Deep State of Hydrogen in Crystalline Silicon: Evidence for Metastability

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After proton implantation into *n*-type silicon at 45 K, a bistable hydrogen center with a band-gap level $E_c - E_t = 0.16$ eV is observed by deep-level transient spectroscopy. The center anneals at ~ 100 K under zero bias with a decay constant $\nu = (3.0\times10^{12}\ \mathrm{s}^{-1})\exp[(-0.29\ \mathrm{eV})/k_BT]$ and at ~ 210 K under reverse bias with $\nu = (1.3\times10^{8}\ \mathrm{s}^{-1})\exp[(-0.44\ \mathrm{eV})/k_BT]$. In both cases the center regenerates by forward-bias injection at low temperatures. The decay without (with) reverse bias reflects capture of one (two) electron(s). The metastability is ascribed to hydrogen jumps between bond-center and tetrahedral sites as a result of changes in charge states.

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The properties of hydrogen impurities in silicon have been studied intensively in the past,[1] and the subject is still one of broad interest. There are several reasons for this, among others that hydrogen neutralizes acceptors[1] and donors[1] and passivates electronic levels related to various impurities[1] and intrinsic defects.[1] Hydrogen has been found in a variety of configurations in crystalline silicon.[1-7] The microstructure of these centers continues to represent a challenge, although experimental[4-7] and theoretical progress[8,9] has been made recently.

Theory predicts that isolated neutral and positively charged hydrogen atoms occupy the bond-center site[8,9] (BC site), while negatively charged hydrogen enters the interstitial tetrahedral site[8] (T site). Several observations are in favor of this model: (i) Muon-spin resonance experiments identified two types of muonium,[10] "anomalous" muonium located at the BC site,[11] and "normal" muonium located at the T site.[10] (ii) Channeling measurements[6] showed that deuterium atoms implanted at low temperatures occupy the BC or the T site. (iii) Infrared-absorption studies[3] revealed a Si-H stretching mode at 1990 cm^{-1} after proton implantation at 80 K, in agreement with the value of $1945\pm100\ \mathrm{cm}^{-1}$ calculated for neutral bond-center hydrogen.[8] (iv) Electron paramagnetic resonance (EPR) experiments[4] identified a trigonal hydrogen-related center, *AA*9, involving two equivalent silicon atoms.

According to the calculations of Van de Walle *et al.*,[8] the Fermi-level position determines the energetically favorable charge state, H^-(T) in *n*-type and H^+(BC) in *p*-type silicon. Total-energy curves for H^+, H^0, and H^- in *n*-type silicon are sketched in Fig. 1. As can be seen, ion-implanted hydrogen may, at low temperatures, be trapped in the H^0(BC) configuration, although H^-(T) represents the global minimum in total energy. In this context, it may be noted that ion implantation at low temperatures normally leaves the sample in a non-equilibrium situation. If the temperature is raised, H^0(BC) will transform into H^-(T) by a thermally activated jump, combined with the capture of one electron. In the depletion layer of a reverse-biased diode, H^0(BC) converts into H^+(BC), and the transformation into H^-(T) will proceed with a higher activation barrier since H^+ has a stronger energy variation than H^0 in the configuration space. In principle, H^0(BC) and H^+(BC) can be regenerated at low temperatures by injection of holes, and it may therefore be possible to cycle between the various configurations. Thus isolated hydrogen in silicon may be a metastable (bistable) center, as pointed out previously.[12]

H^0(BC) is expected to act as a deep donor with an electron level in the upper half of the band gap,[8] but experimental evidence for this species is still lacking. The donor level may be revealed in a diode structure by deep-level transient spectroscopy[13] (DLTS). In combination with annealing studies, this technique may also be applied to investigate metastability. A number of hydrogen-related deep levels in silicon are known.[1,14,15] However, none of these have been properly assigned to specific defect structures, nor has metastability been observed. A particularly interesting deep donor denoted *E*3′ was reported by Irmscher, Klose, and Maass.[15] The

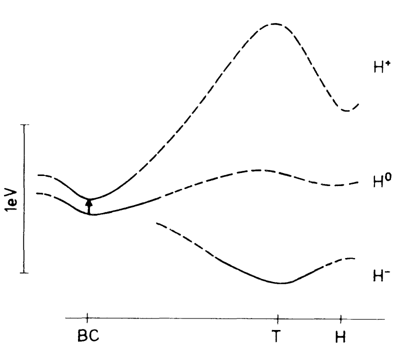

FIG. 1. Sketch of the total-energy curves for H^+, H^0, and H^- in *n*-type silicon, based on Van de Walle *et al.* (Ref. 8). The arrow indicates the activation enthalpy for the ionization of H^0.

$E3'$ center was formed at 77 K during proton implantation and annealed out at about 100 K in n-type and 250 K in p-type Czochralski-grown material. Since the $AA9$ center[4] and the 1990-cm^{-1} Si-H mode originating from hydrogen at BC sites[3,6] also anneal out in this temperature range, the $E3'$ center is a plausible candidate for $H^0(BC)$.

In this Letter we establish that the $E3'$ signal originates from a metastable (bistable) hydrogen-related donor. All our findings comply with the properties of $H^0(BC)$ as deduced from theoretical calculations.[8]

Capacitance-voltage (C-V) and DLTS experiments were carried out on proton- (or deuteron-) implanted silicon diodes, p^+n diodes for Czochralski-grown (Cz) material, and Schotky diodes for float-zone-grown (FZ) crystals. The resistivity of the n-type layer varied from 1 to 100 Ω cm, corresponding to phosphorous concentrations in the range from $5\times10^{13}/cm^3$ to $5\times10^{15}/cm^3$. The proton (deuteron) implantation was performed at about 45 K, with doses in the range $(0.5\text{–}3)\times10^{10}/cm^2$. The DLTS measurements were performed with a Semitrap DLS-82E instrument.[16] The deep levels in the space-charge region are filled by a voltage pulse, and from the magnitude and the time constant of the ensuing capacitance transient, the density and emission rate of the traps can be derived. The thermal emission rate e_n is given by

$$e_n = c_n N_c \exp(\Delta S_n/k_B)\exp[-(E_c-E_t)/k_BT] , \quad (1)$$

where c_n is the capture rate, N_c is the effective density of states in the conduction band, ΔS_n is the ionization entropy, and E_c-E_t is the ionization enthalpy.

A strong DLTS signal is observed after the implantation. The value of c_n is large,[17] $c_n > 4\times10^{-8}$ cm^3s^{-1}, and $E_c-E_t=0.16\pm0.01$ eV after correction for the Poole-Frenkel effect.[18,19] No similar signal is observed in samples implanted with helium to an equivalent damage level, and the signal disappears in 5 min at about 100 K when no bias is applied to the sample. These findings reproduce[19] the previously reported $E3'$ data,[15] showing that we are dealing with the same defect.

We find that the $E3'$ signal accounts for the majority ($\geq 70\%$) of the implanted ions, independent of whether FZ or Cz material is used. Also, $E3'$ forms equally well in 1- and 100-Ω cm phosphorous-doped material. These facts indicate that neither oxygen nor phosphorous participates in the defect but do not rule out the possibility that other impurities such as, e.g., carbon[20] are involved.

The zero-bias annealing stage at 100 K reflects a reversible transformation into a state invisible by DLTS. After cooling below this stage, the $E3'$ signal can be retrieved by injection of minority carriers during forward bias. In the first annealing-injection cycle, typically 30% of the initial signal amplitude is lost, whereas succeeding cycles are closed. A series of isothermal annealing experiments has been carried out. Since annealing does not proceed under reverse bias in this temperature range, each measurement could be controlled by switching the bias on and off. The annealing is exponential in time, consistent with a first-order process. At a given temperature, the annealing in the case of deuterium is slower than that of hydrogen. This strongly indicates that the $E3'$ defect involves a hydrogen atom. To exclude that the observed difference originates from, e.g., different damage structures, an isothermal annealing measurement has been carried out on a diode implanted to the same depth with equal doses of protons and deuterons. It is found that the decay is indeed composed of two exponential components which are consistent with the single-isotope results. Thereby $E3'$ can be unambiguously assigned to a hydrogen-related defect. The Arrhenius plots of the decay constants are shown for both isotopes in Fig. 2. The preexponential factor in the case of hydrogen is $\nu_H=3.0\times10^{12}\pm0.5\times10^{12}$ s^{-1} and the activation barrier $\Delta E_H=0.293\pm0.003$ eV.

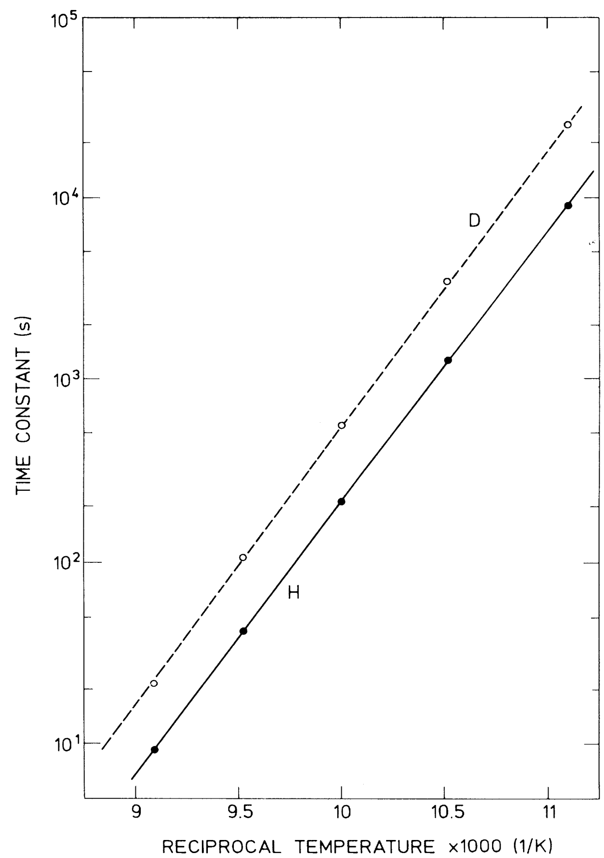

FIG. 2. Arrhenius plot derived from annealing of $E3'$ generated by proton or deuterium implantation at 50 K. Although the DLTS signals are indistinguishable in the two cases a shift in the annealing temperature occurs as shown. The solid curve corresponds to $\nu_H=3.0\times10^{12}$ s^{-1}, $\Delta E_H=0.293$ eV and the dashed curve to $\nu_D=\nu_H/\sqrt{2}$, $\Delta e_D=0.30$ eV.

Under reverse-bias conditions, the $E3'$ signal anneals in 5 min at about 210 K. Again, the signal can be retrieved by minority-carrier injection at lower temperatures, indicating that the same defect state is formed after annealing under either condition. This DLTS-invisible state is stable up to ≈ 250 K, above which temperature the $E3'$ signal cannot be retrieved. The reverse-bias annealing at 210 K is found also to proceed by a first-order process, with the preexponential factor $\nu_H = 1.3\times10^8 \pm 0.6\times10^8$ s^{-1} and the activation enthalpy $\Delta E_H = 0.44 \pm 0.01$ eV.

The value of the preexponential factor ν_H observed for the zero-bias stage has the right order of magnitude for a vibrational frequency, as expected for a process governed by a single atomic jump. Furthermore, the difference in the decay rates for hydrogen and deuterium indicates that hydrogen (or deuterium) is the jumping entity. In that case, the preexponential factors should be related approximately by the harmonic relation $\nu_H = \sqrt{2}\nu_D$. The deuterium data in Fig. 2 have been analyzed with $\nu_H = 3.0\times10^{12}$ s^{-1} and the value of ν_D fixed according to the relation above. This leads to an activation barrier $\Delta E_D = 0.30$ eV which is slightly larger than the hydrogen value, reflecting the isotope shift of the zero-point energy. Thus the data in Fig. 2 can be analyzed consistently on the assumption that the zero-bias stage proceeds via a single jump of hydrogen.

The 210-K stage observed under reverse-bias conditions reflects the annealing of the ionized $E3'$ center. The observed preexponential factor $\nu_H = 1.3\times10^8$ s^{-1} is inconceivable, with a single atomic jump controlling the step alone. From the C-V measurements described below it is inferred that two electrons per $E3'$ center are captured during the process. Since essentially no electrons are available under reverse-bias conditions, the "low" preexponential factor may be tentatively explained by the capture process(es) acting as the rate-limiting step.

In order to determine the charge state of the trap, free-carrier profiles have been deduced from C-V measurements carried out at 65 K after carrier injection and after subsequent annealing. Prior to the annealing of $E3'$, the free-carrier profile depends on the C-V ramp frequency ω_r. For frequencies which are much higher than the $E3'$-trap emission rate, $\omega_r \gg e_n$, only a compensating damage profile is observed in the region corresponding to the projected proton range. At low frequencies, $\omega_r \ll e_n$, the carrier profile contains a contribution from a sharp distribution of ionized donors.[21,22] The profile associated with $\omega_r \gg e_n$ has been subtracted from that corresponding to $\omega_r \ll e_n$ and the result, obtained after 170-K preannealing under reverse bias, is shown by the upper curve in Fig. 3. Although this charge profile is distorted and shifted owing to the binding of the electrons to the trap, the area under the curve represents approximately the number of $E3'$ centers per unit area.

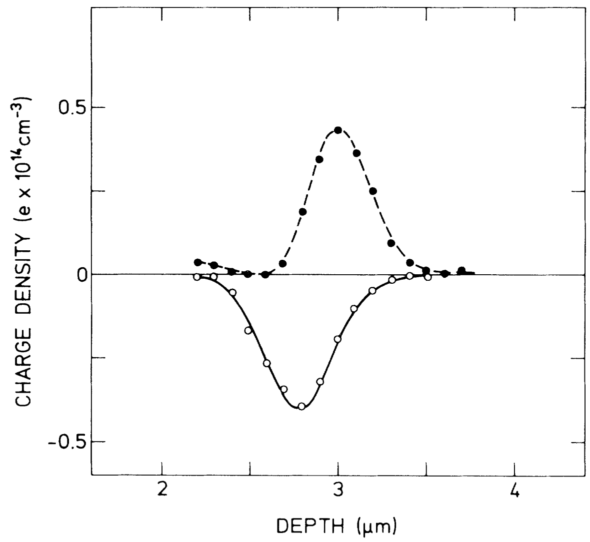

FIG. 3. Change in charge profile during reverse-bias annealing of $E3'$ at 190 K. The charge profiles corresponding to the ionized $E3'$ center present before annealing (upper curve) and to the DLTS-invisible state present after annealing (lower curve) are shown. The profiles display the excess charge relative to the nonionized $E3'$ center.

The corrected areal trap density is estimated to be 1.8×10^9 cm^{-2}, in agreement with the density 1.7×10^9 cm^{-2} estimated from the DLTS signal. Allowing for the losses due to injection ($\approx 30\%$) and preannealing ($\approx 60\%$), the trap density corresponds to $\approx 75\%$ of the implanted dose, 9×10^9 cm^{-2}. Thus close to one $E3'$ level is created per implanted proton. After reverse-bias annealing of $E3'$ at 190 K the free-carrier profile is independent of ω_r. The charge profile shown by the lower curve in Fig. 3 is obtained after subtraction of the free-carrier profile measured prior to annealing with $\omega_r \gg e_n$. In this case, the areal density is 1.9×10^9 cm^{-2}, again roughly equal to the trap density for $E3'$. However, note that the free charge has been reduced. Thus the DLTS-invisible state contains one (two) additional electron(s) compared with the nonionized (ionized) $E3'$ center. The charge profiles shown are in quantitative agreement with similar profiles obtained for zero-bias annealing when interference from a second deep donor ($E_c - E_t = 0.10$ eV), which also anneals at ≈ 100 K, is taken into account.

To summarize, we have shown that the $E3'$ center involves hydrogen (most likely isolated), is metastable, and acts as an electron trap located in the upper part of the band gap. The thermally induced conversion at ~ 100 K (~ 210 K) under zero- (reverse-) bias conditions is associated with capture of one (two) electron(s) and is thus consistent with a transformation between a neutral (positive) metastable configuration and a negative ground state. The metastability explains the previous lack of evidence for a band-gap level of isolated hydrogen in silicon and the reversible conversion observed may help to close the loop in our understanding of this important species. The crucial point in this context is the potential of linking the present experiments to more structure-sensitive techniques such as EPR, infrared-absorption spectroscopy, and channeling. As a matter of fact, the existing data[3,4,6,23] may already indicate such a link, which should be pursued. At the present stage, all the observed properties are in agreement with the theoretical results[8] for the isolated hydrogen impurity in crystalline silicon, which were briefly summarized in the introductory remarks of this presentation. Accordingly (see Fig. 1), we suggest that the $E3'$ signal originates from the metastable hydrogen donor $(0,+)$ at the bond-center position, which transforms reversibly into the acceptor or valence-band resonance $H^-(T)$ at the interstitial tetrahedral site.

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