Direct Observation of Electron Capture and Reemission by the Divacancy via Charge Transient Positron Spectroscopy

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(Received 22 November 2012; published 25 March 2013)

Electron capture during forward bias and reemission at zero bias by divacancies in the depletion region of a silicon diode structure at room temperature have been studied for the first time using monoenergetic positrons. The positron response increases essentially linearly with electron current, as a result of increased positron trapping by negatively charged divacancies. The measurements indicate that $\leq 1\%$ of the divacancies become negatively charged in the steady state at a forward bias of 1 V. Changes in the mean positron response when applying a square wave bias to the sample (1 V forward bias and 0 V, duty cycle 1:4, times at 0 V in the range 0.1–100 μs), were consistent with a rapid conversion of doubly to singly charged divacancies (in $\sim 10^1$ ns), followed by slower defilling of the singly charged divacancies with a time constant of $\sim 10^1$ μs. These ac measurements allow determination of the relative populations of singly and doubly charged divacancies. The results provide confirmation of consistency between the positron's response to the silicon divacancy and previously extracted capture and emission kinetics determined through charge transient measurements and assigned to the same defect. The possibility of combining these two, orthogonal techniques suggest a promising new and powerful approach to defect spectroscopy in which the structure and electrical properties of a defect may be determined in a single measurement.

DOI: 10.1103/PhysRevLett.110.136401 PACS numbers: 71.55.Cn, 61.72.jd, 78.70.Bj, 85.30.Kk

The study of point defects in silicon (Si) remains an area of intense activity. The use of such lattice imperfections is common in device engineering and extends to applications such as carrier lifetime modification [1], impurity diffusion retardation [2], impurity gettering [3], and even Si photonics [4].

The emission and capture of charge carriers in Si is well described by Shockley-Reed statistics [5], whereas Simmons and Taylor expanded these ideas to a system of arbitrary traps in a semiconductor subjected to nonequilibrium conditions [6]. For a single trap there are four possible transitions: electron capture, electron emission, hole capture, and hole emission described, respectively, by the rates $v\sigma_n n N_t(1-\alpha)$, $e_n N_t \alpha$, $v\sigma_p p N_t \alpha$, and $e_p N_t(1-\alpha)$. Here n is the electron density, p is the hole density, N_t is the defect concentration, α is the probability of defect occupation by an electron, v is the electron thermal velocity, σ_n is the capture cross section for electrons at the defect, and σ_p is the capture cross section for holes; e_n and e_p are the probabilities for the emission of electrons and holes, respectively. It can be shown that the fraction of occupied defect sites is given by [6]

$$\alpha = (\bar{n} + e_p)/(e_n + \bar{n} + \bar{p} + e_p), \tag{1}$$

where $\bar{n} = v\sigma_n n$ and $\bar{p} = v\sigma_p p$.

In a p-n diode under forward bias, minority carriers are injected across the junction. If the device contains defects in the region of the junction, occupancy for minority carrier trapping defect sites will be nonzero. The direct measurement of the occupancy fraction for these defects is nontrivial. However, the measurement of the emission rate from the filled defects does not normally depend on the occupancy fraction and thus the filling of minority trapping defects using a forward bias pulse, and their subsequent emptying via the removal of that forward bias allows information on the nature of the trap to be obtained via transient charge measurement. The neutral Si divacancy has an associated energy level that resides in the upper half of the band gap and thus divacancies on the p side of a p-n junction may be considered minority trapping defects.

There exist a number of studies of the Si divacancy using transient charge measurement, most often deep level transient spectroscopy (DLTS) [7]. A selection of these studies provides values for σ_n, which can vary from 1 to 3×10^{-15} cm^{-2} [8,9] and an energy level of $\sim E_c -$ 0.4 eV [10]. Markevich *et al.* [11] used DLTS to measure emission rates at low temperatures for the singly and doubly negatively charged divacancy V_2 (i.e., $V_2{}^-$ to $V_2{}^0$ and $V_2{}^{2-}$ to $V_2{}^-$ transitions) for electron-irradiated Si, the two trap levels being 0.41 and 0.23 eV below the conduction band, respectively. Extrapolating their results to room temperature yields mean state lifetimes of 33 μs and 13 ns, respectively.

Because positrons are efficiently trapped by divacancies in Si, and their trapping rate depends on the charge state of the defect [12,13], variable-energy positron annihilation spectroscopy (VEPAS) is a strong candidate for probing changes in the V_2 charge state in the depletion region of Si diode structures under different bias conditions. In 2006 [14] Beling *et al.*, recognizing this potential, proposed an approach they termed "vacancy-sensing positron DLTS (PDLTS)," which they considered to be the one variation of PDLTS with great potential use. To overcome the main barrier against successful implementation of the technique—that the electric field required to change the charge state of the vacancy defects also drifts the positron away from the volume of interest—they proposed, but did not implement, the use of a Schottky diode with high injection, under forward bias, to provide free carriers from the rear of the sample to be trapped in defects.

In the current work, we use an n-p junction to inject carriers from the n side to the low-doped p side of a sample that has $\sim 10^{17}$ cm^{-3} defects. The combination of the low-doped p side with the much higher concentration of defects, plus the fact that the n-p diode is a minority carrier device (with an enormous injection of free electrons when in forward bias), means that any electric field in the device is not large enough to sweep the positrons out of the volume of interest, while the defect concentration is large enough to obtain a measurable positron signal. This design of sample diode allows us, for the first time, to perform the vacancy-sensing PDLTS experiment.

The sample used is represented by Fig. 1. The diode structure was formed by a phosphorus-doped ($>10^{19}$ cm^{-3} peak concentration) Si region 5 mm in diameter and 600 nm in depth from the top surface of a 4-μm-thick boron-doped (10^{15} cm^{-3}) Si layer epitaxially grown on a similarly doped substrate. A 100-nm-thick SiO_2 layer surrounds the diode. The bias was applied across the diode by a sprung wire to a 300-nm-thick Al contact on the n-type Si surface, the gold-coated back surface of the Si substrate being permanently grounded. The depletion region extends from the n-Si/p-Si interface for approximately 0.5–1 μm at zero bias. Divacancies were introduced into the diode by blanket 1.5 MeV boron ion (B^+) implantation at a dose of 10^{13} cm^{-2}; their presence is denoted by the small open circles on the diagram, and their depth distribution is represented by results from the simulation program SRIM [15].

The B^+ ion dose was chosen so as not to destroy the diode properties of the structure—i.e., to create an average V_2 concentration in the depletion region of $\sim 10^{17}$ cm^{-3} [16]. This was verified by measuring the I-V characteristics of identical diodes with and without B implantation; in reverse bias the current increased to 320 and 50 μA at 5 V, and in forward bias to—1 mA at -0.3 and -0.6 V, respectively. The chosen B^+ dose was several orders of magnitude lower than that required for amorphization; neither the implanted B, which is located well beyond the region of interest, nor native B, C, and O, whose concentrations are more than two orders of magnitude lower than that of the V_2, can form dominant complexes

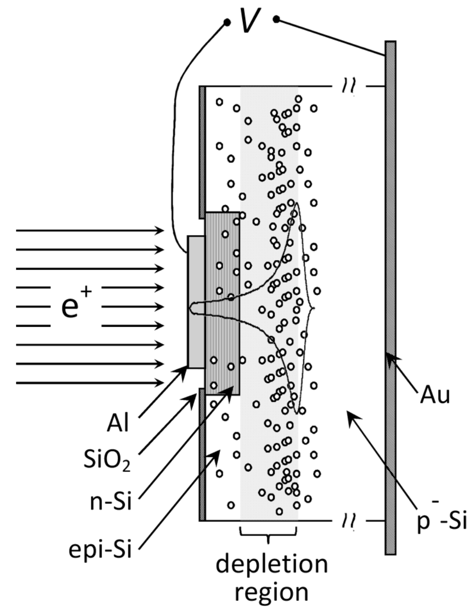

FIG. 1. Schematic sample diagram. Horizontal dimensions are to scale; on the same scale, vertical dimensions are reduced by a factor of 10^3. The bell-shaped curve represents the results of a SRIM simulation of vacancy depth profile [15]. The small circles are sketched to represent vacancy-type damage.

with the V_2; and small vacancy clusters do not form unless the ion dose is close to the amorphization threshold [16] or after annealing to several hundred °C [17]. Finally, we have performed DLTS measurements on similar samples, which show that the overwhelmingly dominant defect acting as a midgap trap is the divacancy.

VEPAS was performed on the unimplanted and implanted diodes using a 4-mm-diameter positron beam. Initial measurements of the Doppler-broadened line shape parameter S [18] as a function of incident positron energy E demonstrated that at $E = 18$ keV the measured value of S represented the mean value characteristic of the depletion region.

With E fixed at 18 keV, S was then measured for diode bias voltages from -1 to $+10$ V (Fig. 2). The small decrease in S at high reverse bias (i.e., when the applied voltage is positive) reflects the decrease in the positron trapping rate as the positron (drift) velocity increases. However, the significant change in S seen from 0 to -1 V (forward) bias reflects the increase in the fraction of divacancies, which have trapped one or two electrons as the diode current increases. The increase in S shows an approximately linear dependence on diode current above ~ 1 mA (Fig. 3). The observed increase in S reflects the increase in the trapped positron fraction resulting from the higher specific trapping rate for positrons in negatively charged V_2 [12,13,19].

The mean (neutral) ${V_2}^0$ concentration C in the depletion region for the implanted diode under zero bias can be estimated [16] to be 4.4×10^{17} cm^{-3} from the measured

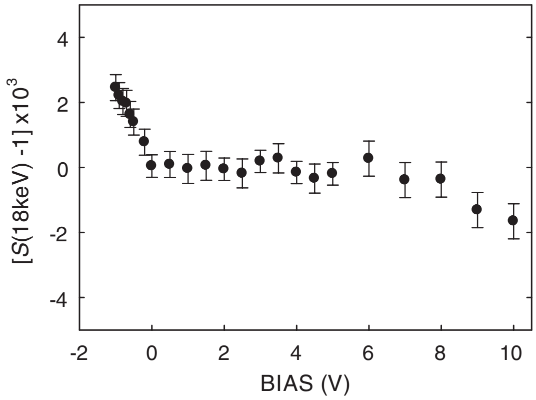

FIG. 2. ΔS (18 keV) for the implanted diode as a function of bias. ΔS is the difference between S (18 keV) for the implanted diode and its mean value under low reverse bias conditions, multiplied by 10^3.

S value for the defected region normalized to the bulk value ($S = 1.020$) and the S value characteristic of V_2 ($S_D = 1.036$). The trapped positron fraction, f_0, is $(S - 1)/(S_D - 1) = 57\%$. When -1 V bias is applied, S increases to 1.0223 and the trapped fraction f is 64%.

Now if f_0 and f_C are the fractions trapped in neutral and charged V_2, we can write

$$f_0 = \{1 + \lambda/[\nu_0(1 - \alpha)C]\}^{-1}, \quad (2)$$

$$f_C = [1 + \lambda/(m\nu_0\alpha C)]^{-1}, \quad (3)$$

where λ is the positron decay rate in undefected Si (4.54×10^9 s^{-1}), ν_0 is the specific positron trapping rate for ${V_2}^0$ (6.8×10^{14} s^{-1}) and $m\nu_0$ for ${V_2}^-$ and/or ${V_2}^{2-}$. If one then substitutes the values above for f, λ, ν_0, and C, one can solve the resulting quadratic equation to obtain α as a function of m. This yields the result that, under forward bias of -1 V, α is only of the order of a few percent; e.g., if $m \geq 10$ [19] then α is below 1%.

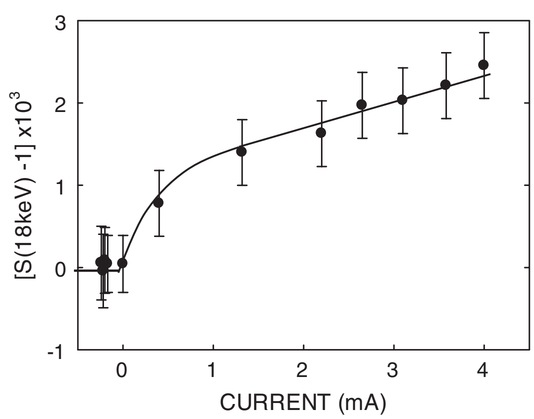

FIG. 3. ΔS (18 keV) for the implanted diode as a function of current. ΔS is the difference between S (18 keV) for the implanted diode and its mean value under low reverse bias conditions, multiplied by 10^3.

In order to estimate α the structure described here, under bias of -1 V, has been simulated using the software code ATLAS (Silvaco). ATLAS calculates α in a manner consistent with Ref. [6]. The sensitivity in defect occupancy is dominated here by the coupled parameters representing the electron and hole capture cross sections (σ_n and σ_p). If we assume that the dominant defect is ${V_2}^0$ (in the unbiased case) at 5×10^{17} cm^{-3}, one can reasonably assign $\sigma_n = 2 \times 10^{-15}$ cm^{-2} [8,9] and a trap level of 0.4 eV below the conduction band [10]. Figure 4 shows the concentration of ionized defects as a function of depth for a range of values of σ_p. It is clear that if $\alpha \sim 1\%$, $\sigma_p \sim 1 \times 10^{-15}$ cm^{-2} or greater, a value at the upper end of expectation, but not unreasonable.

First measurements of the defilling rate of charged V_2 have been made by applying a square-wave bias to the diode, as shown schematically in Fig. 5. -1 V was applied for 20% of the duty cycle, as the filling rate is considered to be so fast ($\sim$ ns) that the V_2 can be considered to be in the equilibrium charged state throughout this part of the cycle. When the bias is removed, for a preset time T, the number of charged V_2 decreases exponentially with a time constant τ whose value depends on the charge state. This occurs as a result of electron emission and hole capture in the now present depletion region. $\Delta S(0)[= 0.0023(1)]$ was measured at regular intervals by alternating the diode bias (in dc mode) between -1 and 0 V and measuring S in each state to a high level of accuracy, multiplying by 80% before using as the $T = 0$ value on a plot of $\Delta S(T)$ values determined using the square-wave bias technique.

Figure 6 shows the experimental results for the square-wave measurements. $\Delta S(T)$ precipitously falls at $T < 100$ ns. This is consistent with the defilling of ${V_2}^{2-}$ to ${V_2}^-$ with a decay time of 13 ns, obtained by extrapolating low-temperature Arrhenius plots using data from

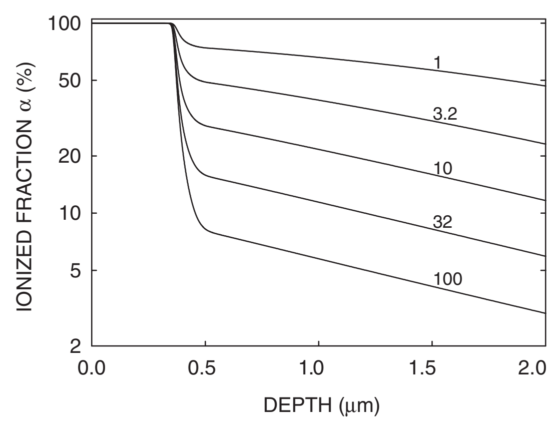

FIG. 4. Simulation results, for the diode structure used in these studies under a bias of -1 V, for the fraction of charged V_2 as a function of depth: plot labels are hole capture cross sections in 10^{-17} cm^2: trap energy level = 0.4 eV: trap (V_2) concentration = 5×10^{17} cm^{-3}: electron capture cross section = 2×10^{-15} cm^2.

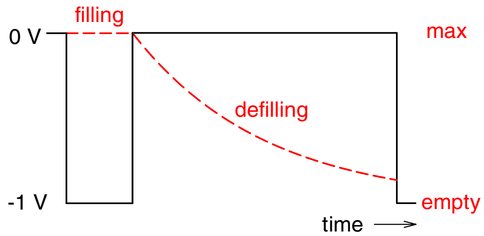

FIG. 5 (color online). Solid (black) line: diode bias, with a duty cycle of 1:4 (on:off). Typical time periods: 1–50 μs. Filling in the "on" state is assumed to be essentially instantaneous in the time scales used, and defilling in the "off" state is represented by an exponential decrease of charged V_2 concentration, represented by the dashed (red) line.

Refs. [7,11]. Therefore we can compute $\Delta S(T)$ as follows, considering all the charged V_2 to be V_2^- at $T = 0$ and emptying with a single time constant τ_1. During any T, the fractional positron response to V_2^- is determined by $F_C(T)$, the fractional area beneath the exponential in the defilling rectangle:

$$F_C(T) = (\tau_1/T)[1 - \exp(-T/\tau_1)]. \quad (4)$$

The change in S, $\Delta S, = [S - S(0)]$, is proportional to the fraction of positrons trapped in V_2^-. Thus

$$\Delta S(T)/\Delta S(0) = [1 + \lambda/(\nu_1 \alpha C)]/\{1 + \lambda/[\nu_1 \alpha C F_C(T)]\}, \quad (5)$$

where ν_1 is the specific positron trapping rate for V_2^-.

The solid line in Fig. 6 uses $\tau_1 = 10$ μs in the expression for $F_C(T)$, which is of the same order as the value of 33 μs for the V_2^- to V_2^0 transition obtained by extrapolating the DLTS data of Ref. [11] to room temperature. It should be stressed that the present data only suggest that $\tau_1 \sim 10^1$ μs; the nonzero measurement at $T = 100$ μs suggests that a τ_1 of $\sim$30 μs is possible.

Information can be extracted from Fig. 6 about the specific positron trapping rates for, and the relative populations of, singly and doubly charged V_2. Let the almost instantaneous decrease of ΔS near $T = 0$ be represented by the ratio $R = \Delta S(0)/\Delta S(100\ \text{ns})$. ΔS is proportional to the fraction of positrons trapped in the charged defects, i.e., $[1 + \lambda/\nu C_C]$, where C_C is the corresponding concentration of charged defects. If C_C is small, as is indicated by the low value of α, then $\lambda/\nu C_C \gg 1$ and $\Delta S \propto \nu C_C$. We can therefore write

$$\begin{aligned} R &\approx [n\nu_1(1 - \beta)C_C + \nu_1 \beta C_C]/[\nu_1 C_C] \\ &= [n + \beta(1 - n)], \end{aligned} \quad (6)$$

where $n\nu_1$ is the specific positron trapping rate for V_2^{2-} and β is the fraction of charged defects in the V_2^- state at $T = 0$. If one assumes a value for n then measurement of R yields a value for β. Figure 6 gives $R = 3.5$; this suggests $n = 3.5$ and $\beta = 0$—i.e., all of the charged defects at

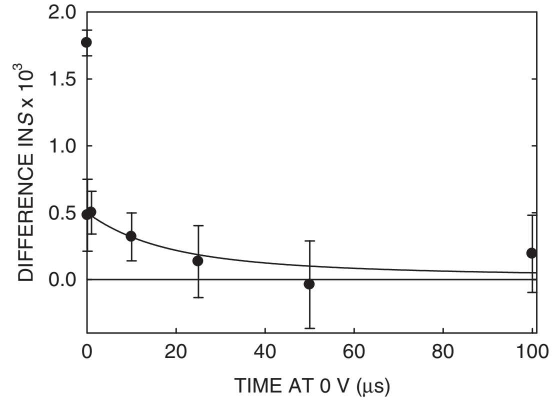

FIG. 6. ΔS (18 keV) as a function of time spent at 0 V (in each duty cycle—see Fig. 6). The solid line represents a defilling time constant (for singly charged V_2) of 10 μs.

$T = 0$ are in the V_2^{2-} state; a value of $\beta < 1$ would require $n > 3.5$, which is inconsistent with earlier evidence [19].

In summary, charge transient positron spectroscopy has yielded information on negatively charged V_2 in a Si n-p diode structure. In forward bias the positron response increases as $\leq 1\%$ of the defects become negatively charged. By applying a square-wave bias to the diode the emptying of the divacancies at room temperature was studied and the results were consistent with the V_2^{2-} to V_2^- transition having a time constant $\tau \sim 10^1$ ns followed by the much slower V_2^- to V_2^0 transition with $\tau \sim 10^1$ μs. This ac technique allows direct estimation of the relative populations of singly and doubly charged V_2 in the biased diode.

This is the first demonstration of a technique that provides both structural information on a defect and its electrical properties (i.e., the carrier capture and emission rates and the determination, with the aid of simulations, of electron and hole capture cross sections for V_2 in an n-p diode under forward bias). This method may be applied to a range of defects in various semiconductor structures and, with the extension to temperature variable measurements, the energy of the level within the band gap may be extracted.

This work was supported by the Natural Sciences and Engineering Research Council of Canada. The Bath positron group is supported by EPSRC, UK.

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