Non-Arrhenius Reorientation Kinetics for the B-H Complex in Si: Evidence for Thermally Assisted Tunneling

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(Received 27 July 1994)

The B-H complex in Si can be aligned by stress and reorients with an activation energy of roughly 0.2 eV. We combine new measurements of the reorientation kinetics of the B-H complex made by the stress-induced dichroism technique with previous internal friction results to show that the reorientation kinetics are non-Arrhenius. These results support Stoneham's suggestion [Phys. Rev. Lett. **63**, 1027 (1989)] that reorientation occurs by thermally assisted tunneling. We have also discovered the remarkable fact that the reorientation rate for B-D is greater than that of B-H for $T > 57$ K.

PACS numbers: 61.72.Ji, 78.30.Hv, 78.50.Ge

The thermally activated reorientation of acceptor-hydrogen complexes in semiconductors is well known [1–8]. The activation energies for reorientation are typically a few tenths of an eV. The best studied example is the B-H complex in Si for which the reorientation kinetics have been studied by stress-induced dichroism [1] at low temperature (≈65 K) and internal friction [7,8] at high temperature (≈130 K). Adiabatic total energy surfaces have been calculated theoretically for the B-H complex [9], and the agreement of the measured activation energy for reorientation with the calculated barrier height is excellent.

In spite of what appears to be good agreement between experiment and theory, Stoneham [10,11] has suggested that the reorientation of the acceptor-H complexes is by a thermally assisted tunneling mechanism and that a model in which the hydrogen jumps over a barrier is inappropriate. This is well known to be the case for hydrogen diffusion in metals [12] and has been studied for many years. One of the classic signatures of quantum diffusive motion of light interstitials in metals is non-Arrhenius hopping kinetics. Here, by combining new stress-induced dichroism data with previous results obtained by internal friction [7,8], we show for the first time that the reorientation kinetics of the B-H complex are non-Arrhenius and thereby provide experimental support for a tunneling mechanism for reorientation. Further, the reorientation kinetics of the B-H and B-D complexes *have been measured together in the same samples* to convincingly show that the activation energies for reorientation are different and that the reorientation rate of the B-D complex is faster than that of B-H above 57 K.

The samples for most of 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 7×10^{14} cm^{-2}. The implants were activated by a rapid thermal anneal at 1200 °C for 60 s. Oriented bar-shaped samples with dimensions $2 \times 2 \times 9$ mm^3 were prepared for stress studies. Both hydrogen and deuterium were introduced into each sample at 120 °C in a Technics Planar Etch II plasma reactor. In order to check that our results were independent of the sample fabrication procedure and doping level, stress samples were also prepared with a lower implantation dose, i.e., 2×10^{14} cm^{-2} at 30, 100, and 180 keV, and from bulk-doped material with $[\mathrm{B}] = 2 \times 10^{17}$ cm^{-3}. In the latter case, hydrogen was introduced by annealing the samples at 1250 °C in a sealed ampoule that contained 0.66 atm of hydrogen gas [13,14].

Infrared absorption measurements were made with a Bomem DA3.16 Fourier transform spectrometer. Stress was applied with a push-rod system that was cooled in an Oxford Instruments CF1204 cryostat. The stress apparatus and sample were cooled by He contact gas to insure temperature uniformity. The sample temperature was measured with a Chromel–Au:0.07-at. %-Fe thermocouple that was attached directly to the sample. The calibration of the thermocouple was checked in liquid N_2 for each sample measured.

It is well known that the B-H and B-D complexes in Si have trigonal symmetry and hence four crystallographically equivalent orientations [15]. A uniaxial stress, applied along a ⟨110⟩ or ⟨111⟩ direction, for example, makes the different orientations inequivalent. At elevated temperatures (≳60 K) the B-H and B-D complexes can reorient and will be preferentially aligned by an applied stress [1]. In the inset of Fig. 1 we show the absorption bands due to the H and D stretching vibrations of the B-H and B-D complexes that were measured at 65 K with polarized light for a sample that contained both centers. Prior to these measurements, a stress of 450 MPa had been applied along the [110] direction while the sample was cooled from room temperature to 65 K. Immediately after the stress was removed, absorption spectra were measured with light polarized parallel and perpendicular to the stress direction. The inequivalence of the populations of different orientations induced by the applied stress causes the differences in the absorption of light polarized parallel and perpendicular to the stress direction shown in Fig. 1. (At 65 K the stress-induced alignment did not

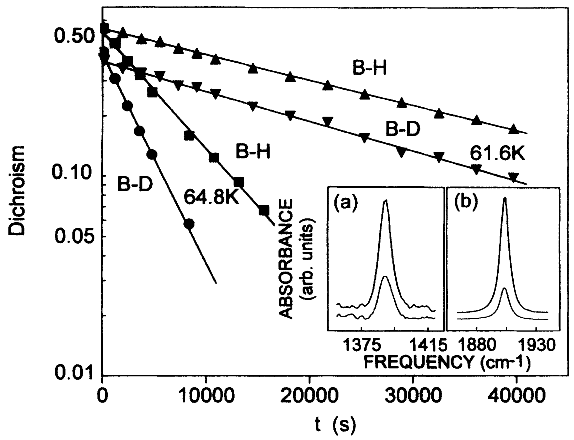

FIG. 1. Decay of the stress-induced dichroism for the 1903 cm^{-1} band of the B-H complex and for the 1390 cm^{-1} band of the B-D complex. Polarized absorption spectra for the (a) B-D and (b) B-H complexes are shown in the insets.

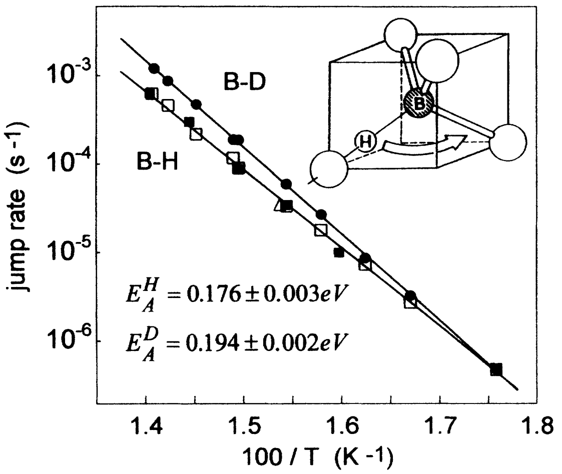

FIG. 2. Hydrogen and deuterium jump rates vs T^{-1} for the B-H and B-D complexes. Activation energies that correspond to the solid lines are shown. The open boxes and filled circles are the jump rates for H and D, respectively, that were measured for B implanted samples in the present work. The filled squares are the previous data of Stavola *et al.* (Ref. [1]). The open triangle is the jump rate for a sample that contained B-H complexes throughout its bulk. The heights of the open boxes correspond to the uncertainty in the measured rates. In the inset, the H jump from one bond-centered site to another is shown for the B-H complex.

have sufficient time to decay appreciably while the absorption measurements were made.) A convenient measure of the stress-induced anisotropy in the vibrational absorption bands is the dichroism which is defined as $D \equiv (\alpha_\perp - \alpha_{//})/(\alpha_\perp + \alpha_{//})$. Here, the α are the absorption coefficients measured at the peaks of the H and D stretching bands.

To determine the reorientation kinetics of the B-H and B-D complexes, we have measured the kinetics for the decay of the stress-induced dichroism. The stress was released and absorption spectra were measured with polarized light as a function of time at several fixed temperatures. In Fig. 1, $\ln D$ vs t is plotted for the B-H and B-D absorption bands for two different temperatures. The dichroism disappears as the B-H and B-D complexes redistribute among their equivalent orientations in the absence of applied stress. It is straightforward to show that the decay of the dichroism is described by

$$\frac{dD}{dt} = -4kD\,, \tag{1}$$

where k is rate of hydrogen (or deuterium) jumps from one bond-centered site adjacent to the B to another specific site (see the inset in Fig. 2). Hence, the slope of a plot of $\ln D$ vs t is $4k$. Plots of $\ln k$ vs T^{-1} for the B-H and B-D complexes are shown in Fig. 2 for the temperature range $56.9 < T < 71.1$ K. The jump-rate date measured previously by Stavola *et al.* [1] are also shown in Fig. 2. Our new data are in agreement with the previous results and extend their range to rates that are a factor of 20 slower [16]. In this temperature range the H and D jump rates are fit extremely well by the Arrhenius expressions,

$$k_\mathrm{H} = (1.87 \times 10^9\ \mathrm{s}^{-1})\exp[(-0.176 \pm 0.003\ \mathrm{eV})/kT]\,, \tag{2a}$$

and

$$k_\mathrm{D} = (7.58 \times 10^{10}\ \mathrm{s}^{-1})\exp[(-0.194 \pm 0.002\ \mathrm{eV})/kT]\,. \tag{2b}$$

Only our new data points were used for these fits. The errors in the activation energies are the standard deviations for the fits shown in Fig. 2.

It is surprising that the reorientation rate for the B-D complex is greater than that for B-H for temperatures greater than 57 K. We are confident in this result, because the reorientation rates for B-H and B-D were measured together in the same samples. Several different kinds of samples were used and precautions were taken to eliminate experimental artifacts. Seven of the data points shown in Fig. 2 were for samples that had been implanted with a B dose of $7 \times 10^{14}\ \mathrm{cm}^{-2}$ at each energy. Two data points were measured for a sample that had received a lower B implantation dose, i.e., $2 \times 10^{14}\ \mathrm{cm}^{-2}$ for each energy. The data point shown by an open triangle in Fig. 2 was for a bulk-doped sample into which H was diffused at high temperature. The rates we have measured are well described by Eqs. (2a) and (2b), independent of the different sample preparation conditions. Finally, we had measured the reorientation rate at several temperatures for one sample and then turned it by 180° to insure that the reorientation rate for centers in the implanted layer on the side of the sample facing the spectrometer's globar source was not affected by the spectrometer light. Again the results were well described by Eqs. (2a) and (2b).

The reorientation of the B-H complex in Si has been measured by internal friction experiments at higher temperatures (~120–150 K) by two groups. Berry and Pritchert [7] have reported an activation energy of 0.226 eV, and Cannelli *et al.* [8] have reported an activation energy of 0.22 ± 0.01 eV. The reorientation rates measured by these two groups only differ by 20%. In Fig. 3 the reorientation rates measured by Cannelli *et al.* [8] are plotted together with our new stress-induced dichroism results. These data span over 11 decades.

An extrapolation of the internal friction results of either group to 70 K gives a reorientation rate that is in good agreement with the reorientation rates measured at the highest temperatures by stress-induced dichroism. The dashed line shown in Fig. 3 is the result of a fit to the internal friction data and the two points measured at highest temperature by stress-induced dichroism (71.1 and 70.3 K). This line corresponds to the following Arrhenius relationship [17]:

$$k_H = 4.06 \times 10^{12}\ \mathrm{s}^{-1} \exp[(-0.223 \pm 0.006\ \mathrm{eV})/kT]. \tag{3}$$

A comparison of the activation energies in Eq. (2a) and Eq. (3) shows that the reorientation rates measured for the B-H complex by internal friction and stress-induced dichroism cannot be described by a single Arrhenius expression. The reorientation rate measured by stress-induced dichroism at 56.9 K is greater than that calculated from Eq. (3) by a factor of 6.7, whereas the relative error in the experimentally measured rate should be less than ±15%.

A reorientation mechanism that involves jumps over a barrier would yield a single activation energy and cannot explain the observed deviation from Arrhenius behavior. Thus we consider Stoneham's suggestion [10,11] that reorientation occurs by a thermally assisted tunneling mechanism. A reduction in the activation energy at lower temperature for reorientation of the B-H complex and an exponential prefactor [$1.87 \times 10^9\ \mathrm{s}^{-1}$ in Eq. (2a)] that is much smaller than a typical phonon frequency is very similar to what has been observed for hydrogen diffusion in metals where tunneling is believed to play an important role [11,12].

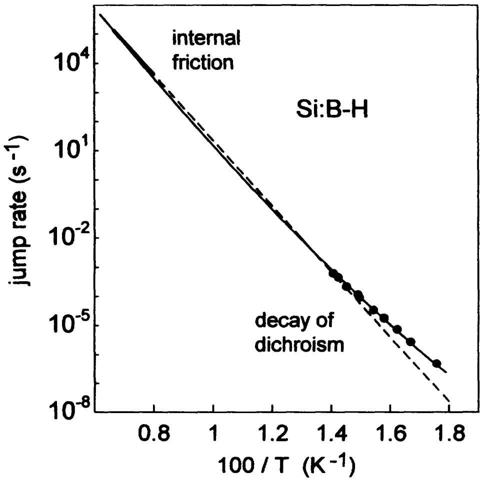

FIG. 3. Hydrogen jump rate vs T^{-1} for the B-H complex. The filled circles are the rates measured in the present work. The thick solid line corresponds to the jump rates measured by Cannelli *et al.* (Ref. [8]). The heights of the filled circles on this plot are twice our estimate of the uncertainty in the measured jump rate.

A theory for the quantum diffusive motion of light interstitials in solids was developed by Flynn and Stoneham [18]. In this model, there is a self-trapping distortion that localizes the light interstitial at a specific lattice site and, because neighboring sites are inequivalent, prevents simple tunneling (i.e., tunneling that is not thermally activated). Thermal fluctuations give rise to a coincidence geometry in which tunneling from site to site can occur. In this theory the jump rate depends on three parameters, the thermal energy E_A to access the coincidence geometry, a tunneling matrix element J, and the Debye temperature θ_D. Numerical integration is required to apply the Flynn-Stoneham theory [19] to the reorientation rate data measured for the B-H complex in Si. A fit of the theory to the data was accomplished by allowing variations in E_A and θ_D, and then by calculating J to fit the internal friction result at 150 K (Ref. [20]). Our best fit, shown by the solid line in Fig. 3, was obtained for $E_A = 0.267$ eV, $J = 56$ meV, and $\theta_D = 187$ K. The Flynn-Stoneham theory reproduces the curvature in the Arrhenius plot of the reorientation data reasonably well. The similarity pointed out by Stoneham [10,11] of the reorientation kinetics for B-H in Si to the reorientation of OH and NH in Nb (Refs. [21] and [22]) is striking. For these centers in Nb, the reorientation kinetics are non-Arrhenius and the jump rates are described well by the Flynn-Stoneham theory with parameters that are very close to those determined for Si:B-H here. For example, for Nb:OH, $E_A = 0.207$ eV, $\theta_D = 257$ K, and $J = 111$ meV (Ref. [22]).

The fit by the Flynn-Stoneham theory [18,19], shown in Fig. 3, is suggestive but does not prove that this is the best model for the reorientation process. We are aware that the theory of hydrogen diffusion in metals is highly developed [12] and also that other models will produce non-Arrhenius behavior. For example, the reorientation of nitrogen in diamond was explained by a model in which tunneling from one orientation to another occurs in vibrational excited states that are thermally populated [23]. The physical appeal of the Flynn-Stoneham theory is the important role played by the lattice distortion caused by the light interstitial. It is well known that hydrogen in a bond-centered configuration induces a large outward relaxation of its heavier neighbors that will inhibit simple tunneling.

At first sight, our result that the reorientation rate for the B-D complex is greater than for B-H would appear to contradict a tunneling mechanism for the reorientation. However, if we extrapolate to temperatures lower than

57 K, then k_H will become greater than k_D as is expected for a tunneling mechanism. The larger activation energy for B-D reorientation is expected for thermally assisted tunneling, because the decrease in slope of the Arrhenius plot should occur at lower T for the heavier isotope. At present we only have speculative ideas about why the B-D complex reorients more quickly than B-H for $T > 57$ K. One possibility is that the larger zero point amplitude of the longitudinal H-stretching vibration for the B-H complex causes there to be a larger outward relaxation of the H atom's B and Si neighbors than for the B-D complex and that this affects the reorientation rates. An explanation of this surprising reverse isotope effect observed for the reorientation rates remains as a challenge. A study of the B-D complex by internal friction should shed more light on this problem.

In conclusion, we have shown that the reorientation kinetics of the B-H complex in Si are non-Arrhenius which strongly suggests that the motion of H in the acceptor-H complexes occurs by thermally assisted tunneling and is similar to the quantum diffusive motion of H in metals. The hydrogen in a few centers in semiconductors has been known to undergo simple tunneling [24,25], and muons have been shown to tunnel in semiconductors [26]. Our new results show how the reorientation of the acceptor-H complexes fit into this picture. Further, we note that the diffusion of isolated hydrogen in semiconductors has been more difficult to study than the motion of H in the acceptor-hydrogen complexes. The mechanism for diffusion for the charge states for which isolated hydrogen has a bond-centered configuration (for example, H^+ and H^0 in Si) is likely to be similar to the mechanism for reorientational motion of the acceptor-H complexes, because the minimum energy position of the H atom and the calculated energy surfaces [27] are qualitatively similar.

We acknowledge G. D. Watkins, W. B. Fowler, and J. P. Huennekens for helpful discussions. We also thank Su Yue for his assistance with the numerical integrations and S. J. Pearton and J. Lopata for their help with the fabrication of the stress samples that were used in a prior study of the reorientation of the B-H complex and that have proved useful again here. This work was supported by NSF Grant No. 9023419.

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[17] To estimate the error in the activation energy in Eq. (3) we have taken the relative errors in the rates measured by stress-induced dichroism at 71 K and by internal friction at 125 K to be ±20%. The activation energy that corresponds to the steepest line that can be drawn between these data points within the error bars is 0.229 eV.

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