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Acceptor state of monoatomic hydrogen in silicon and the role of oxygen

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We determine the activation enthalpies for electron emission of two near *T*-site hydrogen centers in silicon to be ~0.65 and ~0.79 eV. The deeper center is oxygen related, and stabilized with a binding energy of ~0.5 eV with respect to the shallower center. We verify the negative-*U* behavior of both centers, and demonstrate the crucial role that this behavior and the presence of oxygen have for the migration of hydrogen in silicon. The shallower center is interpreted as the acceptor of monatomic isolated hydrogen, and the deeper center is interpreted as a perturbed version of this acceptor.

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I. INTRODUCTION

Hydrogen atoms migrating in silicon interact readily with crystal imperfections[1] such as intrinsic point defects, native impurities, and shallow donors or acceptors. This reactive behavior involves important technological aspects, because it may eventually lead to the formation or destruction of electrically active defects. Not least, the technological aspects have motivated numerous experimental and theoretical studies of the hydrogen-silicon impurity-host system, in addition its character as a model system for studies of semiconductor defects has challenged many authors. A point of particular interest has been to understand the diffusion of atomic hydrogen which, according to the present theoretical consensus,[2] proceeds via isolated ionic species migrating through interstitial sites of a silicon crystal governed by potential-energy surfaces for the different charge states involved. These potential surfaces have minima at the bond-center (BC) site and at the interstitial tetrahedral (*T*) site, giving rise to a donor level and an acceptor level, respectively. The pathway of migration will then, in a particular case, depend on the position of these levels relative to the Fermi level according to doping type and concentration. *Ab initio* calculations[3,4] predicted that neutral BC hydrogen, $H^0(BC)$, in an *n*-type material represents a local minimum in free energy. However, this minimum-energy configuration is metastable inasmuch as either positive BC hydrogen, $H^+(BC)$, or negative *T*-site hydrogen, $H^-(T)$, represents the global energy minimum for any position of the Fermi level. This implies that the donor level lies above the acceptor level, with the consequence that monatomic hydrogen should behave as a negative-*U* defect in silicon when the H^0 impurity can jump swiftly between BC and *T* sites.

The BC donor level has been identified spectroscopically,[5,6] whereas the position of the *T*-site acceptor level is still debated.[7,8] The authors of Ref. 7 defined the acceptor level as the energy difference between $H^0(BC)+e_c$ and $H^-(T)$, and placed it slightly below midgap on the basis of a kinetics study. As the first step in this work, an initial amount of H^+ was released in a diode space-charge layer from hydrogen-passivated shallow donors by reverse-bias illumination, and converted to H^- by the application of a filling pulse. Then the subsequent thermally induced removal of H^- was recorded as an exponential capacitance transient. The authors ascribed this transient to the first step of the process $H^-(T)\rightarrow H^0(BC)+e_c\rightarrow H^+(BC)+2e_c$ and obtained the activation enthalpy of this step. They found, consistent with the anticipated negative-*U* property, that this enthalpy is larger than that reported earlier[5] for the second step of the process. They further obtained the position of the acceptor level from detailed-balance considerations. Recently our group showed[9] that at least two kinds of BC hydrogen donors exist. One, H(BC), is associated with hydrogen at the BC solution site, the other, $H^0(BC)$-O_i with BC hydrogen weakly bound to interstitial oxygen. Hence the obvious question arises of whether a similar situation applies to the *T*-site acceptor. If so, two different configurations of $H^-(T)$, with and without an oxygen atom nearby, should exist. In this paper we show that this is indeed the case.

II. EXPERIMENTAL DETAILS AND BACKGROUND

A. Summary of previous results

The foundations of the present work are delineated in Ref. 9, where the dynamic properties of the H(BC) and H(BC)-O_i donor centers were examined by the application of deep-level transient spectroscopy (DLTS). A key point in this interpretation (Fig. 9 of Ref. 9) is that $H^+(BC)$-O_i converts to $H^+(BC)$ in oxygen-poor material, whereas in oxygen-rich material the reverse process occurs. The characteristics related to the formation of H(BC) and H(BC)-O_i are particular relevant in the present context and may be summarized as follows. Both centers are abundant after low-temperature proton implantation, giving rise to two signals, denoted $E3'$ and $E3''$, observed when DLTS is applied *in situ* to as-implanted samples. These signals are always present after implantation into the depletion layer of a reverse-biased diode. However, they are almost indistinguishable as far as their electronic properties (i.e., their DLTS signals) are concerned, but can be discerned on the basis of characteristic differences in their formation and annealing properties. When the bias is removed at low temperature (<80 K) the $E3''$ signal disappears instantaneously while $E3'$ is unaffected. If the temperature is raised to 120 K, then also $E3'$ disappears swiftly. However, the total strength of the original

$E3'+E3''$ signal can be recovered. Typically, the original signal accounts for >80% of the implanted protons, and total recovery can be achieved by illumination of the annealed sample while under reverse bias. In this case the restored signal is practically all $E3''$, which accounts for all of the original signal or even slightly more. Also, the original $E3'$ signal can be recovered. This happens when forward-bias is applied to p^+n samples, giving rise to the injection of holes. In this case a minor fraction of the original $E3'$ is not recovered, and no $E3''$ is recovered. However, the remaining strength of the original signal can be recovered as $E3''$ when reverse-bias illumination is subsequently applied. The $E3'$ recovery is accompanied by long-range diffusion even at 65 K, whereas long-range diffusion is not observed in connection with the $E3''$ recovery. The tracking of charge accumulated in the deletion layer shows that both centers prior to the recovery were converted temporarily into singly negatively charged centers. These, so far hidden, centers are thermally stable up to ~250 K where they both anneal.

B. Sample preparation and experimental principle

For the measurements a series of Schottky diodes were prepared on 10–20 Ω cm n-type as-grown Czochralski silicon wafers (either older commercially purchased 2-in. wafers or cut and polished from commercially grown bulk crystals) with a concentration of dispersed interstitial oxygen $[O_i]$ of $\sim 1\times 10^{18}\,\mathrm{cm}^{-3}$. The O_i content was obtained from the absorption of the 1136-cm^{-1} local mode of interstitial oxygen. Since our wafers did not undergo special treatments to denude interstitial oxygen from the wafer surface, the measured concentration is representative of $[O_i]$ in the reverse-bias depletion layer of the diodes. To generate the hydrogen centers and initiate the search for emission from the hidden centers, the individual diodes were implanted with protons at 65 K through the junction (under zero bias) at an energy of ~450 keV, and doses in the range of $10^9-10^{10}\,\mathrm{cm}^{-2}$. The resulting implantation profile is, under these conditions, located in the middle of the depletion layer when 20-V reverse bias. Only $E3'$ is present initially because $E3''$ transforms during the zero-bias implantation. After illumination to generate the total $E3'+E3''$ signal, *in situ* DLTS measurements were carried out to determine the initial strength of this signal for the purpose of normalization.

We anticipate that the hidden centers are identical to $H^-(T)$ and $H^-(T)$-O_i, and expect the annealing to be triggered by thermal electron emission from these centers. The emission may then be observed as a capacitance transient at temperatures slightly below 250 K, at which temperature we know that the hidden centers anneal. Because $E3'+E3''$ completely dominates the DLTS spectra and can be recovered fully from the hidden centers, we may expect a substantial signal, large enough to be detected as a single-shot capacitance transient. Furthermore, with only one (or two) dominating trap(s) present, we may apply the electrical pulse-train method[10] to measure capture barriers.

III. RESULTS AND ANALYSIS

A. Capacitance transients

As depicted in Fig. 1, a single-shot capacitance-transient measurement allowing for long decay times does indeed reveal the emission. The transient shown was recorded with an oxygen-rich hydrogen-implanted diode with about 55% of the implants initially present as H(BC) and the rest as H(BC)-O_i. Both centers were first converted into negative hidden centers by bias removal at 110 K. The capacitance transient was then recorded after reapplication of the bias at 242 K. As can be seen, it consists of two exponential components of about 55% and 45% intensities. We ascribe the fast decay (55%) to electron emission from $H^-(T)$, and label it AT'. The slow decay (45%) is analogously ascribed to emission from $H^-(T)$-O_i and labeled AT''. These assignments are based on the following observations: (1) The negative centers can be (partially) recovered after the application of a filling pulse and a second-shot transient recorded. This second-shot transient is still composed of AT' and AT''. However, now AT'' dominates, with AT' accounting for only ≈20% of the transient. (2) For samples prepared so that essentially only H^+(BC)-O_i is initially present, the fast component AT' is absent in the first-shot transient. However, in this case, the second-shot transient is now found to contain up to ≈20% of the AT' component. These two observations are consistent with the earlier result[9] that the concentration of H^+ slowly diminishes as a result of redistribution in the depletion layer and migration to sinks in the temperature range 210–260 K. At a given temperature, steady-state conditions are established with most monatomic hydrogen present as H^+(BC)-O_i, and a smaller fraction present as H^+(BC). Thus when the filling pulse is applied both H^- centers are formed in accordance with the amounts of their

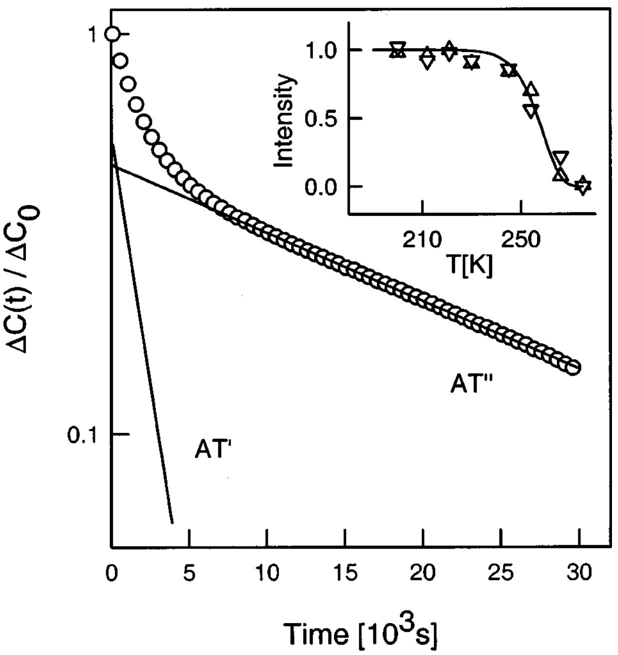

FIG. 1. Single-shot capacitance transient obtained at 242 K revealing two exponential components AT' and AT''. The inset depicts the isochronal annealing of the center responsible for AT'', ∇ with bias and Δ without bias. The data are obtained with as-grown Cz silicon with $\sim 1\times 10^{18}\,\mathrm{cm}^{-3}$ of interstitial oxygen as derived from the absorption of the 1136-cm^{-1} local mode of O_i.

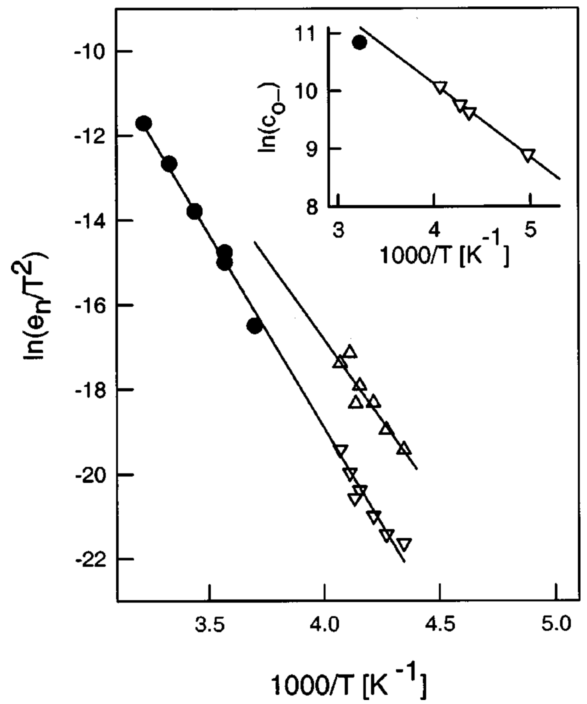

FIG. 2. Arrhenius analysis of AT'' (∇) and AT' (Δ) emission rates yielding the barriers ~0.79 and ~0.65 eV, respectively. The data (●) of Ref. 7 are included. The inset depicts the temperature dependence of the capture to the center responsible for AT'' including a data point from Ref. 7. The capture barrier is ~0.11 eV.

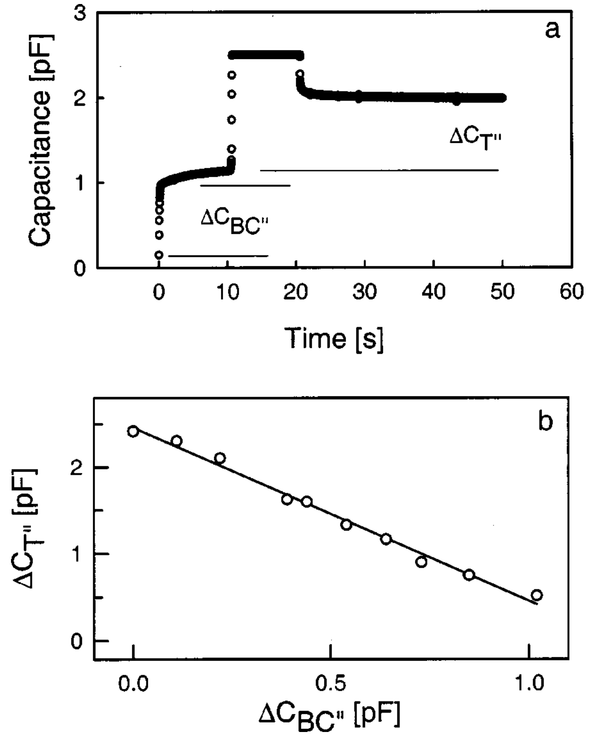

FIG. 3. Illustration of the correlation between the $E3''$ signal and the reservoir for the AT'' signal. (a) The pulsing sequence to obtain $\Delta C_{T''}$ and $\Delta C_{\mathrm{BC}''}$, as explained in the text. (b) $\Delta C_{T''}$ vs $\Delta C_{\mathrm{BC}''}$.

respective precursors $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ and $\mathrm{H}^+(\mathrm{BC})$. From the transients AT' and AT'' measured at different temperatures, we derive the Arrhenius plots depicted in Fig. 2. We note the remarkable agreement over many decades between our AT'' data and those obtained in Ref. 7. The linear-regression analysis yields the activation $\Delta H'' = 0.79 \pm 0.03\,\mathrm{eV}$ for the emission from $\mathrm{H}^-(T)$-O_i, and $\Delta H' = 0.65 \pm 0.10\,\mathrm{eV}$ for the emission from $\mathrm{H}^-(T)$.

B. Negative-*U* property

The electron emission enthalpies found for $\mathrm{H}^-(T)$-O_i and $\mathrm{H}^-(T)$ exceed those of the corresponding BC donor states, in accordance with the expected negative-U property. However, to demonstrate this property more directly, we shall examine the correlation between the amount of charge bound as $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ and $\mathrm{H}^-(T)$-O_i. For this purpose a reverse-biased sample was prepared to contain $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ predominantly. The $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ was then partially converted to $\mathrm{H}^-(T)$-O_i by the application of a filling pulse with the number of the converted centers being controlled by the pulse duration. The remaining $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ gives rise to a capacitance transient (the $E3''$ signal) following the filling pulse. The amplitude of this transient [see Fig. 3(a)] is a measure of the amount of charge emitted in the process $\mathrm{H}^0(\mathrm{BC})$-$\mathrm{O}_i \rightarrow \mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ and is denoted $\Delta C_{BC''}$. An illumination pulse applied immediately after the $E3''$ transient has leveled off causes a shift in steady state capacitance which we denote $\Delta C_{T''}$. This capacitance shift measures the charge change as the $\mathrm{H}^-(T)$-O_i configuration converts back to the $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ configuration. Then, choosing different filling-pulse lengths to vary the relative amounts of $\mathrm{H}^0(\mathrm{BC})$-$\mathrm{O}_i$ and $\mathrm{H}^-(T)$-O_i, we obtain the linear correlation between $\Delta C_{T''}$ and $\Delta C_{BC''}$ depicted in Fig. 3(b), which reveals that two electrons are emitted when $\mathrm{H}^-(T)$-O_i is converted optically to $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$. A hypothetical acceptor level, defined as the enthalpy difference between a metastable configuration $\mathrm{H}^0(T)$-$\mathrm{O}_i + e_c$ and $\mathrm{H}^-(T)$-O_i, cannot lie above the BC donor level. In this case the emission from $\mathrm{H}^-(T)$-O_i would occur prior to the application of the illumination pulse, and the slope of the observed correlation should be one instead of two. The negative-U property implies that $\mathrm{H}^0(\mathrm{BC})$-$\mathrm{O}_i$ and subsequently $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ are swiftly formed after thermal electron emission from $\mathrm{H}^-(T)$-O_i. In accordance with this the AT'' transient should have twice the amplitude of the $E3''$ transient. We find that the AT'' amplitude is larger than that of $E3''$, but only by a factor of about 1.5.

To obtain further information, we measured the reverse-bias capacitance as function of increasing temperature (TSCAP), which revealed the capacitance step shown in Fig. 4. The step is depicted as the intensity ratio between AT'' and $E3''$ by normalizing to the initial $E3''$ signal. Although this ratio is definitely larger than 1, it is clearly less than the expected value of 2. We explain this as follows: The emission is described as a stepwise process $\mathrm{H}^- \rightarrow \mathrm{H}^0 + e^- \rightarrow \mathrm{H}^+ + 2e^- \rightarrow$ ''leak'', where we assume that the first step in the sequence is rate controlling and introduce a leakage term to account for the redistribution of H^+ in the space-charge layer. From our earlier study[9] we know that release of H^+ for

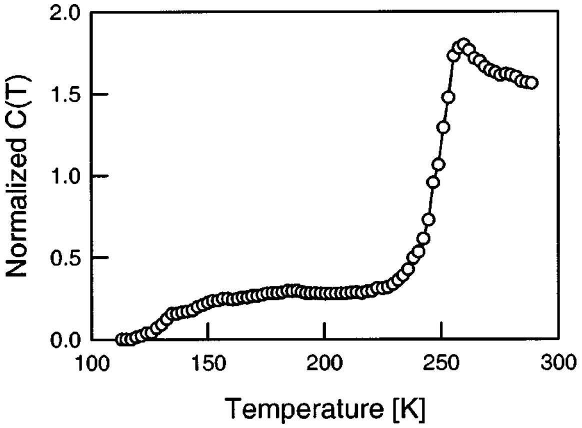

FIG. 4. Normalized TSCAP step revealing the *effective* removal of a hydrogen-associated negative charge from the depletion layer during AT'' emission.

trapping at sinks or drift toward the junction occur with an activation enthalpy of 0.73 eV. The capacitance transient monitors the charge change according to $(2[\mathrm{H}^-]+[\mathrm{H}^0]+[\mathrm{H}^{\mathrm{leak}}])\times\overline{e}$, where the term $[\mathrm{H}^{\mathrm{leak}}]$ accounts for the effective loss of positive charge caused by the redistribution of H^+ during the recording of the transient. If $[\mathrm{H}^0]$ and $[\mathrm{H}^{\mathrm{leak}}]$ were negligible at all times, the AT'' capacitance transient would be exponential with a total amplitude corresponding to twice the $\mathrm{H}^-(T)$-O_i concentration. The leakage term could explain the loss in signal. However, a detailed analysis indicates that the actual loss, if explained by $[\mathrm{H}^{\mathrm{leak}}]$ alone, would cause the transient to become measurably nonexponential in contrast to the observations. Hence, we look for an additional explanation which we may find by noting that the isothermal annealing of $E3''$ is nonexponential, and may be decomposed in fast and slow components. If only the slow component is used for normalization of the TSCAP data, the step is increased by about 20%. Considering the fact that two analogous $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ complexes are known to exist,[11] we may assume that only the slow component is connected with AT''. This possibility is further substantiated by the fact that the TSCAP data actually disclose a second smaller step at lower temperature. This step is not present after room-temperature annealing and may partly account for the missing amplitude (see Fig. 4). The results establish the one-to-one correspondence $E3''\leftrightarrow AT''$, and hence support the assignment of AT'' to $\mathrm{H}(T)$-O_i. The results further establish the negative-U behavior of the $\mathrm{H}(T)$-O_i defect.

C. Two-step capture and emission

Next we discuss the capture cross-section barrier which could be measured for AT'' but not for AT''. The capture from $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ to $\mathrm{H}^-(T)$-O_i proceeds as a two-step process via the neutral charge state according to the rate conditions $c(+\rightarrow 0)\gg c(0\rightarrow -)\gg e(-\rightarrow 0)$. With these conditions fulfilled, the H^+ population decreases gradually to form H^- via H^0 while thermal equilibrium persists between H^+ and H^0. In accordance with the analysis of Ref. 7, the measured reciprocal capture time is given by $1/\tau=\sigma_a\langle v\rangle n_e F_0 = c(0\rightarrow -)F_0$, where $F_0=[\frac{1}{2}\exp(E_d-E_F)+1)]^{-1}$. The inset of Fig. 2 depicts the derived capture rates $c(0\rightarrow -)$ as a function of T^{-1}, from which the capture barrier $\Delta E_c=0.11\pm 0.04\,\mathrm{eV}$ is obtained. We note that the data point of Ref. 7 fits in when renormalized to match our carrier density.

We note that the barrier (0.79 eV) for the emission from $\mathrm{H}^-(T)$-O_i is larger than the barrier (0.73 eV) determined previously[9] for release of hydrogen from $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$. This has the consequence that the annealing of the $\mathrm{H}^-(T)$-O_i center should be controlled by the electron emission independent of the sample bias during annealing when a swift transfer to $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$ takes place. We have obtained the $\mathrm{H}^-(T)$-O_i annealing stage by recording the temperature dependence of the ability to recover $E3''$ by illumination. This isochronal stage has been included as an inset in Fig. 1. The parameters $\nu''=7\times 10^7\,\mathrm{T}^2\,\mathrm{s}^{-1}$ and $\Delta H''=0.79\,\mathrm{eV}$ describing the AT'' transient agree with the parameters $\nu''=5\times 10^7\,\mathrm{T}^2\,\mathrm{s}^{-1}$ and $\Delta H''=0.80\,\mathrm{eV}$ describing the best fit to the isochronal data.

IV. DISCUSSION

A. Energy levels

We define the oxygen-perturbed acceptor level as the energy difference between $\mathrm{H}^0(\mathrm{BC})$-$\mathrm{O}_i+e_c$ and $\mathrm{H}^-(T)$-O_i, and place it at $0.68\pm 0.08\,\mathrm{eV}$ below the conduction band by subtraction of the capture barrier from the activation enthalpy. For the solution site $\mathrm{H}^-(T)$, the situation is more complicated. We can state an activation enthalpy ΔH of about 0.65 eV but must use indirect arguments to estimate the level position. As mentioned earlier, we found that repeating the transient causes the $\mathrm{H}^-(T)$-O_i signal to become dominant. This indicates that the activation enthalpy obtained for the solution site is actually the barrier against the release of hydrogen from $\mathrm{H}^-(T)$ to migrate as H^0 through T sites. This migration may proceed swiftly as has been shown,[9] and (most) of the released hydrogen eventually traps at the oxygen-perturbed BC sites as $\mathrm{H}^+(\mathrm{BC})$-$\mathrm{O}_i$. In this form hydrogen is bound by an additional binding energy[9] of about 0.29 eV relative to the regular solution BC site. The consequence of the fast migration and trapping at oxygen is that the concept of an acceptor level defined as the energy difference between $\mathrm{H}^0(\mathrm{BC})+e_c$ and $\mathrm{H}^-(T)$ loses its meaning in practical terms, since it cannot be realized experimentally. Nevertheless, we may obtain an estimate for the total energy of $\mathrm{H}^-(T)$. The activation enthalpy for $\mathrm{H}^0(\mathrm{BC})\rightarrow\mathrm{H}^0(T)$ is known[9] (0.295 eV) and the barrier for the reverse process $\mathrm{H}^0(T)\rightarrow\mathrm{H}^0(\mathrm{BC})$ has been estimated[9] (~0.2 eV). Furthermore, the swift diffusion observed under carrier injection[9] indicates a small barrier of ⟨0.1 eV for migration of H^0 through T sites. Combined with the measured activation enthalpy these figures show that the total energy of $\mathrm{H}^-(T)$ is 0.40–0.60 eV lower than that of $\mathrm{H}^0(\mathrm{BC})+e_c$. It should be noted that our measured barrier for escape from the T-site complies with the activation enthalpy of the process $\mu^-(T)\rightarrow\mu^0(T)+e^-(0.56\,\mathrm{eV})$ reported in a recent muonium study.[12]

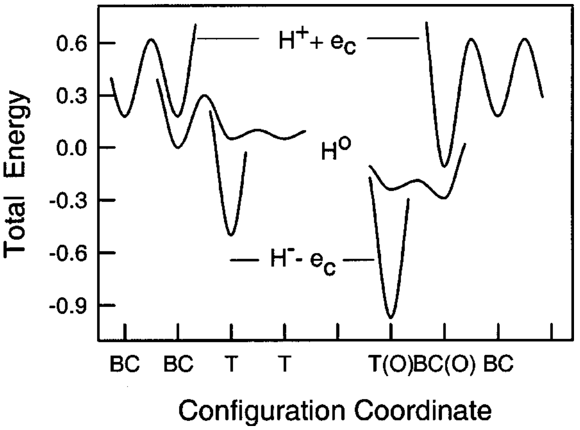

FIG. 5. Experimental configuration diagram for the three charge states of isolated and oxygen-perturbed monatomic hydrogen in the silicon lattice. The zero of the energy scale is chosen to be equal to the total energy of neutral hydrogen at the bond-center position.

B. Configuration scheme and hydrogen migration

In our previous work[9] we presented a sketch of the total-energy variations of the three charge states H^-, H^0, and H^+ along paths connecting neighboring BC and $\dot{T}$ sites in configuration space, including the modifications caused by the oxygen perturbation. In this sketch the H^- energy curves were tentative. With the acceptor levels known the scheme can now be further quantified as shown in Fig. 5, where the minims and saddle points of the configuration potentials are fixed to a common energy scale by means of all available experimental data,[9] taking H^0(BC) at zero energy. The sketch complies qualitatively with the theoretical consensus[2] as far as the regular solution sites are concerned. The possibility of the swift migration of injected H^0 to oxygen traps, as indicated by the sketch, was foreseen by molecular-dynamics simulations.[13] In these simulations the hydrogen ends up at a BC site in the strain field of O_i, as also observed experimentally. Further calculations[14] indicate that the barrier for H^0 migration is in the range 0.5–0.15 eV which is consistent with the present analysis. A point that is still debated is whether or not the $H^0(T)\rightarrow H^0$(BC) barrier is significantly higher than the migration barrier. The effective formation of the oxygen-perturbed sites provides strong evidence on the importance of that barrier.

C. Comparison with previous experiments

The experimental evidence presented in Fig. 2 indicates that our results and those of Ref. 7 are closely related. Indeed, the two experiments have much in common. In both cases monatomic hydrogen is released from traps by illumination under bias, and converted to H^- by the application of a flooding pulse. In our case the hydrogen source is oxygen-trapped hydrogen, whereas the source in the experiment of Ref. 7 is hydrogen trapped at the shallow donor. The main difference is that the temperature of the illumination and the temperature of the signal recording are lower in our case. The similarity of the two experiments, and the consistency of the combined Arrhenius analysis indicated in Fig. 2, suggests that our AT'' oxygen-related transient and the transient reported in Ref. 7 may have the same origin. On this basis, notwithstanding that the content of oxygen in the interstitial form may be different in the two cases as a result of differences in the post-growth wafer treatments, we suggest that the acceptor state identified in Ref. 7 is actually the oxygen-perturbed version of monatomic T-site acceptor. We emphasize that we do not dispute the basic scenario proposed in the original work to generate the occupied acceptor states. We only suggest the slight modification that hydrogen released from shallow donors under the reverse-bias illumination starts out as fast migrating H^0 through the open areas of the lattice. The implied rapid conversion to H^+ under reverse-bias conditions must occur near BC sites, where the energy of the positive charge state is low. Now the migration through T sites occurs very quickly[9] (a jump rate $>10^4\ s^{-1}$ at 65 K) whereas the rate constant for direct conversion to H^0(BC) is small[9] ($<10^{-2}\ s^{-1}$ at 65 K). The consequence of this is that migrating hydrogen swiftly encounters a strained BC site in the proximity of interstitial oxygen and forms $H^+(BC)\text{-}O_i$. Because this configuration is stabilized with respect to the regular BC site by ~0.29 eV,[9] with an escape barrier of ~0.73 eV, the hydrogen will be held up for some time. When the ensuing flooding pulse is applied,[7] the held-up hydrogen forms $H^-(T)\text{-}O_i$. The crucial point is the height of the barrier opposing the transformation $H^0(T)\rightarrow H^0$(BC) as compared to the barrier for jump between adjacent T sites. With $[O_i]\sim 10^{18}\ cm^{-3}$ (as in our case) we find that a barrier difference as low as 0.15 eV would be sufficient to produce primarily $H^-(T)\text{-}O_i$ by an illumination-flooding cycle carried out even at room temperature (as in the experiment of Ref. 7). For this to be true also for oxygen-lean material ($[O_i]10^{16}\ cm^{-3}$) the barrier difference must be larger (~0.3 eV). Such a large barrier difference would comply with the barrier for the process $\mu^0(T)\rightarrow\mu^0$(BC) (0.38 eV) reported in the muonium study[12] and with the small barrier (0.5–0.15 eV) for H^0 migration obtained by molecular-dynamics simulations.[14] Furthermore, the critical dependence on oxygen concentration could possibly explain the failure of Ref. 8 to reproduce the transient of Ref. 7. In this connection it should be noticed that the intervening of carbon[15] may be important. The authors of Ref. 8 further questioned the swift downhill transition $H^0(T)\rightarrow H^+$(BC) implied in the analysis of Ref. 7. Also, this point may be resolved by reference to the role of interstitial oxygen. Our analysis indicates that this direct conversion is not needed because of the fast migration and conversion to $H^+(BC)\text{-}O_i$.

V. CONCLUSION

To conclude, we have shown that T sites in the proximity of interstitial oxygen act as trapping centers for H^- in the same way as BC sites with oxygen nearby act as trapping centers for H^0 and H^+. The escape of hydrogen from the T-site traps is initiated by thermal electron emission. We have obtained the activation enthalpy and the capture rate for the process, and determined the position of the oxygen-perturbed acceptor level. This level is, in accordance with the negative-U behavior of the system, defined as the enthalpy difference between $H^0(BC)$-$O_i + e_c$ and $H^-(T)$-O_i. We have further obtained the activation enthalpy for the escape of isolated H^- hydrogen from the T site and estimated the energy of $H^-(T)$ relative to that of $H^0(BC) + e_c$. Our results demonstrate that the presence of interstitial oxygen in silicon plays a crucial role for the migration and annealing of hydrogen at or below room temperature. Interstitial oxygen retards the migration of H^+ and acts as a catalyst for conversion of hydrogen from T sites to BC sites.

Note added in proof: Recently C. Herring *et al.*[16] expanded the work of Ref. 7. The formation of a 0.16-eV donor center of hydrogen in Cz silicon is reported. This center is identified with the $E3'$ center discussed here. However, the authors make no distinction between the regular bond center ($E3'$) and the perturbed bond-center ($E3''$), hence they do not consider in their analysis the effect of local strain on the dynamics and stability of bond center hydrogen. As shown in Ref. 9 an interstitial oxygen impurity generates such a local strain field which can trap interstitial hydrogen and cause the $E3''$ center.

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