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Electronically controlled motion of hydrogen in silicon

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We report on the quantitative study of charge-state-dependent local motion of hydrogen around carbon in Si, which was directly probed by measuring the recovery of stress-induced alignment of a hydrogen-carbon complex by means of deep-level transient spectroscopy under uniaxial stress. We have found that hydrogen jumps from a bond-centered site between C and Si atoms to another with an activation energy of 1.33 eV and a frequency factor of $7.1\times10^{14}\ \mathrm{s}^{-1}$ in the electron-empty charge state while hydrogen jumps much faster in the electron-occupied charge state with a lower activation energy of 0.55 eV and a smaller frequency factor of $3.3\times10^{6}\ \mathrm{s}^{-1}$. We have concluded that the hydrogen-carbon complex captures an electron from the conduction band at its gap state with antibonding character, lowering the barrier and frequency factor for hydrogen motion in the electron-occupied charge state.

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Hydrogen is the lightest element and rapidly moves. Its quantum mechanical motion such as tunneling and zero-point motion is also expected at low temperatures. The motion of hydrogen has received great attention in various fields of solid-state physics and physical chemistry because it affects the properties, phase transitions and chemical reactions of a variety of matter, especially hydrogen-bonded matter, to induce interesting phenomena.[1–8] These examples indicate that the hydrogen motion induces the changes of electronic states of physical, chemical and biological systems and affects their properties and reactions, and also suggest that the changes of electronic states of a proton and neighbors induce the motion of a proton.

The static properties of hydrogen in semiconductors, such as electronic state, stable lattice location, and configuration, have extensively been studied, but only a little information has been obtained on the dynamic properties of hydrogen. The charge-state-dependent motion of hydrogen in Si was observed for the $E3'$ deep-level transient spectroscopy (DLTS) center[9,10] and the AA9 EPR center,[11] both of which were ascribed to isolated hydrogen located at the bond-centered (BC) site between two Si atoms. In these centers, hydrogen moves faster in the electron-occupied charge state than in the electron-empty one. Hydrogen is so mobile and reactive that it is easily trapped by defects and impurities especially at low temperatures. The local motion of such bound hydrogen has been studied by some groups. The dynamical tunneling motion of proton was observed in a few systems, H-Si in Ge (Ref. 12) and H-Be in Si.[13] Such motion alters the multiplicity and symmetry of the electronic ground state. On the other hand, the hydrogen motion around boron in Si is not pure tunneling but thermally assisted tunneling,[14] in which thermal fluctuations induce the coincidence configuration where hydrogen has the same energy for both initial and final sites and can tunnel.[15] Recently, the signatures of electronically controlled motion of hydrogen around carbon in Si have been found.[16–20] The hydrogen-carbon (H-C) complex where hydrogen was located at the BC site between C and Si atoms was observed by DLTS to act as an electron trap with a level at E_c-0.15 eV. In both processes of the dissociation of the H-C complex[16–18] and its stress-induced alignment and subsequent recovery after removing the stress,[19,20] hydrogen was observed to move faster in the electron-occupied charge state than in the electron-empty one. Thus, the above two kinds of hydrogen systems, isolated hydrogen, and hydrogen bound by carbon in Si, have the common features that hydrogen energetically occupies the BC site in electron-empty and electron-occupied charge states and moves faster in the electron-occupied state. Quantitative experimental studies are necessary for the deep understanding of the mechanism by comparing experiments with theoretical work.

In this report, we describe the quantitative study of electronically controlled motion of hydrogen in the neighborhood of a carbon impurity in Si, and demonstrate the unique effects of electronic states of hydrogen and its surroundings on the local motion of hydrogen, which was directly probed by measuring the recovery of stress-induced alignment of the H-C complex by means of DLTS under uniaxial stress. We have found that there are large differences in activation energy and frequency factor for hydrogen motion around carbon between the electron-occupied and electron-empty charge states of the H-C complex. We discuss the origin of such remarkable effects of the charge state.

We used an FZ grown *n*-type silicon crystal with a phosphorus density of $1.7\times10^{14}\ \mathrm{cm}^{-3}$. The oxygen and carbon densities were less than 1×10^{16} and about $1\times10^{16}\ \mathrm{cm}^{-3}$, respectively. Samples were cut into a square pillar with dimensions of $1\times1\times6\ \mathrm{mm}^3$, the longest of which was parallel to $\langle 100\rangle$, $\langle 110\rangle$, or $\langle 111\rangle$ directions. Hydrogen or deuterium injection was performed by chemical etching at 20 °C for 5 min. Capacitance DLTS measurements were performed typically at a rate window of $114\ \mathrm{s}^{-1}$. Uniaxial compressive stresses up to 1.2 GPa were applied to the samples along their longest dimension during DLTS measurements and annealing experiments for stress-induced alignment. We applied reverse bias voltage (V_R) to the Schottky junction to control the charge state of the H-C complex during the annealing. Other details were the same as published previously.[17–20]

Our previous experiments showed that the DLTS peak of the H-C complex split into two under $\langle 111\rangle$ and $\langle 110\rangle$

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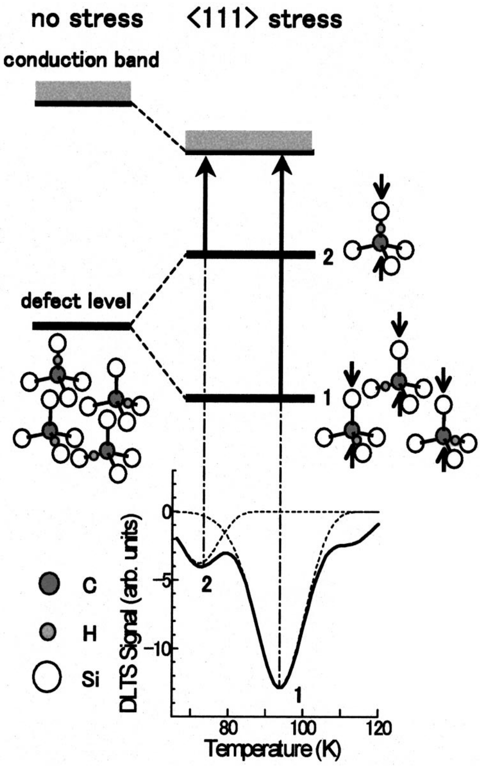

FIG. 1. A typical spectrum recorded under a ⟨111⟩ stress of 1 GPa and its interpretation from the viewpoint of the lift of orientational degeneracy of the H-C complex under the stress. A solid curve represents the experimental data and two dotted curves represent the fitting of two split peaks, labeled as 1 and 2. An unidentified peak around 115 K is not related to the complex. Vertical arrows represent the thermal emission of a trapped electron from the defect level to the conduction band, producing the DLTS peaks.

stresses with intensity ratios of 1:3 and 1:1, respectively, which were the ratios of the low temperature peak to the high temperature peak.[19] We observed no splitting under ⟨100⟩ stress. Such peak splitting is due to the lift of orientational degeneracy of the complex. The observed intensity ratios suggest the C_{3v} symmetry of the H-C complex, and are consistent with a structural model where a hydrogen atom occupies the BC site between C and Si atoms. This model is also consistent with the results of recent theoretical calculations.[21–23] A comprehensive illustration explaining the above description is shown in Fig. 1, where the intensity ratios of 1:3 clearly indicates that compressive stress raises the energy of the gap state of the complex, suggesting its antibonding character.

In Fig. 1, if the temperature is high enough for hydrogen to move, the high-energy configuration with the level 2 is expected to change into the low-energy configuration with the level 1 by a hydrogen jump, making the DLTS spectrum have a single peak (peak 1). This is called stress-induced alignment. When the applied stress is subsequently removed, the four configurations of the H-C complex become energetically equivalent. This drives the complex to take four configurations with the same probability through the random jumps of hydrogen, causing the recovery of stress-induced alignment. Such stress-induced alignment along ⟨111⟩ and ⟨110⟩ stresses and subsequent recovery were actually observed in our previous experiments,[20] where the effect of the isotopic substitution of deuterium for hydrogen on the recovery rate proved that the recovery of stress-induced alignment was certainly due to hydrogen motion.

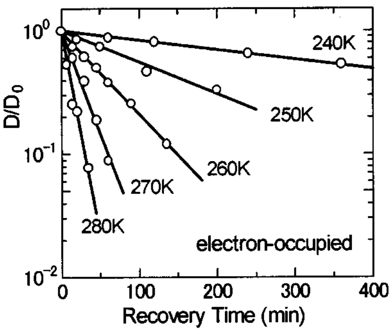

FIG. 2. The recovery of ⟨110⟩-stress-induced alignment due to isothermal annealing with $V_R = 0$ V to make approximately 2% of H-C complexes in the electron-occupied charge state at temperatures of 240–280 K. The ordinate represents normalized degree of alignment D/D_0, which is defined in the text.

We have performed a series of isothermal annealing experiments to obtain quantitative results of the recovery of ⟨110⟩-stress-induced alignment of the H-C complex. Figure 2 shows the results of experiments performed at temperatures of 240–280 K under neither reverse bias nor stress for the recovery of stress-induced alignment. Under this bias condition, approximately 2% of H-C complexes were in the electron-occupied charge state at temperatures of 240–280 K. The ordinate represents normalized degree of alignment D/D_0. Here, D is defined as

$$D = (N_1 - N_2)/(N_1 + N_2), \tag{1}$$

where N_1 and N_2 are the densities of H-C complexes with configurations corresponding to high- and low-temperature DLTS peaks under ⟨110⟩ stress, respectively, and are proportional to the signal intensities of respective DLTS peaks. D_0 is the initial value of D. If all of the H-C complexes are aligned in the low-energy state responsible for the high-temperature peak, D is equal to unity, and when the recovery is completely finished, D reaches zero.

We consider random jumps of hydrogen among four energetically equivalent BC sites adjacent the carbon atom. If we define n_1, n_2, n_3, and n_4 as the densities of hydrogen atoms occupying the four BC sites, then the rate equation describing the time variation of n_1 is written as

$$dn_1/dt = k(-3n_1 + n_2 + n_3 + n_4), \tag{2}$$

where k is the jump rate of hydrogen (or deuterium). Similar equations also hold for the time variations of n_2, n_3, and n_4. If we apply ⟨110⟩ stress perpendicular to the C-H-Si bonds with densities n_3 and n_4, the energy of these bonds becomes lower than that of the C-H-Si bonds with densities n_1 and n_2. This results in that $N_1 = n_3 + n_4$ and $N_2 = n_1 + n_2$, and therefore

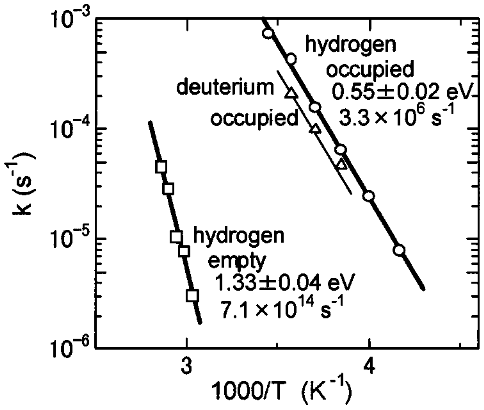

FIG. 3. Arrhenius plots of k for hydrogen in the electron-occupied (circles) and electron-empty (squares) charge states and for deuterium in the electron-occupied charge state (triangles). The activation energies and frequency factors determined by the fitting for hydrogen motion are indicated beside thick solid lines. A thin solid line represents a fitting with an activation energy fixed to 0.55 eV for deuterium motion, giving a smaller frequency factor by a factor of 0.6 than that for hydrogen motion.

$$dD/dt = -4kD. \tag{3}$$

The total densities N_1+N_2 of split DLTS peaks of the H-C complex remained constant with only a few percent of variation during the annealing. This means that hydrogen (or deuterium) jumped from one BC site to another without little dissociation of the complex. When we applied a reverse bias of 7 V to the Schottky junction to make the charge state of the complex completely electron empty, the recovery of alignment was remarkably slowed down, so that much higher recovery temperatures were necessary. At such high temperatures (330–350 K), considerable parts (6–36 %) of the complexes were dissociated during the recovery of alignment. However, the dissociation reduced both N_1 and N_2 by the same factor, and therefore did not affect D. Since the slope of a respective line in Fig. 3 is $4k$, we can make the Arrhenius plot of k for hydrogen motion in the electron-occupied charge state, as shown by circles in Fig. 3. Here, other two Arrhenius plots are shown for hydrogen motion in the electron-empty charge state (squares) and for deuterium motion in the electron-occupied charge state (triangles). A remarkable feature is that the activation energy and frequency factor for hydrogen motion is greatly reduced by changing the charge state of the H-C complex from electron-empty to electron-occupied states.

A likely mechanism of such charge-state-dependent motion of hydrogen is proposed and discussed below. In the electron-empty charge state, the magnitude of a frequency factor (7.1×10^{14} s^{-1}) is consistent with the usual atomic jump frequency. The activation energy, 1.33 eV, is much higher than those (0.43–0.44 eV) of both local motion[11] and long-range diffusion[9] of isolated hydrogen in Si. The difference, 0.9 eV, may arise from the binding energy between hydrogen and carbon. In other words, there is a higher energy barrier for hydrogen motion in the C-H-Si system than in the Si-H-Si one. If the H-C complex captures an electron from the conduction band at its gap state with antibonding character, the complex raises its electronic energy by the energy difference between bonding and antibonding states, typically 1 eV and more. On the other hand, in both of C-H-Si and Si-H-Si systems, hydrogen may feel similar potentials at the saddle points between adjacent BC sites, because hydrogen is located apart from C and Si atoms. Therefore, the electron capture considerably lowers the energy barrier for hydrogen motion in the electron-occupied charge state. The captured electron lies in the gap state with the antibonding character, which makes the C and Si atoms relaxed outward to lower the energies of the C-H-Si system. When hydrogen reaches the saddle point, all atoms around it are appropriately relaxed to lower the energy of the saddle-point configuration, further reducing the energy barrier. In this way, hydrogen motion is limited by the electron capture and subsequent slow atomic relaxation. In other words, hydrogen waits for the events of electron capture to jump more quickly. The capture rate c of an electron from the conduction band is described by

$$c = n\sigma v_{\mathrm{th}}, \tag{4}$$

where n is the electron density, σ is the cross section of electron capture, and v_{th} is the thermal velocity of an electron. Based on their numerical values ($n = 1.7\times10^{14}$ cm^{-3}, $\sigma = 5\times10^{-16}$ cm^2, $v_{\mathrm{th}} = 2\times10^7$ cm/s) determined under the experimental conditions, we can obtain an estimate for the capture rate as 2×10^6 s^{-1}, which is quite consistent with the magnitude of the frequency factor for hydrogen motion in the electron-occupied charge state.

In conclusion, we have reported on the quantitative study of the charge-state-dependent local motion of hydrogen around carbon in Si, which was directly probed by measuring the recovery of stress-induced alignment of the H-C complex by means of DLTS under uniaxial stress. We have found that there are large differences in activation energy and frequency factor for hydrogen motion between the electron-occupied and electron-empty states of the H-C complex. We have concluded that the H-C complex captures an electron from the conduction band at the gap state and raises its electronic energy to lower the barrier for hydrogen motion in the electron-occupied charge state. Thus, the hydrogen motion is limited by the electron capture, explaining a very low frequency factor. The present work presents a typical example of electronically controlled motion of hydrogen in the neighborhood of an impurity in semiconductors, and demonstrates the unique effects of electronic states of hydrogen and its surroundings on the local motion of hydrogen.

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