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Alternating donorlike-acceptorlike configurationally bistable defect in irradiated phosphorus-doped silicon

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Using deep-level transient spectroscopy we have detected a new configurationally bistable defect in heavily phosphorus-doped silicon, electron irradiated at room temperature. The center has the unique property of being electron attractive in one of its configurations and hole attractive in the other. The activation energies for electron and hole emission for the corresponding traps are determined as 0.42 and 0.15 eV, respectively. The configurational transformation of this center can be activated by the cool-down of the sample under applied zero, forward, or reverse bias, but also by certain electrical pulsing schemes. A general model for the bistable defect as a close deep donor-acceptor pair is suggested, where the configurational transformation is accompanied by a partial internal charge transfer in the neutral charge state of the complex defect.

Bistability of defects in semiconductors—and related phenomena such as persistent photoconductivity—are of great current interest. Examples of bistable defects include *DX* centers in $Al_xGa_{1-x}As$ and $GaAs_xP_{1-x}$ (Ref. 1), *EL*2 in GaAs,[2] and in Si the *C* center,[3] and the Fe-acceptor pairs.[4] Recently, two defects exhibiting configurational bistability have been observed in electron-irradiated Si. These are the interstitial carbon-substitutional-carbon pair,[5–7] and a defect in *p*-type Si irradiated at 80 K which is tentatively identified as the substitutional boron-vacancy complex.[8] However, radiation-induced defects in Si which can exist in more than two configurations, and possessing families of associated metastable states were also reported.[9,10]

The existence of configurationally multistable defects was first revealed by electron paramagnetic resonance (EPR) studies of the oxygen-vacancy pair in Si.[11] Later, multistability was probed using photocapacitance techniques, as in the photocapacitance quenching effect of *EL*2 in GaAs.[2] More recently, deep-level transient spectroscopy (DLTS) has proved quite informative when extended to study the alternating structures of bistable centers via their representative electronic states.[12]

In this Rapid Communication we report the DLTS detection of a new configurationally bistable defect center in highly phosphorus-doped *n*-type Si electron irradiated at room temperature. When contrasted to previously reported bistable centers, this center is unique in the sense that its electronic character alternates between being an electron trap in one configuration to being a hole trap in the other. In all bistable or metastable centers reported in Si thus far, the hole-attractive[3,4,8] or the electron-attractive[5–7,9,10] nature of the center is conserved in all of its observed configurations.

The samples used in this study were cut from float-zone (FZ) *n*-Si single crystals heavily doped with phosphorus ($\sim 1.0\times10^{17}$ cm^{-3}). They were provided by Wacker Chemitronics in the form of thin slices with ⟨100⟩ orientation. A Schottky-barrier (SB) contact on the sample was fabricated by Au evaporation. Ohmic contacts were made using Al-Ga alloy. The samples were irradiated with 2.0-MeV electrons at room temperature to a total dose of 1.0×10^{16} e^-/cm^2. DLTS data were retrieved using a standard experimental setup.[13]

It has been shown that the degree of minority-carrier injection in a SB diode is substantially increased provided the barrier height is large and the diode is forward biased.[14–16] This fact, if properly utilized, allows for the DLTS detection of minority-carrier traps in SB diodes, as recently demonstrated by many workers.[17–20] The barrier heights in our samples, as determined from *CV* measurements, lie in the range 0.70–0.90 eV. The capacitance transients were produced in reverse-biased diodes with forward-bias pulses. By so doing we were able to probe both electron and hole traps in our samples. A more elaborate description of the experimental methods involved is reported elsewhere.[21]

Typical DLTS spectra of the defect states observed are shown in Fig. 1. An electron trap $E(0.42)$ and a hole trap $H(0.15)$ are detected, with electron and hole emission activation energies of 0.42 and 0.15 eV, respectively. These traps, apparently reported here for the first time, arise from two configurations of a single defect. This is shown to be true in Figs. 1(a) and 1(b) which show DLTS spectra recorded following sample cool-down under zero- and reverse-bias conditions, respectively. In order to examine this effect more thoroughly, the sample was first cooled from 300 K to a temperature *T* at zero bias; then it was kept for a short time *t* at *T* under a fixed applied bias, and finally cooled rapidly to 77 K. Representative data of such an isochronal ($t = 3$ min) process performed at a reverse bias of 5 V are included in Fig. 2 (solid lines). Remarkably, a clear transmutation behavior of the two DLTS peaks is observed to occur: cooling the sample with an applied reverse bias from above 200 °C [as shown in Fig. 1(b), solid line] causes the decay of the $H(0.15)$ signal, and the correlated growth of $E(0.42)$, whereas below 200 °C [Fig. 1(b), dashed line] the opposite effect is observed to occur. The sum of the two peaks remained constant, i.e., $\Delta H(0.15) = -\Delta E(0.42)$, to within less than 10% of its maximum value (Fig. 2). This phenomenon was found to be reversible; the spectra are reproducible

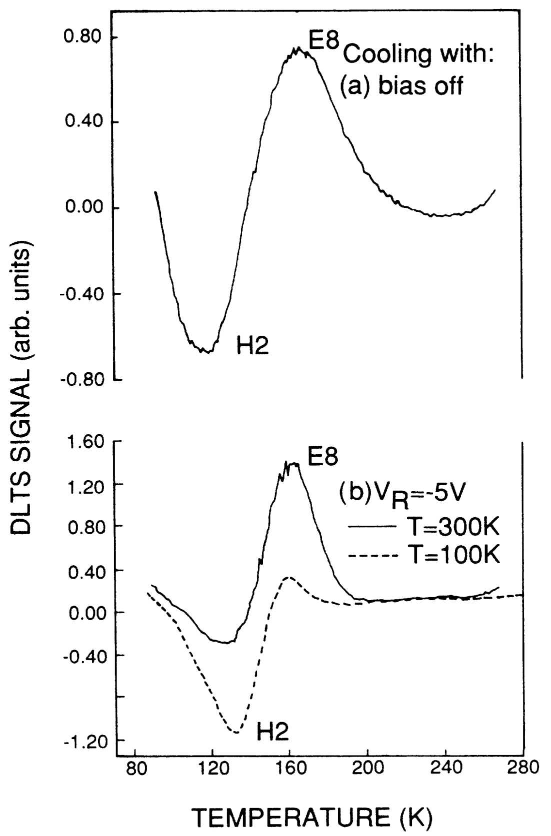

FIG. 1. DLTS spectra taken at a rate window of 6.25 s^{-1}, and an injection pulse width of 60 ms. In (a) the sample is cooled down to liquid-nitrogen temperature with bias off, whereas in (b) the sample is kept for 3 min at an applied reverse bias of 5 V at the indicated temperature before being rapidly cooled down to liquid-nitrogen temperature.

within an error of ± 2 K in temperature and ~10% in the signal intensity, provided the appropriate cooling conditions were applied.

All of the above experimental features exhibited by these two states are typical for configurationally bistable defects.[3,5,6,10] However, when compared to the previously observed bistable centers in Si, the center reported here is distinguishable in the sense that in one configuration it behaves as an electron trap, while in the other configuration the center becomes a hole trap. This is clearly shown by the opposite senses of the two DLTS signals $E(0.42)$ and $H(0.15)$.

In order to reveal whether the observed traps are acceptorlike or donorlike, it is necessary to estimate their carrier-capture cross sections, and hence decide on the charge-state transitions that take place at each of the states $E(0.42)$ and $H(0.15)$. Capture cross sections are commonly determined by reducing the width of the injection pulse t and measuring the decrease in the capacitance transient or the trapped carrier density. That is, for an initially empty electron trap

$$n_T = N[1-\exp(-t/\tau)] , \qquad (1)$$

where n_T is the trapped electron density, N is the the trap density, and the trap filling time τ is expressed in terms of the electron-capture cross section σ_n and its thermal velocity v_n as

$$\tau^{-1} = \sigma_n v_n n_0 , \qquad (2)$$

where n_0 is the free-electron density. Identical equations, with obvious notational changes, apply for hole traps. However, the injected density (p_0) of holes, being minority carriers, must be calculated from the external current. Figure 3 shows some of the observed DLTS spectra

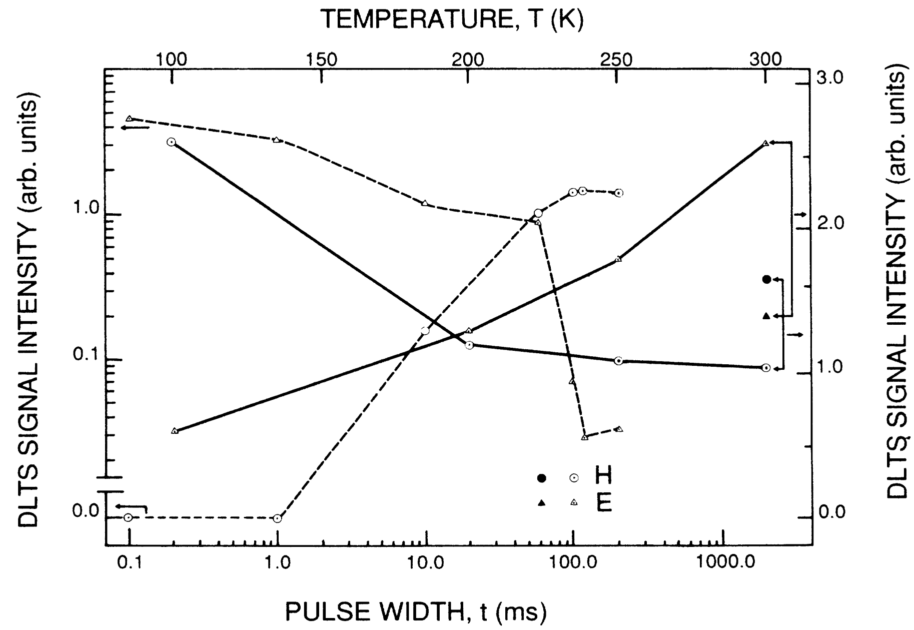

FIG. 2. The DLTS signal intensity plotted vs (i) the temperature (T) at which the sample is kept for 3 min at an applied reverse bias of 5 V before being rapidly cooled down to liquid-nitrogen temperature (solid lines); (ii) the injection pulse width t (dashed lines). The solid symbols represent a zero-bias cool-down of the sample from 300 K to liquid-nitrogen temperature.

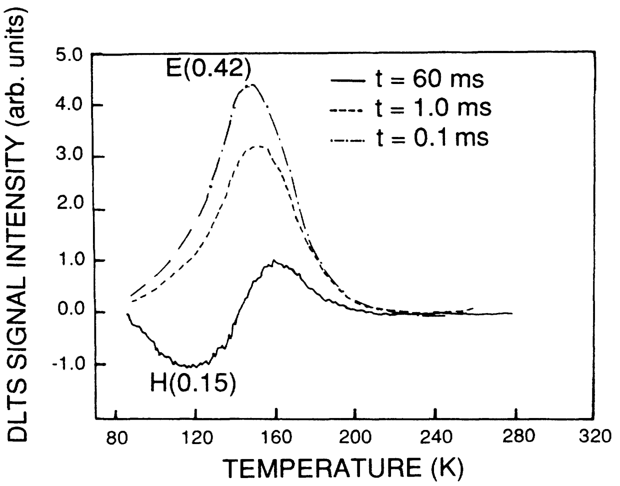

FIG. 3. DLTS spectra recorded at a rate window of 6.25 s^{-1} and different injection pulse width *t*.

recorded for injection pulses of different width *t* (much less than the time between pulses). Prior to recording of the spectra, the diode is cooled down to 77 K at zero bias.

In general, one gets smaller DLTS peaks for shorter pulse widths, since the traps do not have sufficient time for carrier capture: as *t* is increased, the traps are exposed to free carriers for a longer period of time, allowing for more traps to capture a carrier as given by Eq. (1). Contrary to what is usually observed, the signal intensity of $E(0.42)$ decreases with increased *t* as is shown in Fig. 3. Correspondingly, the signal intensity of $H(0.15)$ increases with increased pulse width, however, not in conformity with Eq. (1). Furthermore, the combined total signal intensity of $E(0.42)$ and $H(0.15)$ remained virtually constant for $t > 10$ ms. For a pulse width of 10 ms and below, the concentration of $E(0.42)$ increased considerably, whereas that of $H(0.15)$ decreased below our detection limit. The variations of the trap signal intensities with pulse width, taken under otherwise identical recording conditions, are contained in Fig. 2.

Moreover, it should be noted that such significant variations in the trap signal intensities are effected by relatively small changes in *t*, only in the range of ms. It is, therefore, concluded that the alternation of the center between its two configurations can be activated as well by specifically chosen bias pulsing schemes. This effect is similar, but perhaps not identical, to earlier observations on a bistable center,[22] later identified as an interstitial carbon-substitutional-carbon pair.[5-7] It is, therefore, difficult to differentiate between changes in the trap signal intensity as a function of *t* caused by the configurational transformation of the center, on one hand, and its efficiency in trapping carriers in each configuration on the other hand. Accordingly, estimations of the carrier-capture cross sections for such a center based on the variable pulse width method become untenable.

Alternatively, capture cross sections could be extracted from emission-rate data for the traps, as displayed in Fig. 4. We estimate for the hole-capture cross section σ_p of

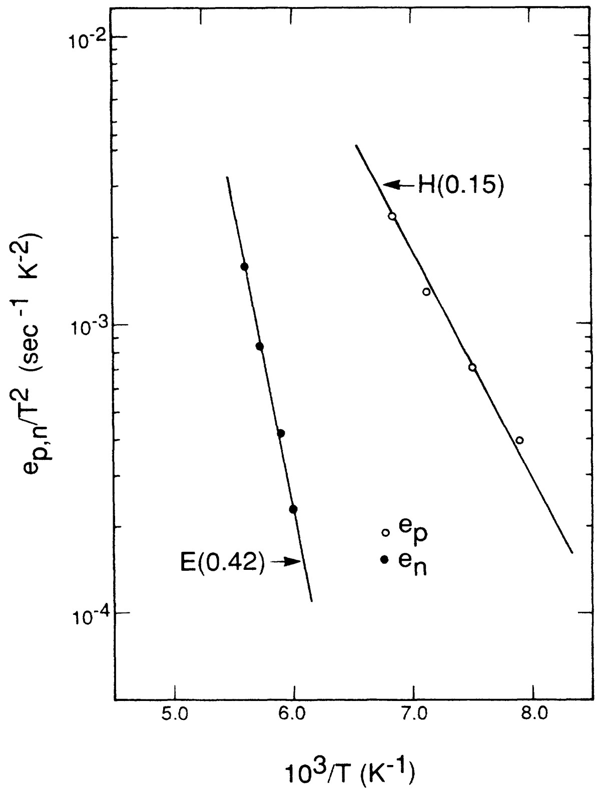

FIG. 4. The temperature dependence of the emission rates for the observed traps.

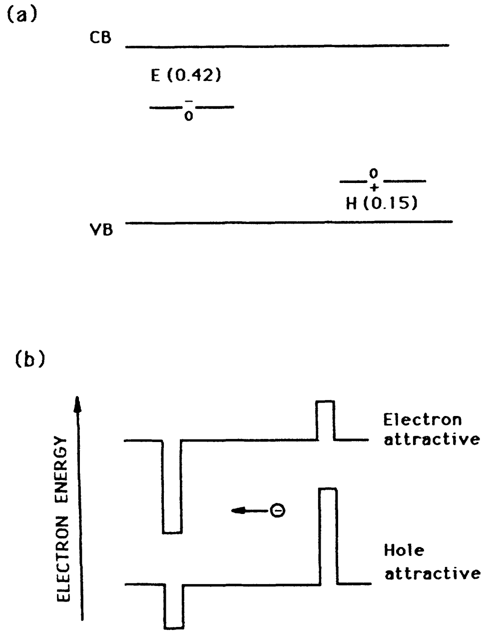

FIG. 5. (a) Trap levels for the defect in the band gap; and (b) a simple sketch of the suggested changes in the defect potential, comprised of an electron-attractive and a hole-attractive part, with a different cancellation in the two different configurations due to a partial internal charge transfer at the defect upon the structural rearrangement.

$H(0.15)$ and the electron-capture cross section σ_n of $E(0.42)$ values in the order of 10^{-18} cm^2 and 10^{-15} cm^2, respectively. The magnitude of these values suggests that the transitions for the hole capture in $H(0.15)$ and the electron capture in $E(0.42)$ are, respectively, between positive and neutral $(+/0)$ and negative and neutral $(-/0)$ charge states of the defect center in its two configurations.[23] It is, hence, phenomenologically deduced that the defect center changes from being donorlike to being acceptorlike as it transforms from one configuration to the other.

The presently available data are insufficient to provide a definite structural picture of the defect in its various configurations. A general model for a bistable defect that would show the observed properties involves a close pair of a deep donor and a deep acceptor. If the relaxation of the defect between the two configurations promotes a partial-charge transfer so as to predominantly leave an electron-attractive potential in one case, and a hole-attractive potential in the other configuration, the observed properties could be reproduced. This is schematically illustrated in Fig. 5. Lacking the defect identity, it is premature to speculate whether the electronic energy changes involved are due to bond rearrangements, alternating sites for an interstitial, or other effects.

We tentatively conclude from the search for this defect in differently doped irradiated FZ silicon, that the defect involves P as one of its constituents. Also the defect is observed to disappear following 30 min annealing at 200 °C. These observations may suggest that a plausible candidate for the deep acceptor in the pair is the phosphorus-vacancy center,[24] which has similar annealing characteristics and, incidentally, possesses an electron trap located at a similar energy position in the gap as the one observed in this study. As for the deep donor component of the pair, the involvement of P is also very likely. This is due to the fact that we were not able to observe this bistable center in FZ samples of P content in the range 10^{15}–10^{16} cm^{-3}, where the P-vacancy center is known to be dominantly generated.[5,10] Complexes involving more than one P atom have been previously reported in heavily P-doped Si.[25]

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