Inverted Order of Acceptor and Donor Levels of Monatomic Hydrogen in Silicon

N. M. Johnson, C. Herring,* and Chris G. Van de Walle
Xerox Palo Alto Research Center, Palo Alto, California 94304
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The acceptor level $\epsilon_A$ of monatomic hydrogen ($^2$H) in crystalline silicon has been located at $\epsilon_A \approx \epsilon_m + 0.00$ eV, where $\epsilon_m$ is the midgap level, more than 0.3 eV below the recently identified donor level. Thus, hydrogen has a large negative “effective Coulomb energy.” We obtain $\epsilon_A$, via the principle of detailed balance, from separately measured electron emission and capture rates, assuming that the processes $H^+ + 2e^- \rightarrow H^-$ proceed by a brief residence in the ground state of $H^0$. Such routes seem indicated by ab initio calculations of the energies of $H^+$, $H^0$, and $H^-$ for various atomic positions and relaxations.

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The properties of hydrogen in solid solution in crystalline silicon have for some years been at the leading edge of progress in understanding the broader and technologically important field of hydrogen in semiconductors [1]. However, despite intensive research in the last decade, the numerical descriptors necessary for a quantitative understanding of this behavior have only gradually been isolated and measured. The donor and acceptor levels of monatomic interstitial hydrogen are prominent examples. In the earliest years it was commonly assumed that dissolved hydrogen existed only in the neutral charge state $H^0$. Then it was discovered that in p-type silicon the rapid drift of hydrogen in an electric field required the presence of $H^+$, and the revised model allowed $H^+$ and $H^0$, dependent on the position of the Fermi level with respect to a donor level $\epsilon_D$, which was presumed to be somewhere in the middle of the energy gap but with a large uncertainty in its precise location [2]. A few years ago the field drift of hydrogen released by the thermal dissociation of P-H complexes was measured [3] and interpreted as evidence for the existence of an $H^-$ species. It was subsequently shown [4] that $H^-$ is, in fact, the stable form when the Fermi level is positioned 0.3 eV above the midgap level $\epsilon_m$, and possibly also at lower positions. Thus, the hydrogen acceptor level $\epsilon_A$ is below $\epsilon_m + 0.3$ eV, and if $\epsilon_D$ is higher than $\epsilon_A$ (the “negative-$U^m$ case” [5], for which two $H^0$s can lower their energy by changing to $H^+$ and $H^-$) the stronger condition must obtain

$$\epsilon \equiv (\epsilon_D + \epsilon_A)/2 < \epsilon_m + 0.3\text{ eV}. \quad (1)$$

Recently, evidence has been presented [6] that a level observed earlier in low-temperature studies of hydrogenated silicon [7–10] with deep-level transient spectroscopy (DLTS), and designated $E^3'$, is identical with the +0 transition of the center known as A49 observed by electron paramagnetic resonance in similarly treated material [11], and identified as neutral hydrogen in a bond-center site; this center appears to be the isotopic analog of “anomalous muonium” in silicon [12]. Since the $E^3'$ level lies only $\sim 0.20$ eV below the conduction band [8,10], acceptance of this identification implies that $\epsilon_D \geq \epsilon_m + 0.35$ eV. Thus, Eq. (1) applies and gives $\epsilon_A \leq \epsilon_m + 0.25$ eV. Hydrogen is thus a “negative-$U$” impurity in silicon, a property that had indeed been tentatively predicted by ab initio theoretical calculations [13].

The purpose of this Letter is to provide the first explicit experimental determination of $\epsilon_A$, and thereby quantitatively establish the negative-$U$ character of isolated hydrogen in silicon. For a negative-$U$ system there is, of course, a difficulty with the normal method of locating an acceptor level by measuring the dependence of its charge state on Fermi level $\epsilon_F$, since the impurity goes from being nearly all positive to nearly all negative when $\epsilon_F$ passes through $\bar{\epsilon}$; $\epsilon_D - \epsilon_A$ affects the charge-state statistics only in the always-small concentration of $H^0$. Even for the positive-$U$ case, measurements with $\epsilon_F$ as close to $\epsilon_m$ as expected for $\epsilon_A$ would be difficult since the material would be nearly intrinsic. The method used here avoids this difficulty by focusing attention on the kinetics of the transitions,

$$H^0 + e^- \rightarrow H^-, \quad (2a)$$
$$H^- \rightarrow H^0 + e^-, \quad (2b)$$

whose rates, related by the principle of detailed balance, are, respectively [2],

$$r_{0-} = \sigma_{0e}v_en_e \quad (3)$$

and

$$r_{-0} = r_{0-}[(\nu_0Z_0) / (\nu_-Z_-)] \exp [(\epsilon_A - \epsilon_F)/kT], \quad (4)$$

where $\sigma_{0e}$ is the cross section for capture of an electron by $H^0$, $v_e$ is an average thermal velocity for electrons, $n_e$ is the free electron concentration, $\nu_0$ and $\nu_-$ are the number of ground state configurations for $H^0$ and $H^-$, respectively, in a primitive cell, and $Z_0$ and $Z_-$ are the vibrational partition functions associated with $H^0$ and $H^-$, respectively. We obtain $\epsilon_A$ by inserting measured values of $r_{-0}$ and $r_{0-}$ into (4).

Actually, we are not able to directly measure $r_{-0}$ and $r_{0-}$. One of our experiments measures the spontaneous
conversion of $\text{H}^-$ to $\text{H}^+$, the other the absorption of two electrons by $\text{H}^+$. These give the rates of the reactions
\begin{align*}
\text{H}^+ + 2e^- &\rightarrow \text{H}^-, & (5a) \\
\text{H}^- &\rightarrow \text{H}^+ + 2e^-, & (5b)
\end{align*}

instead of the rates of (2). However, we assume that each of the processes (5) consists of a fast step and a slow step occurring sequentially, the fast step involving an interconversion of $\text{H}^0$ with $\text{H}^+$, and the slow (hence rate determining) step being the appropriate process of (2). Specifically, we assume the rates of (2a) and (2b) to be essentially the same as those of (5a) and (5b), respectively. This assumption is correct provided that (i) the processes (5) both proceed via an essentially equilibrium state of $\text{H}^0$ and (ii) the rates of $\text{H}^0 \leftrightarrow \text{H}^+ + e^-$ are very fast compared with the corresponding rates for $\text{H}^- \leftrightarrow \text{H}^0 + e^-$ in (5). In the discussion of ab initio calculations to be given below, we shall argue that both these conditions should be valid if, as the calculations seem to indicate, the stable configurations of $\text{H}^+$ and $\text{H}^0$ both have the hydrogen at a bond-center site, with no metastable site for $\text{H}^0$.

The quantity $\tau_{-0}$ was determined by analyzing near-room-temperature capacitance transients; it was found to be only slightly in excess of a lower limit obtained by a simplified analysis [4]. Experimentally, minority carriers (holes) are introduced for a fraction of a second into the depletion region of a reverse-biased, previously hydrogenated, Si:P Schottky diode, by use of back-side illumination [4]. These holes dissociate a small fraction of the P-H complexes in this region and hasten the conversion of the freshly released atomic hydrogen into $\text{H}^+$. After the hole pulse, the bias is reduced to zero for a long enough time (e.g., 10 ms) to convert all the $\text{H}^+$ to $\text{H}^-$ by process (5a), except in a narrow near-surface region. As shown in Fig. 1, the diode capacitance $\Delta C^-(t)$ after restoration of a sizable reverse bias rises with time because the conversion back to $\text{H}^+$ by process (5b) dominates over the inward drift and eventual recombination of the $\text{H}^-$. The drift contribution to $(d\Delta C^-/dt)_{t=0}$ is negative and can be determined from the transient $\Delta C^+$ (upper curve) that is observed in the absence of a flooding pulse and from the known [4,10] mobilities of $\text{H}^+$ and $\text{H}^-$. Results from measurements at several temperatures are plotted in the inset of Fig. 1.

The rate $r_{0-}$, or equivalently the rate of process (5a), was determined by studying the amount of conversion of $\text{H}^+$ to $\text{H}^-$ due to zero-bias pulses of very short duration $\tau_n$. A set of such capacitance transients $\Delta C_n(t)$ recorded at 310 K is presented in Fig. 2. The inset shows the exponential decay of the normalized values of $\Delta C_n(0)$ toward their long-time $\Delta C_\infty(0)$ ($\tau_n=10$ ms) limit, which yields the electron capture time $\tau_e (\equiv 1/r_{0-})$ for process (2a).

The acceptor level $\varepsilon_A$ can now be determined from Eq. (4). A variety of theoretical calculations [14] agree that the minimum-energy configuration for $\text{H}^0$ (as well as for $\text{H}^+$) has the hydrogen at a bond-center site (with outward silicon relaxation); hence with spin degeneracy the number of sites in a primitive cell is $\nu_0 = 8$. Similarly, $\nu_\perp = 2$ for $\text{H}^-$ at the tetrahedral interstitial site. Near room temperature, both $Z_0$ and $Z_\perp$ can be assumed to be near unity. The $r_{0-}$ obtained from the slope of the semilogarithmic plot in Fig. 2 is of course an average over a modest range of values corresponding, via (3), to the range of electron concentrations $n_e$ that existed in the depth interval over which hydrogen was released and sampled by the capacitance measurement. The entire set of runs depicted in Fig. 2 induced an increase in the active donor concentration of $<10\%$ with an average of $\approx 5.6 \times 10^{15}$ cm$^{-3}$. For this value of $n_e$, $\varepsilon_F - \varepsilon_m$ at 310 K is 0.33 eV. Thus (4) gives

$$\varepsilon_A \approx \varepsilon_m + 0.00 \text{ eV}. \quad (6)$$

That is, the acceptor level is coincidentally located essentially at midgap. This is our main result.

With the DLTS result quoted earlier for the donor level, $\varepsilon_D \approx 0.20$ eV, (6) reveals that isolated hydrogen is
FIG. 2. Capacitance transients $\Delta C_n(t)$ after dissociation of P-H complexes by a hole pulse at a reverse bias of 20 V, immediate reduction of the bias to zero for a duration $\tau_n$, and imposition of a new reverse bias of 6 V. The $\Delta C$ values for each $\tau_n$ are normalized by a value $\Delta C_n^+(0)$ which for $\tau_n=0$ represents an extrapolation of the observed curve to $t=0$ to eliminate the effect of a small initial thermal transient, and which for the other $\tau_n$'s represents this extrapolation plus normalization to the actual amount of hydrogen released in the $n$th run. The latter normalization was enabled by inserting a short (10 ms) delay between the hole pulse and the zero-bias pulse. The inset shows the exponential decay of the $t=0$ values (corrected for the small thermal transient) toward their long-time (10 ms) limit, which yields the electron capture time $\tau_c (\equiv 1/r_{0-})$.

a negative-$U$ impurity with

$$U \equiv \varepsilon_A - \varepsilon_D \approx -0.36 \text{ eV},$$

(7)
a remarkably large value comparable, for example, to that for interstitial boron in silicon [15]. Then the energy $\varepsilon$, describing the Fermi level position at which monatomic hydrogen changes from being nearly all positive to nearly all negative, is

$$\varepsilon \approx \varepsilon_m + 0.18 \text{ eV},$$

(8)
a value consistent with (1). The prediction (8) could perhaps be directly tested by studying charged hydrogen distributions in junctions under zero bias.

As was noted earlier, the conclusions (6)–(8) are based on the assumptions (i) and (ii) stated immediately after (5). Support for these assumptions is provided by calculations of total energy as a function of lattice configuration, with a first-principles density-functional pseudopotential technique previously described [13]. These calculations yield energy surfaces for hydrogen in the positive, neutral, and negative charge states, that is, the energy of the system as a function of the coordinates of the hydrogen atom, with the Si atoms fully relaxed for each hydrogen position. The diagram in Fig. 3 displays, for each charge state, how the energy of this fully relaxed configuration changes as the hydrogen position is moved, along the path shown in the inset, from the bond-center (BC) site to the tetrahedral (Td) site. This path has the property that for the lowest energy charge state, the energy is very nearly a minimum with respect to displacements of the hydrogen normal to the path. To make the energy curves for the different charge states comparable, they have been made to refer to the same total charge in all cases, specifically, H$^-$, H$^0$ plus one electron at the bottom of the conduction band, and H$^+$ plus two such electrons. The energies shown have been taken directly from the density-functional calculations, with no correction for the well-known error in the band gap ($E_G = 0.48 \text{ eV}$ in the calculation).

Correction of the just-mentioned error might shift the relative heights of the three curves by a significant fraction of an eV, but would probably have much less effect on their individual shapes. In particular, the calculated three-dimensional energy surface gives no indication of metastable sites for H$^0$. Therefore, if the system makes a transition from H$^-$ to H$^0$, it will coast downhill to the global minimum at BC. This should happen quickly, before there is time for a fluctuation to the higher energy necessary to reach the H$^+$ curve. Hence assumption (i) seems likely to be the case for the electron-emitting transitions. For the electron-absorbing ones, H$^+ + e^-$ will generate H$^0$ in a configuration that needs only a small downhill readjustment to reach that of ground-state H$^0$, so assumption (i) seems justifiable here as well.

Because of the smallness of the configurational change between the ground states of H$^0$ and H$^+$ (merely an
increase of about 0.04 Å in the Si-H distance on going from H$^+$ to H$^0$), it seems unlikely that any sizable configurational-energy barrier exists for H$^0$ ↔ H$^+$ transitions. On the other hand, the fact that the Arrhenius slope of 0.84 eV in Fig. 1 significantly exceeds the ground-state energy difference of about 0.56 eV between H$^-$ and H$^0 + e^-$ implies that there is an extra configurational-energy barrier of ~0.3 eV, even for electron capture by H$^0$ [16]. This can well be consistent with Fig. 3, since the H$^0$ and H$^-$ curves may well correspond to quite different Si lattice relaxations for H positions where their energies are similar. Thus assumption (ii) seems likely also to be true.

In summary, it has been experimentally demonstrated that monatomic hydrogen in silicon has a large negative effective correlation energy, $U \approx -0.36$ eV, with the donor level situated ~0.20 eV below the conduction band minimum and the acceptor level coincidentally located essentially at midgap. In addition, the activation energy for electron emission from H$^-$ was shown to be 0.84 eV, which implies a configurational-energy barrier of ~0.3 eV for electron capture by H$^0$. This picture is consistent with the microscopic model of isolated, interstitial hydrogen derived from total-energy calculations.

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* Permanent address: Department of Applied Physics, Stanford University, Stanford, CA 94305.
[16] It should be noted that this configurational-energy barrier for electron capture by H$^0$ corresponds to and agrees in magnitude with the activation energy for "zero-bias" annealing of the E$^3$' center reported in [9].