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Structure of the boron-hydrogen complex in crystalline silicon

A. D. Marwick and G. S. Oehrlein
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

N. M. Johnson
Xerox Palo Alto Research Center, Palo Alto, California 94304

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The lattice site occupied by the boron and hydrogen atoms in hydrogenated crystalline silicon is investigated by use of ion channeling and nuclear-reaction analysis. After hydrogenation, boron atoms are found to be displaced from substitutional sites. Analysis of the data indicates that the shift is 0.22 ± 0.04 Å. The hydrogen atoms are found to preferentially occupy the bond-center site. These findings are consistent with a structure for the boron-hydrogen complex in which the hydrogen atom occupies a site between a silicon and a boron atom, while the boron atom relaxes back towards a threefold-coordinated position. The data are compared with recent predictions of the structure of the B-H complex in silicon.

Evidence for the association of hydrogen and boron in crystalline silicon comes from observations of the loss of electrical activity of B in hydrogen-doped silicon[1] and diffusion measurements which show that hydrogen is trapped in regions containing boron.[2] ir absorption data[3] show a line with a frequency close to that of the Si—H bond, and a hydrogen-deuterium isotope shift[2] that is also consistent with Si—H bonding. It has been proposed[3] that these data can be explained by the formation of a B-H pair in which the H essentially satisfies the dangling silicon bond adjacent to a substitutional B atom, while the B becomes threefold coordinated. Further evidence that passivation is accompanied by the formation of B-H pairs is found in the observation[4] that the luminescence signal of excitons bound to B and other acceptors is suppressed by hydrogenation. Total-energy cluster calculations of the structure of the B-H complex have been made by two groups, with differing results. DeLeo and Fowler[5,6] find that the H atom lies near the bond-center site on the line between the B and neighboring Si atom, while the B atom relaxes in the opposite direction, i.e., along a ⟨111⟩ direction, by 0.5 Å. However, another calculation, by Assali and Leite[7,8] predicts that the B atom remains close to a substitutional site while the H occupies an antibonding position between the B atom and the tetrahedral interstitial site. Both these calculations predict an ir absorption mode with a frequency close to that measured by Pankove, Carlson, Berkeyheiser, and Wance,[1] though detailed comparison with the more comprehensive data of Stavola, Pearton, Lopata, and Dautremont-Smith[9] is not yet available. Recently a third structure has been proposed,[10] based on tight-binding calculations, in which the hydrogen atom occupies an antibonding site on one of the *silicon* atoms adjacent to a fourfold coordinated boron. In view of these different calculated structures of the boron hydrogen complex it is clearly desirable to obtain more information on its structure and properties, and that of other dopant-hydrogen complexes.

In this study we were able to make a critical test of the calculated structures by determining the lattice position of the deuterium atom in deuterium-passivated boron-doped silicon, and also to test the quantitative prediction of DeLeo and Fowler of a 0.5-Å shift of the boron atom. The technique we used, lattice location by ion channeling,[11] can discriminate between the different interstitial sites potentially occupied by solute atoms (as previous studies of hydrogen in undoped silicon have shown[12,13]), while also being able to detect small displacements of impurity atoms from substitutional sites as long as they exceed about 0.1 Å. Boron was detected by the B (p,α) ion-induced nuclear reaction,[14] and small displacements of the B atoms off lattice sites in hydrogenated samples were measured from the narrowing of the channeled dip in the nuclear reaction yield. For deuterium atom location the $^{2}\mathrm{H}(^{3}\mathrm{He},\alpha)$ reaction was used.

Samples were prepared by boron implantation and annealing, followed by exposure to atomic hydrogen. Both (100) and (111) wafers were implanted with boron ions to doses in the range $1\text{–}5\times10^{15}$ cm^{-2}, at energies of 30 and 100 keV. Because of considerations outlined later, only data from implants of 10^{15} cm^{-2} at 30 keV into (100) wafers are given here. These samples were annealed at 1000 °C for 30 min. This procedure yielded starting material in which the boron atoms were as nearly fully substitutional as we could measure, and which 1 MeV He channeling showed to be highly crystalline. Angular scans through the ⟨111⟩ and ⟨110⟩ axial channels in this starting material, taken with a 670-keV H^{+} beam, are shown in the upper parts of Figs. 1 and 2. The Si yield in these figures was obtained by integrating the backscattered energy spectrum over the range of energies corresponding to the depths within which most of the boron atoms were contained. Hydrogenation of the samples was performed by exposure to atomic hydrogen or deuterium at a sample temperature of 150 °C. Two different sets of apparatus were used for the hydrogenation. One, in which the source of atomic hydrogen was a remote microwave gas discharge, has been described previously.[15] In the other, samples were placed on a heated platen on the target electrode of a plasma etching system, but were shielded from the plasma. The lattice position of boron has been measured in samples from both sets of equipment, with similar

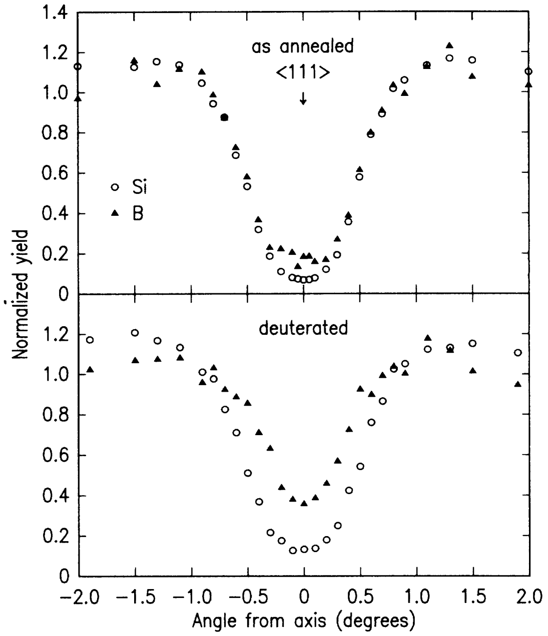

FIG. 1. ⟨111⟩ channeling dips from samples containing implanted boron, with and without exposure to atomic deuterium. The yields of elastically backscattered 670-keV protons from silicon, and of α particles from the B (p,α) nuclear reaction, are plotted. The yields are normalized to a "random" value obtained by averaging over indicence angle. The data show that the B atoms in the hydrogenated material have been displaced slightly from their sites.

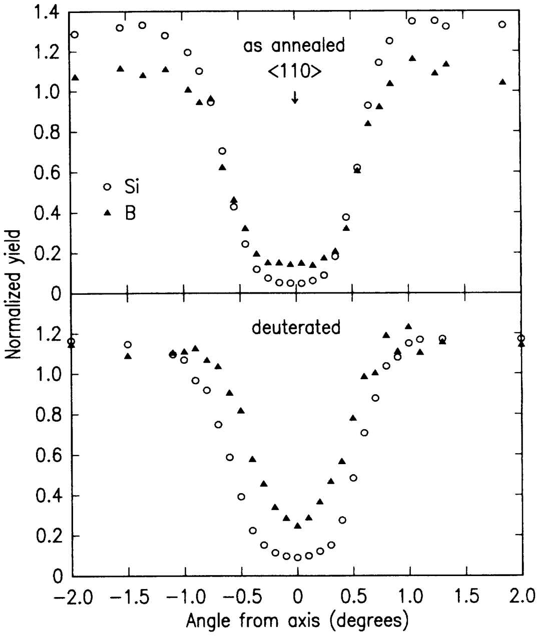

FIG. 2. ⟨110⟩ channeling dips before and after exposure to atomic deuterium. As in the ⟨111⟩ case, boron atoms are slightly displaced from lattice sites by hydrogenation in a deuterium plasma.

results. Deuterium lattice location was done on the samples made with the remote microwave discharge.

Characterization of the samples confirmed that the boron-containing layer was fully doped with hydrogen, and that the electrical passivation of the B atoms was almost complete. Boron and deuterium depth profiles were measured with secondary-ion mass spectroscopy. In agreement with previous work, the hydrogen and boron profiles were found to have a similar shape, with peak concentrations falling at the same depth. However, in samples prepared using the plasma system for hydrogenation the concentration of deuterium was much greater than that of boron, whereas in other work the ^{2}H and B concentrations have been found to be comparable.[2] This discrepancy is consistent with the temperature of the sample in the plasma system being somewhat higher than the nominal value of 150 °C. The ratio of deuterium-to-boron concentration in the samples from this system for which data are reported here was about four. In samples prepared in the remote microwave discharge system the hydrogen concentration in the boron-containing region is comparable with the boron concentration, as reported previously.[2] Electrical passivation of the boron was monitored by the increase in sheet resistance following passivation, which indicated at least 90% passivation. This was confirmed by spreading resistance profiling in selected samples.

Channeling measurements were made to determine the positions in the lattice occupied by the boron and deuterium atoms. For boron atom location we used a 670-keV H$^+$ beam, and for ^{2}H location a 700 or 750-keV ^{3}He beam, collimated in both cases to 0.03°. The reaction products from the respective nuclear reactions were collected in large-area detectors close to the sample, which was mounted on an *XY* stage on a computer-controlled two-axis goniometer accurate to at least 0.02°. The large-area detectors were covered with Mylar to exclude scattered beam ions. A separate collimated detector was used to monitor elastically backscattered ions.

Fladda, Bjorkqvist, Eriksson, and Sigurd[16] have shown that H$^+$ irradiation is itself sufficient to displace B atoms from substitutional sites, and our tests have shown that the ^{2}H atoms are also readily redistributed by the analyzing beam. Great care was taken to minimize these effects in our data. The beam dose to the sample was kept small by taking each point in the angular scans on a fresh spot. Separate scans were made on different areas to locate the B and ^{2}H atoms. In the data reported here the fluence of H$^+$ or ^{3}He$^+$ per point was 6×10^{14} cm^{-2}. The degree to which the analyzing beam disturbed the substitutional boron can be gauged from Figs. 1 and 2, where it can be seen that the minimum yield for B is of order 15%, indicating that a similar proportion of the B atoms in the sample were affected by the probing beam at the dose per point used. The material implanted at 30 keV to 10^{15} cm^{-2} was found to offer the best channeling behavior and thus the greatest sensitivity to B atom displacements induced by hydrogenation. Where the boron implant was made to a dose of 5×10^{15} cm^{-2}, the analyzing beam dose for the same counting statistics was smaller, but the higher-dose implants caused a higher level of residual disorder, and hence poorer channeling. In material implanted to 10^{15} cm^{-2} at 100 keV, the peak boron concentration was lower, and as found by Fladda *et al.*[16] the probability of beam-induced displacement of the B atoms was greater. Thus, best results for B atom location were obtained from samples boron implanted to 10^{15} cm^{-2} and furnace annealed, which were also used for the ^{2}H location runs.

A further check was made to guard against the possibility that B-H pairs were more sensitive than B atoms alone to the damage introduced by the probing beam. In this test 2 cm^2 of a fully passivated sample was uniformly irradiated with a scanned beam of 670-keV protons to the same fluence employed in the channeling analysis, and the sheet resistance of the irradiated area measured. The sheet resistance increased slightly, either because the residue of unpassivated B atoms was affected by the damage, or because ^{2}H atoms from other sites were detrapped and retrapped at unpassivated boron atoms. This result shows that the B-H pairs in the sample were not broken up by the beam to any significant extent.

The results of the channeling analysis for boron atom location (Figs. 1 and 2) show the distinct narrowing of the channeled dip in a boron yield in both the ⟨111⟩ and ⟨110⟩ axial channels after hydrogenation, as also shown by the angular widths at half minimum shown in Table I. In the nonhydrogenated starting material the B and Si dips are almost identical except for the difference in the minimum yield caused by beam-induced displacements of the B atoms, as already discussed. This similarity shows that the B atoms lay in the walls of the channels in substitutional sites. The narrowing of the channeled dip in the B yield following hydrogenation shows that B atoms were made to protrude from the Si rows into the channels. A slight increase in the Si minimum yield showed the presence of a small amount of additional lattice disorder in some hydrogenated samples.

The size of the displacement of the B atoms from lattice sites can be estimated from the data by using calculations of the shape of the channeling dip as a function of the position of the B atom in the lattice. These are most reliably done by Monte Carlo methods, but we have carried out a preliminary analysis of the ⟨111⟩ data using semianalytical methods in the statistical equilibrium approximation[17] to derive the distribution of transverse energies of the channeled ions, with a channel potential obtained from the "standard" row continuum potential[17] and a correction for thermal vibrations of the lattice atoms. The details of the calculation are similar to those described by Matsunami and Itoh.[18] For each angle of incidence of the beam, the distribution of the flux of the channeled ions across the ⟨111⟩ channel was calculated, and convoluted with the solute atom distribution to give the close encounter probability, which is proportional to the measured nuclear reaction yield. For comparison with the experimental data we assumed that the boron atoms were displaced along ⟨111⟩ directions, in accordance with the expected symmetry of the B-H complex, based on the results of the cluster calculations already referred to, and the

TABLE I. Angular widths of channeling dips.

Axis	Condition	Si (deg)	B (deg)
⟨111⟩	As annealed	0.98 ± 0.03	0.99 ± 0.06
	Deuterated[a]	1.04 ± 0.03	0.74 ± 0.06
⟨110⟩	As annealed	1.10 ± 0.03	1.16 ± 0.06
	Deuterated[a]	1.20 ± 0.03	0.84 ± 0.06
	Deuterated[b]	1.10 ± 0.03	0.71 ± 0.06

[a] Plasma system.

[b] Remote microwave discharge.

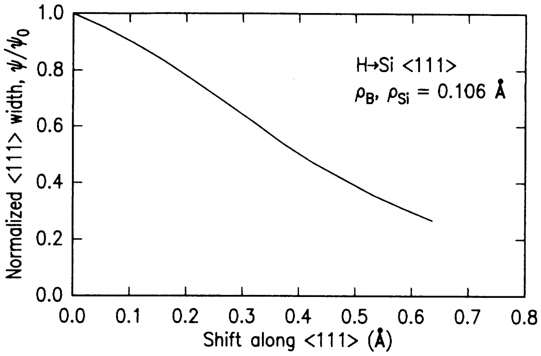

FIG. 3. Narrowing of the angular width of the ⟨111⟩ channeling dip caused by displacements of an impurity atom along a ⟨111⟩ direction. ρ is the thermal vibration amplitude used in the calculation.

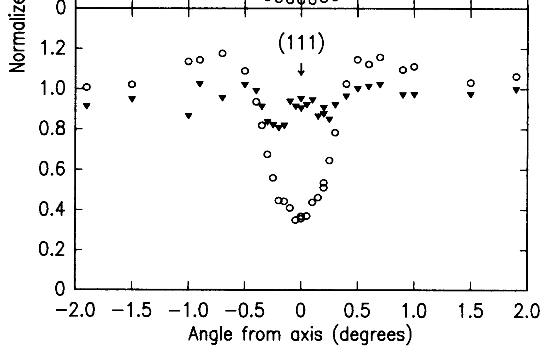

FIG. 4. Angular scans across the ⟨110⟩ axial channel, and the (111) planar channel, taken with a 700-keV ^{3}He$^+$ beam, showing the yield of the ^{2}H(^{3}He,α) nuclear reaction and that of ^{3}He$^+$ ions backscattered from silicon atoms. These data indicate that the bond-center site is preferred by the hydrogen.

finding that the Be-H pair in Ge has a ⟨111⟩ axis of symmetry.[19] Results of these calculations are shown in Fig. 3. Comparison with the experimental data for the ⟨111⟩ given in Table I shows that the B atom shift in the deuterated samples was 0.22 ± 0.04 Å.

Results of the ^{2}H atom location experiments are shown in Fig. 4, in which angular scans across the ⟨110⟩ axis and (111) plane are presented. These measurements were made in a sample from which about 1000 Å had been removed by wet chemical etching. This procedure was designed to remove the near-surface damaged layer[15] which, as secondary-ion mass spectroscopy profiling has shown, contains most of the deuterium initially present in the sample. The etching was found to reduce the deuterium content of the sample to about 40% of that in a control sample, while increasing the amplitude of the channeling dips in the ^{3}H yield. In other samples which had not been etched a similar though smaller improvement in the channeling data was observed on increasing the ^{3}He$^+$-beam energy from 700 to 750 keV in order to use the energy dependence of the nuclear-reaction cross section to discriminate against deuterium near the surface.

The ^{2}H location data in Fig. 4 can be interpreted qualitatively by geometrical considerations, supported by the calculated scans given by Nielsen.[13] The dip in the nuclear reaction yield in the ⟨110⟩ direction rules out the tetrahedral and hexagonal sites for the ^{2}H, since both these sites lie near the center of this channel and would give rise to an increase in yield. However, the dip is consistent with either the bond-center (BC) or the back bonded (Q) site, as ^{2}H atoms at either of these sites would lie near the channel wall. The (111) data allow us to discriminate between the BC and Q sites, and thus between the calculated structures for the boron-hydrogen complex. The BC site lies in the middle of the (111) planar channel, and ^{2}H atoms at this site will give rise to an increase in nuclear reaction yield, due to flux peaking, when the beam is aligned with the channel. This is indeed what is observed in the experimental data, indicating that the bond-center site is preferred by the ^{2}H atoms. Further analysis will determine whether some of the deuterium is at other sites in addition to the BC site.

This investigation has given information on the lattice position of both the boron and deuterium atoms in deuterated boron-doped silicon. The displacement of the boron atoms from their initially substitutional sites lends weight to the view that B-H pairs are indeed formed in passivated material. The ^{2}H site indicated by the data, the bond-center, supports the structure of the complex originally envisaged by Pankove *et al.*[3] and found to be the lowest-energy configuration in the calculations of DeLeo and Fowler,[5,6] i.e., a hydrogen atom on a site between a silicon and a boron atom, with the latter relaxed back along a ⟨111⟩. However, the B atom displacement inferred from our data is smaller than that predicted by DeLeo and Fowler. Our (111) planar channeling data (Fig. 4) rule out proposed structures in which the hydrogen atom occupies a back-bonded site, either on the boron,[7] or on a silicon atom.[10] We plan to undertake more detailed analysis of the data using Monte-Carlo simulation to derive more precise information about the hydrogen atom site. Studies of the interaction of hydrogen with other acceptors are also in progress.

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