

## Hydrogen Motion in Defect Complexes: Reorientation Kinetics of the B-H Complex in Silicon

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The motion of hydrogen in the B-H complex in silicon has been studied. An applied stress is used to produce a preferential alignment of the B-H complex at temperatures sufficiently high for the H to move within the complex (above  $\sim 60$  K). This alignment of the complexes is detected by comparing the optical-absorption strengths of the H stretching vibration for light polarized parallel and perpendicular to the stress axis. From the kinetics of the decay of alignment after the stress is removed we show that the motion of H from bond-centered site to bond-centered site around the B atom is thermally activated with an activation energy of 0.19 eV.

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Defect complexes in semiconductors that contain hydrogen have been studied extensively.<sup>1</sup> One of the primary interests has concerned the possible motion of the light hydrogen atom in the complex.<sup>2</sup> In some complexes the H is static,<sup>3</sup> in others tunneling motions have been reported,<sup>4,5</sup> and in some cases the nature of the motion is controversial.<sup>6</sup> An impediment to understanding why some hydrogen-containing complexes are static while others are dynamic is that in previous studies the structures of the complexes and hence the atomistic nature of the H motions are unknown. The structure of the B-H complex in Si has been widely debated and has become the best understood among H-containing complexes in semiconductors because of several theoretical<sup>7-11</sup> and experimental studies.<sup>12-14</sup> Here we use a classic technique for measuring the kinetics of defect motion, the relaxation of stress-induced dichroism,<sup>15</sup> to observe the motion of H in the B-H complex and thereby to provide an atomistically well understood case of H motion in a semiconductor defect complex.

Most studies agree that H occupies a bond-centered (bc) site between the boron atom and one of its Si neighbors in the B-H complex.<sup>7,8,10-13</sup> There are four such sites that are crystallographically equivalent. Recently, Denteneer *et al.*,<sup>11</sup> in their *ab initio* calculations, have found that there is a path in which the hydrogen can move about the B from bc site to bc site, with a small activation energy. The bc configuration and the H motion of interest here are shown in Fig. 1.

The H stretching vibrations of the acceptor-H complexes have been studied by infrared-absorption<sup>16</sup> and Raman spectroscopy.<sup>17</sup> The longitudinal H stretching mode of the B-H complex, which we use as a probe of the center's orientation here, lies at  $1903\text{ cm}^{-1}$  at low temperature. This band was the subject of previous uniaxial stress measurements<sup>18</sup> made near 10 K where the H is static. The static properties of the complex under stress complement the current study of the center's dynamics.

Infrared-absorption experiments on B-H complexes re-

quire samples with thin, heavily doped surface layers because the amount of silicon that can be passivated is limited by the diffusion depth of hydrogen at temperatures near  $150^\circ\text{C}$  where the B-H complex becomes unstable. The samples for our experiments were prepared from floating zone silicon that had been ion implanted with B at energies of 30, 100, and 180 keV, each to a dose of  $7 \times 10^{14}\text{ cm}^{-2}$ . The implants were activated by a rapid thermal anneal at  $1200^\circ\text{C}$  for 60 sec. Oriented, bar-shaped samples with dimensions  $2 \times 2 \times 8\text{ mm}^3$  were prepared for stress studies. These samples were then hydrogenated in a Technics Planar Etch II plasma reactor at  $120^\circ\text{C}$  for 6 h.

The infrared absorption was measured with a Nicolet 60SX Fourier-transform spectrometer equipped with a TGS detector. The incident light was polarized with a wire grid polarizer on a KRS-5 substrate. Our apparatus for applying uniaxial stress at low temperatures consists of a push-rod system that is cooled by an Air Products continuous flow cryostat. Force was applied to the push rod by a pneumatic cylinder. This apparatus has been used in many studies and is known to produce a

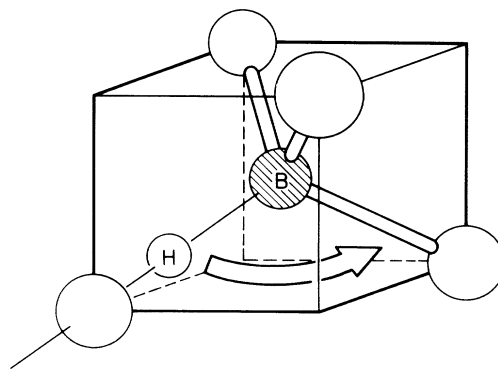


FIG. 1. The bond-centered configuration for the B-H complex in silicon. The hydrogen jump from one bond-centered site to another is shown.

homogeneous, well calibrated uniaxial stress. The temperature of the sample was measured with a Chromel-Au:0.07-at%-Fe thermocouple that was bonded to the sample with silver epoxy.

In Fig. 2 we show the absorption band due to the longitudinal H stretching vibration of the B-H complex, measured near 10 K following different prestressing treatments. For these experiments a stress of  $30 \text{ kg/mm}^2$  ( $2.9 \times 10^8 \text{ N/m}^2$ ) was applied along the directions indicated while the sample was cooled from room temperature to low temperature. At 10 K the stress was removed and absorption spectra for light polarized parallel and perpendicular to the stress direction were measured. In the absence of a prestressing treatment the absorption is isotropic as is shown by the dashed lines in Fig. 2(a). When stress is applied at temperatures where the hydrogen can move from bc site to bc site the hydrogen will preferentially occupy the sites with lowest energy. Upon lowering the temperature further, the preferential alignment of the hydrogen is frozen in and remains when the stress is removed. (The kinetic studies described below show that the complex is static at low temperature.) Because the transition moment of the longitudinal stretching vibration is oriented along the defect axis, the preferential occupation gives rise to the large optical dichroism (difference in the absorption for light polarized parallel and perpendicular to the applied stress) shown for the  $1903\text{-cm}^{-1}$  band after a [110] stressing treatment.

The orientation dependence of the stress alignment effect is consistent with the trigonal symmetry of the B-H complex that has been determined previously in uniaxial stress experiments,<sup>18</sup> channeling experiments,<sup>12,13</sup> and several calculations.<sup>7-11</sup> Stress along the [110] direction

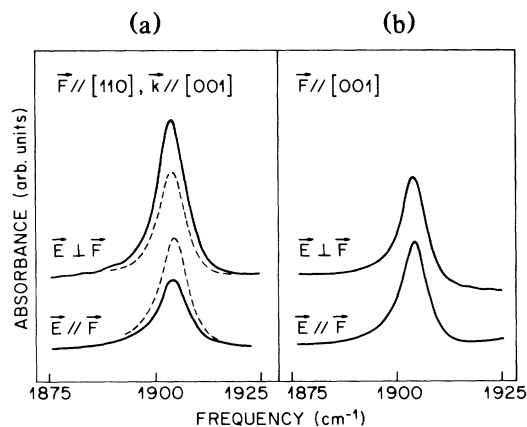


FIG. 2. The H stretching band for the B-H complex measured at 10 K. The spectra were measured subsequent to a prestressing treatment with the stress orientation shown. A stress of  $30 \text{ kg/mm}^2$  was applied at room temperature and maintained while the sample was cooled to 10 K. The spectra were then recorded at 0 stress. [The dashed spectra shown in (a) were recorded for an unstressed sample.]

lifts the orientational degeneracy of the four bc sites about the boron atom and leads to the large dichroism shown in Fig. 2. (While not shown, a [111] stress also makes the four bc sites inequivalent and leads to a dichroism of the expected magnitude.) No alignment of the hydrogen in the complex is observed for a [001] stress direction because all the trigonal [111] axes (which the bc sites are along) are at the same angle to the stress axis and hence remain equivalent. Note that the sites perpendicular to the stress are preferentially occupied (the absorption strength for  $\mathbf{E} \perp \mathbf{F}$  increases upon stressing) as is consistent with the expectation that applied stress will raise the energy of the crowded bc configuration. We find  $n_{\parallel}/n_{\perp} = 0.35$  for a [110] stress of  $38 \text{ kg/mm}^2$  at 77 K and a [001] viewing direction.

To determine the kinetics of the hydrogen motion from bc to bc site adjacent to the B we measure the decay of the stress-induced dichroism at several temperatures. For these experiments we apply a [110] stress at an elevated temperature (77 K) to align the B-H centers and then cool to the measurement temperature with the stress maintained. The stress is released and  $\alpha_{\perp}$  and  $\alpha_{\parallel}$  are measured as functions of time at fixed temperature. As the hydrogen redistributes, the difference between  $\alpha_{\perp}$  and  $\alpha_{\parallel}$  disappears. In Fig. 3 the logarithm of the dichroic ratio  $\mathcal{D} \equiv (\alpha_{\perp} - \alpha_{\parallel})/(\alpha_{\perp} + \alpha_{\parallel})$  is plotted as a function of time for several temperatures.

The rate of change of the occupation  $n_i$  of a specific bc site adjacent to the boron is written as follows for site 1:

$$\frac{dn_1}{dt} = \frac{1}{\tau} [-3n_1 + (n_2 + n_3 + n_4)]. \quad (1)$$

Similar expressions can be written for sites 2, 3, and 4. Here  $\tau$  is the time constant for a single H jump from one bc site to another. For a [110] stress direction and a [001] viewing direction one has

$$\mathcal{D} = (n_1 + n_3 - n_2 - n_4)/(n_1 + n_2 + n_3 + n_4), \quad (2)$$

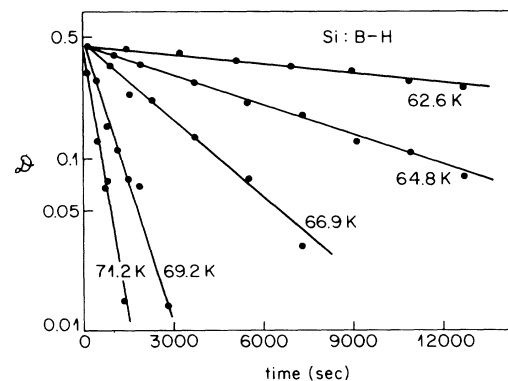


FIG. 3. The decay of the stress-induced dichroism  $\mathcal{D} \equiv (\alpha_{\perp} - \alpha_{\parallel})/(\alpha_{\perp} + \alpha_{\parallel})$  in the  $1903\text{-cm}^{-1}$  band of the B-H complex.

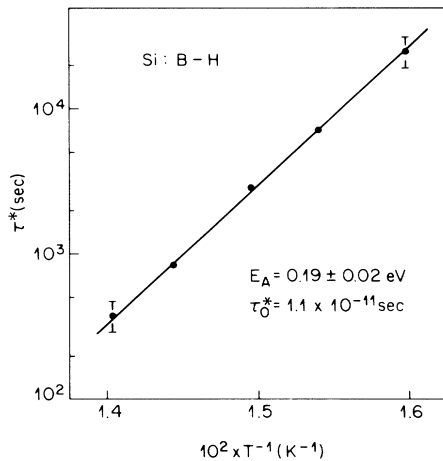


FIG. 4. The time constant for the decay of the stress-induced dichroism vs reciprocal temperature. The activation energy and prefactor corresponding to the solid line are as shown.

where sites 1 and 3 are along  $[11\bar{1}]$  and  $[\bar{1}\bar{1}1]$  axes and sites 2 and 4 are along  $[111]$  and  $[\bar{1}\bar{1}\bar{1}]$  axes. From these expressions it is straightforward to show that

$$\frac{d\mathcal{D}}{dt} = -\frac{4}{\tau} \mathcal{D}. \quad (3)$$

Hence, the time constant for the decay of the dichroism,  $\tau^*$ , which is determined from the slope of one of the lines in Fig. 3, is related to the time constant for a single jump by  $\tau^* = \tau/4$ . To determine the activation energy for H motion we plot  $\ln \tau^*$  vs  $T^{-1}$  in Fig. 4. From our fit to the data we obtain a time constant for a single H jump of

$$\tau = (4.4 \times 10^{-11} \text{ sec}) \exp[(0.19 \pm 0.02 \text{ eV})/kT]. \quad (4)$$

Denteneer *et al.*<sup>11</sup> have calculated an activation energy of 0.2 eV for the motion of H from bc site to bc site in the B-H complex. The agreement with our data is striking.

The prefactor here is the reciprocal of a vibrational attempt frequency and is smaller than expected for a thermally activated jump. (The attempt frequency is expected to be roughly a typical phonon frequency, i.e.,  $10^{13} \text{ sec}^{-1}$ .) However, the relevant frequency for jumping from bc site to bc site is probably the transverse H vibrational frequency which is thought to be small for acceptor-H complexes<sup>16</sup> (of order  $100 \text{ cm}^{-1}$ ) as compared to the longitudinal H stretching frequency of  $1903 \text{ cm}^{-1}$ . While such an argument can explain the small prefactor we qualify these remarks by noting that the prefactor is not well determined by our experiment because it varies greatly for small changes in the activation energy.

We have made measurements for the B-D complex

that are similar to what has been described above for B-H. The motion of D in the complex is also thermally activated with approximately the same activation energy for the decay of the stress-induced dichroism that we observed for H motion above. However, the absolute jump rate is slightly larger for D motion (a factor of roughly 1.5) rather than smaller as we had expected. At present we speculate that interactions between centers may be affecting our measured rates for the high density of centers used in our experiments and that the absolute jump rate might depend on details of the sample fabrication. We are checking this idea and other possibilities in our current work.

We emphasize that the hydrogen moves from bc site to bc site about the boron by thermally activated jumps and that tunneling motions are not involved in our experiments. At 62.6 K, the lowest temperature for which we have measured a time constant for a single H jump, we have found  $\tau = 10^5 \text{ sec}$ . This implies a very small tunneling splitting ( $< 10^{-19} \text{ eV}$ ). We recall that the tunneling splitting was of order 1 meV in the work of Muro and SiEVERS<sup>5</sup> on Be-H complexes where a tunneling model was invoked. What the difference between the Be-H and B-H complexes might be to explain the dramatically different behaviors of the hydrogen migration in the complexes remains an interesting open question.

In summary, we have measured the rate of H motion from bc site to bc site about the B atom in the B-H complex in silicon by a stress-induced optical dichroism technique. The measured thermal activation energy for this H motion is 0.19 eV and is in strikingly good agreement with the theoretically calculated barrier between bc sites of 0.2 eV determined by Denteneer *et al.*<sup>11</sup> This excellent agreement between theory and experiment removes any remaining doubt<sup>9,14</sup> about the correctness of the bond-centered configuration for the complex. Observations of *structurally well understood* H motions like those described here are essential to help further our understanding of the dynamics of H-related complexes. The technique used here can also be used to help understand the possible motions of H in other defect complexes in semiconductors.

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