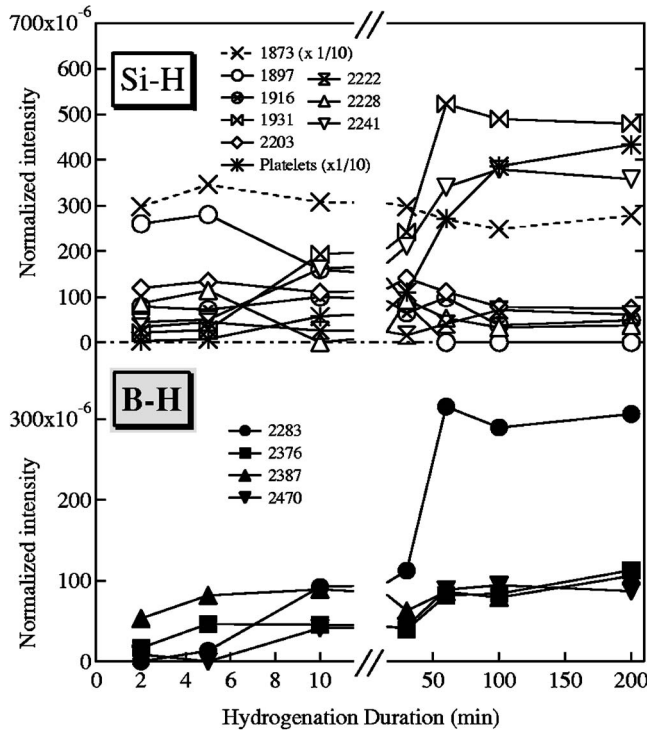


FIG. 8. Dependence of the peak intensities of H-related Raman peaks on the hydrogenation duration. The specimens were implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $5 \times 10^{15} \text{ cm}^{-2}$, followed by hydrogenation at 190 °C.

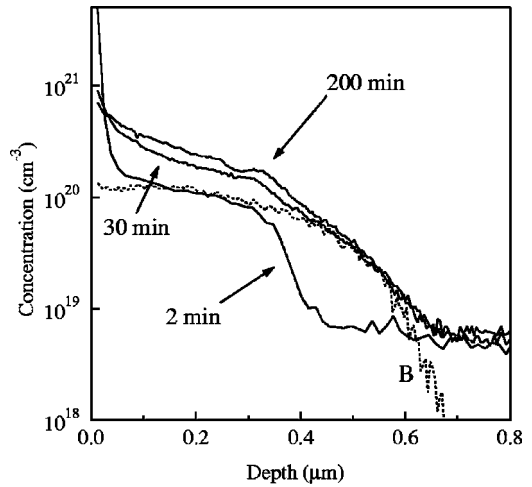


FIG. 9. Depth profiles of the concentrations of B and H introduced into B-doped Si specimens. The depth profile of B was obtained for a Si specimen implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ and annealed at 900 °C. The depth profiles of H were then obtained for B-doped Si hydrogenated at 190 °C.

SIMS measurements were performed to investigate the concentrations of H introduced into specimens for different durations. The results are shown in Fig. 9. The dotted line shows the depth profile of the B concentration in the specimen after activation annealing at 900 °C. In the case of the specimen hydrogenated for 2 min, the depth profile of the H concentration shows a well-defined plateau at B concentrations up to 0.3 μm , then it significantly decreases in the deeper region. The features of the depth profile of the H concentration are in good agreement with earlier SIMS results for B-doped Si.²³ In the case of B-doped Si, positively charged H atoms are effectively trapped by negatively charged B, and therefore the depth profile of the H is similar to that of B.^{7,23} With increasing hydrogenation duration, the concentration of H exceeds that of B by several times. This result suggests the formation of H-related complexes in addition to the H-B passivation center.

D. Resistivity of hydrogenated specimens

In order to investigate the effect of H-related complexes on the B carrier, the resistivities of specimens hydrogenated at different temperatures were measured by four-point probe. The results are shown in Fig. 10. The hydrogenation temperature dependence of the peak intensity of the H-B passivation center, platelets, and B-H complexes (2283 and 2470 cm^{-1}) is also shown in the figure. The increase in resistivity at 120 °C from the value before hydrogenation is due to the passivation of B by H, since the main complex is the H-B passivation center at 120 °C. The passivation efficiency at 120 °C is estimated to be about 45%. The resistivity reaches a maximum between 190 and 220 °C. This increase is mainly due to the promotion of hydrogen passivation of B with increasing concentration of H introduced into the specimens. Subsequently, the resistivity gradually decreases with increasing hydrogenation temperature.

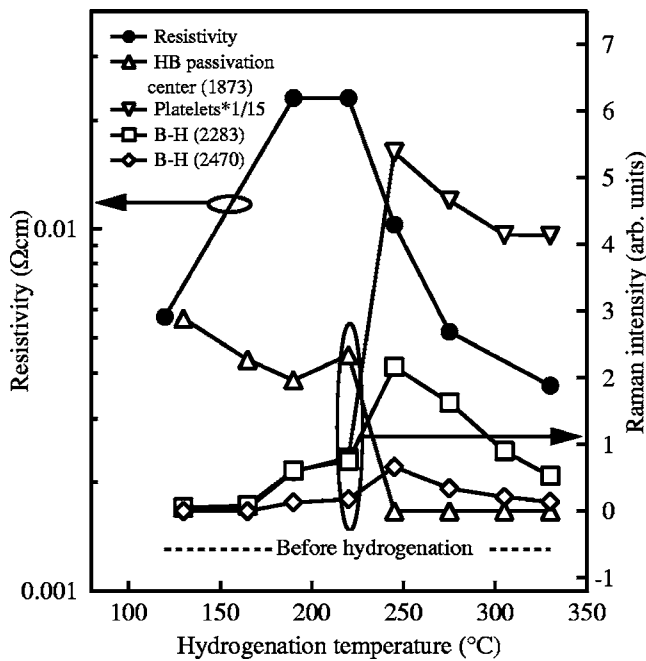


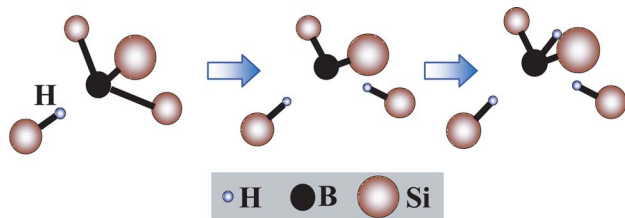
FIG. 10. Dependence of the resistivity of hydrogenated B-doped Si specimens and the peak intensity of the H-B passivation center, platelets, and B-H complexes (2283 and 2470 cm^{-1}) on the hydrogenation temperature. The dotted line shows the resistivity before hydrogenation. The specimens were implanted with 30 keV $^{11}\text{B}^+$ ions at a dose of $1 \times 10^{15} \text{ cm}^{-2}$. Hydrogenation was performed at each temperature shown for 30 min.

IV. DISCUSSION

A. Origin of B-H complexes

In Sec. III, the formation of B-H complexes in which an H atom is directly bonded to a B atom was described on the basis of detailed isotope experiments using both H and B. Here, the origin of the B-H complexes is discussed. Several candidates are considered for the B-H complexes. The first is an H multiple trapping center with a B-H bond, as illustrated in Fig. 11. The second is a complex with B cluster and H atoms. The third is B-H bonds in platelets.

First, we describe the possibility of the first case. The formation of H multiple trapping center without a B-H bond



(a) H-B passivation center (b) Intermediate state (c) B-H complex

FIG. 11. (Color online) Possible model of the B-H complex. In this configuration, the B-H complex is formed via the formation of the H-B passivation center and the subsequent intermediate state. The B-H complex contains three H atoms, one of which bonds to a B atom in the complex.

has already been reported by Korpas *et al.* from a theoretical calculation.¹⁹ In the complex, two H atoms are located at two BC sites between B and the two nearest neighboring Si atoms. The structure is shown in Fig. 11(b) as an intermediate state of the H multiple trapping center with a B-H bond. In their paper, the authors pointed out the possibility of one additional H atom being trapped in the complex, since the B atom is essentially twofold coordinated and carries most (95%) of the odd electrons in the complex. The model in Fig. 11(c) shows a form of the complex with a total of three trapped H atoms. If such a complex with a B-H bond is the origin of the B-H complex, Si-H stretching peaks must be observed in addition to the B-H stretching mode. As already described in Sec. III C, the intensities of the B-H stretching peaks at 2283 and 2470 cm^{-1} showed a similar dependence on the hydrogenation temperature and the duration to those of the Si-H stretching peaks observed at 1931, 2222, and 2241 cm^{-1} . This result suggests that these peaks may be a candidate for the complex shown in Fig. 11(c). The results of the Raman and SIMS measurements shown in Figs. 7–9 also suggest the formation of new complexes with B atoms. The depth profile of the H concentration for the specimen hydrogenated for 2 min shows that B existing up to 0.3 μm is perfectly passivated by H, and some electrically active B exists in the region deeper than 0.3 μm . After hydrogenation for 30 min, the H concentration exceeds the B concentration in the Raman probe region ($\sim 0.5 \mu\text{m}$). The peak intensity of the H-B passivation center, however, does not increase, but rather slightly decreases. This indicates that some H-B passivation centers are transformed into other H-related complexes containing B atoms with increasing H concentration. This result can be interpreted as evidence that H-B passivation centers are transformed into B-H complexes by the reaction of a high concentration of H introduced into the specimens, as shown in Fig. 11.

Next we consider the second case, a B cluster with H atoms. The formation of B clusters in highly B-doped Si is a well-known phenomenon.^{24–26} The characteristics of the B clusters formed by B implantation are as follows. It is known from resistivity and SIMS measurements that B clusters are formed in the case of a doping level of approximately 10^{19} cm^{-3} or more. They are formed by annealing at around 700–790 $^{\circ}\text{C}$ after B implantation. B clusters in specimens doped at a level of less than 10^{20} cm^{-3} have not been detected by high-resolution cross-sectional TEM measurements, suggesting that the clusters only contain a few B atoms. In the case of high B concentration levels such as 10^{21} cm^{-3} , the existence of defects has been observed by TEM measurements.²⁷ The existence of B clusters is observed as an immobile B spike by SIMS measurements, and electrical measurements show that the immobile B spike is electrically inactive. The static B peak is observed to dissolve on a time scale of more than 4 h during annealing at 800 $^{\circ}\text{C}$ after the formation of the B clusters. The doping level of B in this study is in the range for the formation of B clusters, while the annealing temperature for B activation (900 $^{\circ}\text{C}$) is much higher than the formation temperature of B clusters; it is, in fact, in the temperature range at which B clusters dissociate. Indeed, the B profile obtained by SIMS measurements showed no immobile peaks. Based on these

results, the possibility of the second case is considered to be low.

Finally, let us consider the third case, B-H bonds in platelets. As already described, the formation of platelets is enhanced with increasing hydrogenation temperature and duration. The dependence of the formation of platelets on hydrogenation duration is similar to that of the above-mentioned peaks related to the B-H complexes, while that on hydrogenation temperature is different. Hence, the possibility of the third case is rejected for the peaks at 2283 and 2470 cm^{-1} . However, several B-H stretching peaks were observed in addition to the peaks at 2283 and 2470 cm^{-1} in this study. Such peaks can be considered to be candidates for the third case.

B. Effect of H-related complexes on resistivity

The results shown in Fig. 10 demonstrate that H-related complexes affect the resistivity of the specimens. The increase in resistivity is caused by several effects, such as passivation by H, compensation by defects, and a decrease in mobility by scattering due to defects. As already described, the increase in resistivity at 120 °C from the value obtained before hydrogenation is due to the formation of the H-B passivation center, resulting in the H passivation of B. The resistivity was significantly increased by hydrogenation at 190–220 °C, while the peak intensity of the H-B passivation center slightly decreased. On the other hand, the peak intensities of the B-H complexes increased in this temperature range. With regard to the platelets, they were formed from this temperature range and the intensity was significantly increased by hydrogenation at 275 °C. This dependence is quite different from that of the resistivity. Hence, the contribution of the platelets to the resistivity is low in this tem-

perature range. Based on these results, the steep increase in resistivity is due to the formation of the B-H complexes. In the model shown in Fig. 11, the B-H complex is formed via the formation of the H-B passivation center. Consequently, the B acceptor is still passivated by H in the B-H complexes, as seen in the figure.

The resistivity gradually decreased with increasing hydrogenation temperature from 220 °C. The decrease at 245 °C is caused by the decrease in the H-B passivation center. The further decrease in resistivity above 245 °C is mainly due to the decrease in the B-H complexes, since the contribution of the platelets to the resistivity is considered to be low. These results indicate that the increase in resistivity observed in this study is due to the passivation of B acceptors via the formation of the H-B passivation centers and the subsequent B-H complexes, as illustrated in Fig. 11(c); that is, B is also passivated in the B-H complexes by H.

V. CONCLUSION

We performed Raman measurements on B-doped Si with a high concentration of H and observed both H- and B-related peaks. The results of isotope shifts by the replacement of H with D and ^{10}B with ^{11}B clearly confirmed the formation of B-H complexes in which H directly bonds to B in Si. The results of resistivity measurements showed that the B acceptors are passivated via the formation of the B-H complexes, in addition to the well-known H-B passivation center, in B-doped Si.

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