Effect of energetic ions on the stability of bond-center hydrogen in silicon

S. V. S. Nageswara Rao,[1] S. K. Dixit,[2,3] G. Lüpke,[4] N. H. Tolk,[1] and L. C. Feldman[1,2,3]
[1]*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*
[2]*Interdisciplinary Materials Science Program, Vanderbilt University, Nashville, Tennessee 37235, USA*
[3]*Vanderbilt Institute of Nanoscale Science and Engineering, Vanderbilt University, Nashville, Tennessee 37235, USA*
[4]*Department of Applied Science, College of William and Mary, Williamsburg, Virginia 23187, USA*
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We report an observation of low-temperature, athermal, ion-induced decay of infrared-active bond-center hydrogen (BCH) in silicon. Specifically, the infrared intensity of BCH is found to decay monotonically as a function of ion dose with a decay constant determined by the electronic energy deposited by each ion. Our data indicate that ion-induced decay of BCH results in a different final configuration when compared to the thermal decay process. These findings provide insight into the structure and stability of hydrogen related defects in silicon, and thus have implications for the reliability of state-of-the-art semiconductor devices, radiation damage, and ion-beam characterization studies of hydrogen containing solids.

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I. INTRODUCTION

It is well known that hydrogen implanted into silicon at low temperatures comes to rest primarily in the bond-center site.[1–9] In addition, with increased temperature, bond-center hydrogen (BCH) is known to decay and form infrared-active Si-H complexes at various defect sites.[6] In this paper, we report an observation of ion-induced decay of bond-center hydrogen in silicon at cryogenic temperatures. The most significant infrared-active configuration formed under the thermal annealing process (the H_2^* dimer) did not form in this ion-induced athermal process. These results suggest that the ion-bombardment-induced decay of BCH proceeds through a distinctly different channel, in contrast to the usual thermal annealing process.

The stability of Si-H bonds under operational conditions is critical for the long-term operation of many semiconductor devices which rely on hydrogen passivation to remove carrier trap states.[10] Nonthermal dissociation of Si-H bonds is known to be responsible for the hot carrier induced deterioration of metal-oxide-semiconductor field-effect transistors[11,12] and the photodegradation of hydrogenated amorphous silicon (*a*-Si:H) solar cells (Staebler-Wronski effect).[13,14] Recent calculations and experiments suggest that BCH plays an important role as an intermediate stage in the photodegradation of *a*-Si:H (Ref. 15) and growth of nanocrystalline Si (Ref. 16). Moreover, BCH is a well characterized defect studied by a large number of experimental[1–7] and theoretical[8,9] methods and is thus a good candidate for further studies associated with new types of BCH-radiation interaction. We present a detailed study on the effects of energetic ions on the stability of BCH in crystalline silicon.

Stein, in his pioneering work,[3] observed an intense-infrared absorption line (1990 cm^{-1} at ~80 K) after proton implantation into Si at 80 K. The complex was found to be stable only below 200 K and was also found to be unstable even at 80 K if illuminated by above bandgap light, indicative of an electron-hole (*e*-*h*) pair interaction with this complex. Neither the dose dependence nor the end-products of this decay process were reported in Ref. 3. Since low-temperature implantation creates a large number of Si vacancies, and based on the similarity of annealing characteristics of the 1990 cm^{-1} line with vacancy annealing, Stein designated the site as a Si-H complex, whose existence depended on the presence of vacancies. In addition, since vacancy concentrations are modified with *e*-*h* creation, the illumination effect on this site was consistent with this assignment. Later, the 1990 cm^{-1} line was reinvestigated by Budde and was shown to be attributable to the positive charge state of bond-center hydrogen ($H^+_{[BC]}$ or BCH) in silicon (1998 cm^{-1} at 10 K), without invoking a role for vacancies.[6]

To our knowledge, there have been no attempts to study the influence of any radiation on the stability of what is now recognized as BCH in silicon. Here, we present a detailed study on the effects of energetic ions on the stability of BCH in crystalline silicon. Important implications of these results to several previous experiments,[5–7] including ion channeling studies of BCH,[4] will be discussed.

II. EXPERIMENT

Silicon samples used in this study were cut from a high resistivity (16–23 kΩ cm), 1.5-mm-thick, double side polished, float-zone Si (100) wafer. Hydrogen implantations and subsequent ion irradiations were performed at 80 K in a specially designed cryostat using a 2 MV Van de Graaff accelerator. Infrared-absorption measurements were performed at ~7 K using a Bruker-IFS 66v Fourier transform infrared spectrometer with a nominal spectral resolution of 2 cm^{-1}. The cryostat could be removed from (and reconnected to) the accelerator beamline for systematic infrared and ion irradiation studies without altering the sample temperature, maintaining a good vacuum.[1] Unless otherwise specifically mentioned, samples were maintained at or below 80 K during the entire experiment. Energetic protons (800, 750, and 700 keV of 7.5×10^{15} H/cm^2 at each energy) were implanted through an 8 μm Al foil into silicon to create BCH sites close to the surface. Figure 1 shows the nominal profile of hydrogen as calculated using a well accepted simulation program SRIM (the stopping and range of ions in matter[17]). 1.8 MeV ^{3}He

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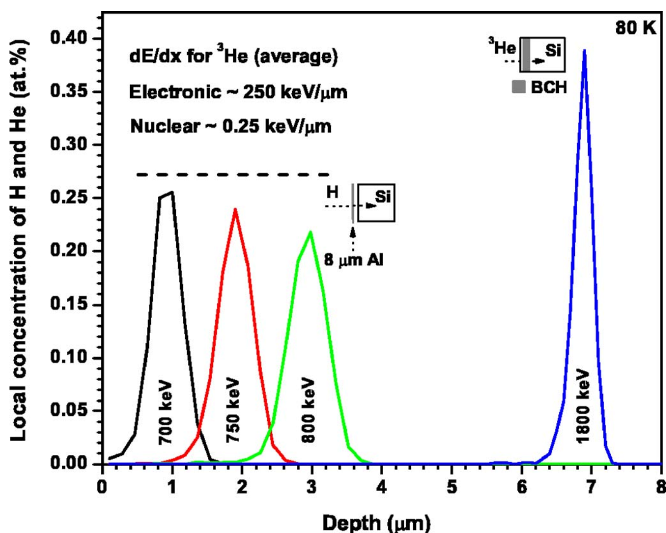
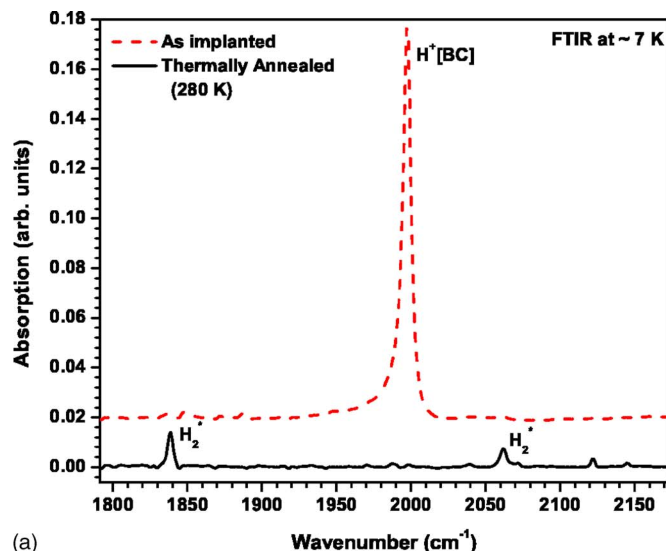


FIG. 1. (Color online) Profiles of implanted hydrogen (BCH) and ^{3}He ions in Si as calculated using SRIM simulations. Also shown are the experimental parameters and conditions along with the average energy loss values of 1.8 MeV ^{3}He ions in the vicinity of BCH.

ions were used to create electronic excitations in the vicinity of the BCH sites. The ^{3}He profile shown in Fig. 1 indicates that the implantation of He ions in the vicinity of the BCH is negligible. The experiment was also repeated using 1.8 MeV ^{4}He instead of ^{3}He, although with a different H profile, in order to study the influence of stopping power. In one of the experiments, 1.5 MeV H was implanted into silicon to study the concentration of BCH as a function of hydrogen dose. Incident ion flux was measured by detecting current ($\sim$200 nA/cm^2 for ^{3}He) directly from the target and the incident power density was kept well below 1 W/cm^2 to minimize heating effects.[5]

III. RESULTS

As shown in Fig. 2(a), low-temperature implantation of protons into silicon results in the appearance of an intense infrared line around 1998 cm^{-1}, which has been assigned by Budde to the positive charge state of bond-center hydrogen.[6] The width of this peak is considerably larger than that of Refs. 1 and 6 because of higher local concentration of BCH which results in local strain. This peak is lost irreversibly upon increasing the sample temperature above 200 K. Concurrently, new infrared lines appear, corresponding to other known H-related defects as shown in Fig. 2(a). A similar sample was prepared and irradiated by ^{3}He ions without warming the sample beyond 80 K to study the effect of ion-beam irradiation on the stability of BCH. Measured changes in the sample temperature during irradiation were never more than 1 K. As shown in Figs. 2(b) and 3, the ^{3}He irradiation causes 95% of the BCH to decay without producing any substantial infrared sensitive peaks in the region of Si-H stretch mode vibrations. We have observed weak peaks corresponding to VH, VH_2, and IH_2 but their intensities are found to be at least an order of magnitude less than those



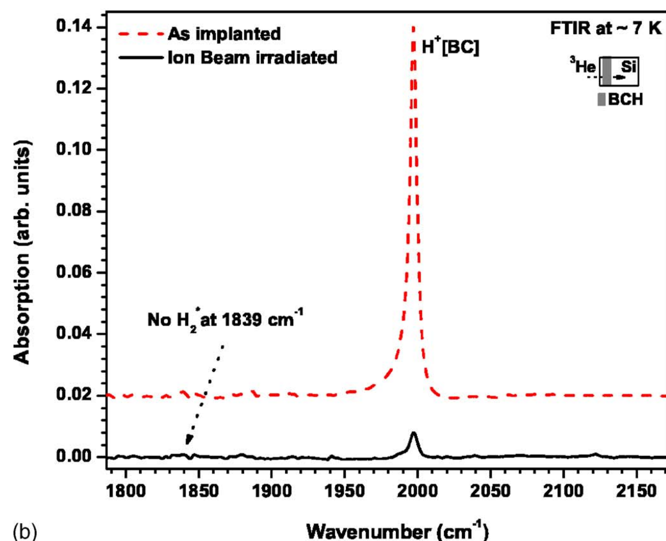


FIG. 2. (Color online) (a) Infrared spectra measured in the region of Si-H stretch mode vibrations immediately after low-temperature implantation of H into Si and after a thermal annealing at 280 K. (b) Infrared spectra measured in the region of Si-H stretch mode vibrations immediately after low-temperature implantation of H into Si and after ion-induced decay of BCH at 80 K. (All spectra were measured at $\sim$7 K. As implanted spectra were displaced by 0.02 arbitrary units on the *y* axis for clarity.)

formed in the thermal process. In particular, we note that this ion-induced decay of BCH, as shown in Fig. 3(a), does not result in the increase of the intensity of 1839 cm^{-1} peak (H_2^*), in marked contrast to the thermally induced decay process. Infrared measurements shown in Fig. 2(a) confirm the fact that the experimental setup is sensitive enough to detect H_2^* and other room-temperature defects. The observation inherently rules out the significance of heating during the irradiation because such heating effects would have produced infrared sensitive H-related defects such as H_2^*. Ion scattering measurements presented in Ref. 4, used to determine the implanted deuterium lattice location, are sensitive to the total amount of D present in the sample and show no

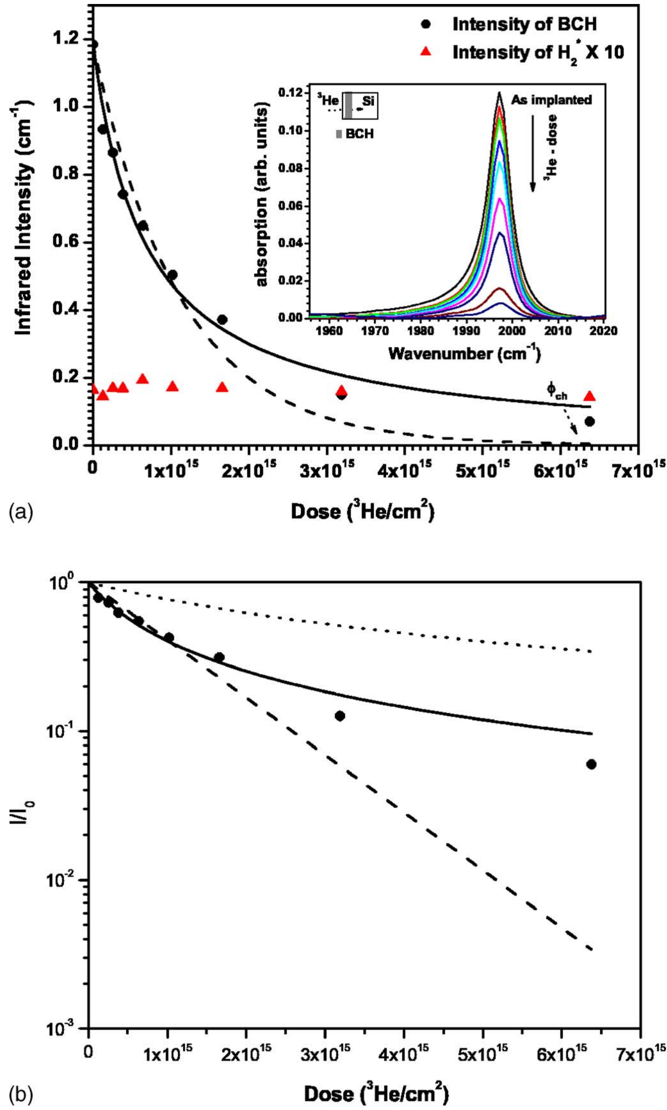


FIG. 3. (Color online) (a) Intensity (I) of 1998 cm^{-1} line as a function of ^{3}He dose showing the ion-induced decay of BCH. The dashed line represents the theoretical fit to Eq. (2) ($I=I_0e^{-k\phi}$) and the solid line represents the theoretical fit to Eq. (4) $[I=I_0/(1+K\phi)]$. The inset shows the individual spectrum measured at each dose value. ($\phi_{ch}\sim 6.25\times 10^{15}$ ^{3}He/cm^2: preirradiation dose used in channeling measurements in Ref. 4.) Also shown is the intensity (multiplied by 10) of 1839 cm^{-1} line of the $H_2{}^*$ dimer as a function of ^{3}He dose showing that the ion-induced decay of BCH does not result in the formation of $H_2{}^*$. (b) Intensity ratio of BCH before and after irradiation (I/I_0) as a function of ^{3}He dose. The dashed line represents the theoretical fit to Eq. (2), the solid line represents the theoretical fit to Eq. (4), and the dotted line is a simulation obtained using Eq. (4) for $K=N_0k^*/5$ to make comparisons with Ref. 4.

significant loss of D from the sample upon ion irradiation. We thus conclude that the physical loss of hydrogen from the sample cannot account for the observed decay of BCH.

An energetic ion passing through any material interacts with the electronic subsystem and the nuclei; the relative probability of these interactions is determined by ion velocity and mass. In Fig. 1 we have shown the calculated (SRIM) values of the average energy loss of 1.8 MeV ^{3}He ions due to electronic and nuclear processes at the depth of the implanted H. Straightforward calculations indicate that only 1% of the Si atoms associated with Si-H-Si centers are expected to be displaced by nuclear scattering. Similarly, the cross section for direct recoil of H from a Si-H-Si bond is also found to be too small to account for the observed loss of BCH. Even if such recoil is produced, it will reimplant at low temperature and thus should not effect the concentration of BCH. The number of vacancies generated while forming BCH by low-temperature implantation of protons in our experiments has been estimated to be ~2 at. % using SRIM calculations. Subsequent ^{3}He irradiation would produce an additional ~0.5 at. % vacancies due to nuclear interactions. As the BCH is stable in the presence of 2 at. % of vacancies, an additional 0.5 at. % is not expected to make it unstable. Hence, it is unlikely that the defect production and displacement damage associated with nuclear energy loss process can account for the ion-induced decay of BCH. So we attribute this effect to the electronic process initiated by energetic ions.

In the first approximation, it is reasonable to assume that the rate of decay of BCH is linearly proportional to the concentration of BCH and the ion dose. Hence,

$$\Delta N_{BC} = -kN_{BC}\Delta\phi, \tag{1}$$

$$\Rightarrow N_{BC} = N_{BC}^0(e^{-k\phi}). \tag{2}$$

Here, N_{BC} is the concentration of BCH at any instant. ΔN_{BC} is the change in N_{BC} due to an incremental ^{3}He dose ($\Delta\phi$). N_{BC}^0 is the initial concentration of BCH obtained by proton implantation (N_{BC} at $\phi=0$). The decay constant k is expected to be a function of electronic energy loss ($[dE/dx]_{\text{ele}}$) of the incident ions. Equation (2) has been verified by measuring the intensity of the 1998 cm^{-1} line as a function of ^{3}He dose and the results are shown in Figs. 3(a) and 3(b). The inset of Fig. 3(a) shows that the peak position of 1998 cm^{-1} line does not change with irradiation dose, indicating that the sample temperature is the same for all measurements. As shown in Fig. 3(a) (dashed line), Eq. (2) provides a reasonable fit to the experimental data. However, we note that the data can be more appropriately characterized by a second-order process, described by the following equation, in which the rate of decay of BCH is proportional to N_{BC}^2 and the ion dose:

$$\Delta N_{BC} = -k^* N_{BC}^2 \Delta\phi, \tag{3}$$

$$\Rightarrow N_{BC} = \frac{N_{BC}^0}{1+K\phi}, \tag{4}$$

where the decay constant $K(=k^*N_{BC}^0)$ is the product of k^* and N_{BC}^0. The solid lines in Figs. 3(a) and 3(b) represent fits of Eq. (4) to the experimental data. Clearly, the ion-induced decay of BCH is dominated by the second-order process. A similar second-order analysis was reported earlier for the isothermal annealing decay of BCH in Si measured by electron paramagnetic resonance,[5] although without mentioning a specific reason for choosing second-order decay. The N_{BC}^2 dependence in Eq. (3) suggests a mechanism in which the observed decay process is governed by the formation of H_2

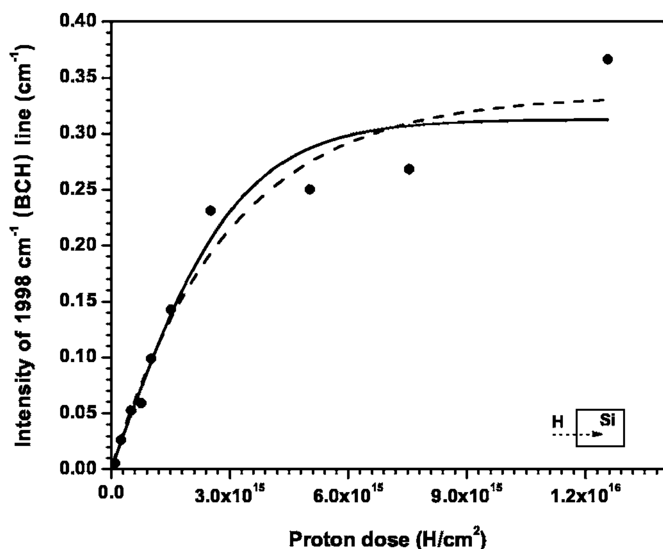


FIG. 4. Intensity of 1998 cm^{-1} line as a function of proton dose showing that the intensity is not a linear function of proton dose. The dashed line is the fit to Eq. (6) and the solid line is the fit to Eq. (8) (fitted to $I=AN_{BC}$ instead of N_{BC}, where the constant A should represent the infrared cross section of $H^{+}{}_{[BC]}$).

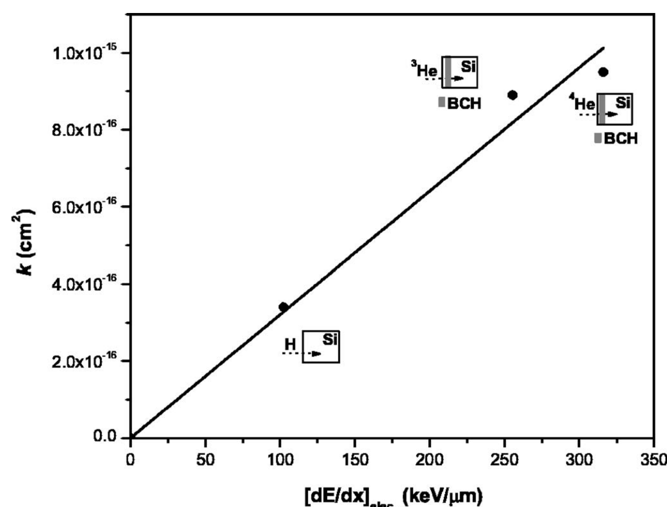


FIG. 5. Rate of decay of BCH (k) as a function of $[dE/dx]_{\rm ele}$ obtained from three different experiments.

molecules. This could be a result of a release of a single H as stimulated by ion bombardment, which then pairs with an existing BCH. The significance of the dotted line shown in Fig. 3(b) will be described in the next section. We found that a similar analysis is also applicable for ^{4}He induced decay of BCH in Si.

Since it is apparent that an energetic ion can stimulate the decay of BCH, it is important to calculate the significance of such effects due to the initial implantation of protons used for creating BCH itself. Figure 4 shows the intensity of the 1998 cm^{-1} line as a function of incident proton dose. The intensity is not a simple linear function of dose. The data shown in Fig. 4 can also be explained by the concepts developed in the previous discussion. We assume that the rate of increase of BCH is proportional to proton dose modified by the subtraction of the ion-induced decay factor defined earlier.

In the case of exponential process,

$$\Delta N_{BC} = \Delta\phi - kN_{BC}\Delta\phi, \tag{5}$$

$$\Rightarrow N_{BC} = \frac{1}{k}(1 - e^{-k\phi}). \tag{6}$$

In the case of second-order process,

$$\Delta N_{BC} = \Delta\phi - k^{*}N_{BC}^{2}\Delta\phi, \tag{7}$$

$$\Rightarrow N_{BC} = \frac{1}{\sqrt{k^{*}}}\frac{1 - e^{-2\sqrt{k^{*}}\phi}}{1 + e^{-2\sqrt{k^{*}}\phi}}. \tag{8}$$

As shown in Fig. 4, both Eqs. (6) and (8) provide reasonable fits to the experimental data, indicating that the ion-induced effects play a prominent role in this case. Finally in Fig. 5, we have plotted the rate of loss of BCH (k) obtained in all three experiments as a function of the electronic energy loss of the corresponding ion beam. Figure 5 indicates that the rate of loss of BCH is directly proportional to $[dE/dx]_{\rm ele}$, suggesting that the electronic excitations triggered by the ion beams are responsible for the observed effects.

IV. DISCUSSION

These results contribute much to the understanding of the stability of BCH as discussed below.

A. Dissociation mechanisms

There are at least three possible mechanisms that can cause the dissociation of hydrogen bonds during the bombardment of energetic ions.

(1) *Electron-hole pairs.* Stein found a 75% reduction in intensity of the 1990 cm^{-1} infrared-absorption peak, now associated with BCH in Si, after 1 h exposure to 1 W filtered output ($E_{\rm photon} \leqslant 3.9$ eV) from a xenon lamp at 80 K.[3] As the probability for direct bond breaking by nonresonant low-energy photons is vanishingly small, the observed illumination effect is likely to be governed by electron-hole pair relaxation processes. Earlier experiments have shown that *e-h* pairs can enhance the low-temperature diffusion of intrinsic defects and impurities in silicon.[5–7,18–21] Hence, it is reasonable to expect a similar effect arising from electron-hole pairs generated by energetic ions, either through a direct effect on the BCH or through the enhanced motion of intrinsic defects.

(2) *Ionization.* Direct breaking of Si-H bonds, either by energetic ions or by secondary electrons generated by ions, can cause the observed decay of BCH.

(3) *Vibrational excitation.* Dissociation of Si-H bonds can be due to vibrational excitation by secondary electrons. A specific example of such phenomenon is the work of Chevallier *et al.*,[22] who attribute the difference in the stability of H/D bonding (within GaAs) to their different response to vibrational excitation caused by secondary electrons created

with UV excitation. Another example of vibrational excitation leading to site instability is the recent resonant desorption measurements of H from Si-H surface bonds using free-electron laser irradiation.[23]

All these three processes can certainly contribute to bond breaking, although the final site of hydrogen cannot be readily predicted.

B. Formation of H_2^*

The new athermal dissociation of BCH does not result in the formation of H_2^* dimer. Budde *et al.*[24] indicated that the most efficient way of forming H_2^* is low-temperature proton implantation combined with thermal annealing rather than a direct room-temperature implantation. Calculations of Estreicher *et al.*[25] indicate that the presence of native defects is required for the formation of H_2^* dimer. This implies that both the presence of native defects and their kinetics are important in trapping hydrogen for forming H_2^* complex. Therefore, we suggest that the lack of H_2^* in this athermal process is due to the poor mobility of defects and host atoms at low temperature. Furthermore, the intrinsic defects produced by initial proton implantation are expected to be annealed out during the subsequent ^{3}He ion irradiation due to ion-beam annealing effects observed in previous channeling measurements.[4,21] Defects produced by ^{3}He ion irradiation are spatially separated from the region of hydrogen. Thus, this reduced concentration of defects in the vicinity of hydrogen may also be a possible reason for not forming the H_2^* defect.

C. Implications for earlier lattice location experiments

Ion irradiation effects on bond-center deuterium were observed in the early channeling lattice location work of Nielsen.[4] In that study, the author observed changes in the lattice location of deuterium as a function of the dose of the probing beam (^{3}He). In order to overcome this problem, samples were preirradiated with ^{3}He ions in a channeling direction at 30 K until the results were independent of the bombardment dose. These *in situ* channeling measurements determined that 80% of low-temperature implanted deuterium is close to the BC sites, in fact, displaced by 0.3 ± 0.1 Å from the BC site. The remaining 20% is close to tetrahedral sites, displaced by 0.1 ± 0.1 Å from the tetrahedral site. It must be noted that our present study reports a decrease in the infrared intensity of $H^+_{[BC]}$ as a function of ion dose. Therefore, it is important to review the correlation between infrared and channeling data presented in Ref. 4. The observed decay in Fig. 3(a) indicates that the preirradiation dose ($\phi_{ch}\sim6.25\times10^{15}$ ^{3}He/cm^2) used in the above mentioned lattice location work is sufficient to cause essentially the complete decay of 1998 cm^{-1} line at 80 K when starting with a hydrogen concentration (BCH) of about 0.25 at. % ($N^0_{BC}\sim0.25$ at. %).

The efficiency of the second-order process [Eq. (4)] depends on the value of N^0_{BC}, which is about five times larger in our experiment than that of Ref. 4. The dotted line in Fig. 3(b), obtained for $K=k^*N^0_{BC}/5$, predicts 65% reduction of $H^+_{[BC]}$ for the preirradiation dose used in the channeling measurements.[4] Thus, our results indicate substantial loss of BCH due to ^{3}He irradiation.

Several isotope dependence studies reported lower dissociation rates for Si-D bonds when compared to Si-H bonds in a variety of configurations and is attributed to the difference in their vibrational properties.[11,13] Although the specific isotope dependence for the dissociation of BCH is not known, it may be important to consider this effect in comparing our results with the channeling study. However, this isotope effect is applicable only if the decay process is governed by the vibrational excitation, which is one of the three possible mechanisms proposed here. Hence, it is not clear whether the lattice location determined in Ref. 4 represents an infrared-active bond-center deuterium or not. Here, it is essential to underline the fact that the lattice location determined in Ref. 4, which has been generally attributed in the literature to BCH,[6–8] was determined after significant ion-beam effects as noted by the authors.

D. Charge state effects

Earlier experiments showed that the presence of *e*-*h* pairs or minority carriers can decrease the activation energy for the thermal dissociation of BCH by altering its charge state (from $H^+_{[BC]}$ to $H^0_{[BC]}$).[5–7] The BCH center was found to decay at lower temperatures ($\sim$160 K) if illuminated by above bandgap light as compared to its normal annealing temperature ($\sim$200 K).[5,7] These studies indicate a possible influence of *e*-*h* pairs on the charge state and the activation energy for decay of bond-center hydrogen. However, the influence of *e*-*h* pairs on the stability of BCH at or below 80 K is not revealed in these experiments. It is important to note that the $H^+_{[BC]}$ can be recovered by removing *e*-*h* pairs from the vicinity of $H^0_{[BC]}$.[5–7] The influence of *e*-*h* pairs on the charge state of BCH may be one of the possible mechanisms for the observed phenomenon.

E. Influence of initial concentration of BCH (N^0_{BC})

Previous experiments, mentioned above, did not report the permanent loss of BCH under the influence of *e*-*h* pairs or minority carriers, in contradiction with Stein's observation[3] of photoinduced irreversible loss of 1990 cm^{-1} line at 80 K. We have verified Stein's result by subjecting one of our samples (Si:BCH) to 890 nm light from a Ti:sapphire laser. 4 h ($\sim$0.3 W/cm^2) of laser illumination at 80 K resulted in a 67% irreversible loss of BCH in Si.

This apparent inconsistency between experiments can be explained in the second-order approximation [Eqs. (3) and (4)]. As discussed earlier, it is known that the presence of *e*-*h* pairs or injected minority carriers can convert $H^+_{[BC]}$ into $H^0_{[BC]}$. Here, we propose that this $H^0_{[BC]}$, under the influence of ion or laser irradiation, may readily hop between BC sites. This is a reasonable assumption because hydrogen diffusion theory predicts that the lowest-energy path for the migration of hydrogen in silicon is mediated through BC sites.[8,12] $H^0_{[BC]}$ relaxes back to $H^+_{[BC]}$ whenever the continuous sup-

ply of carriers is interrupted. This does not result in any net change in the concentration of bond-center hydrogen because the hydrogen is hopping only between BC sites. However, under the ion or *e-h* pair enhanced hopping, if a hydrogen atom encounters another hydrogen atom then they may form a H_2 molecule, resulting in the permanent loss of two BCH centers. The probability of forming such a molecule over a given time (or for a given ion dose) strongly depends on the concentration of BCH itself. The N^2 dependence shown in Figs. 3(a) and 2(b) is in support of this argument. Hence, it is clear that the efficiency of a second-order phenomena depends on the initial concentration of BCH [i.e., N_{BC}^0 in Eq. (4)], which is a few orders of magnitude larger in Stein's experiments,[3] Nielsen's experiments,[4] and our present experiments when compared to that of Refs. 5–7.

Our experiments indicate that the hydrogen released from BCH sites forms a complex whose infrared activity is too weak to be detected in our present experiment. Diatomic molecular hydrogen, a weak infrared-sensitive configuration known to exist in Si,[26] is one of the possible candidate configurations. Ion-induced hopping of H between BC sites can result in the formation of such H_2 molecules and thereby the observed loss of BCH.

V. CONCLUSION

We have reported an observation of low-temperature ion-induced decay of BCH in silicon. The observed phenomenon associated with electronic excitations caused by energetic ions is found to be distinctly different as compared to thermal processes. These results provide important insights into the effects of carrier-enhanced dissociation mechanisms, which is essential for semiconductor science and technology. We have also shown that ion beams can modify the bonding configuration and thereby the structure of the H-containing materials even though they may not affect the total H concentration.

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