## Capacitance transient studies of a metastable defect in silicon

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Capacitance-transient-spectroscopy measurements were undertaken to study the properties of a previously reported, electron-irradiation-induced defect in silicon. This defect has been attributed to the boron substitutional-vacancy pair. It appears in two metastable configurations and exhibits at least three electrical levels in the deep-level transient capacitance spectrum.

## INTRODUCTION

Capacitance-transient spectroscopy<sup>1,2</sup> is generally used to obtain quantitative information, i.e., activation energies and capture cross sections for defects in semiconductors. The above two parameters which provide the identity of a defect level inside the forbidden gap are calculated from the well-known Arrhenius analysis  $[\ln(e/T^2) \text{ vs } 1/T]$ . Capture cross sections can also be found more accurately by using the pulse width variation method.<sup>1</sup>

Capacitance-transient spectroscopy can also be used to study alternate structures of metastable defects through their electronic states.<sup>3,4</sup> The energy levels alter when the configuration of the metastable defects changes due to regulations of their charge state. The above changes result in a transformation of the spectrum. In case that a defect exhibits two metastable configurations, there is a procedure that exists in order to reveal them. It involves annealing of the sample at a certain temperature either with or without the simultaneous application of a reverse bias voltage so that the defect acquires the desired configuration. Then the sample temperature is quickly lowered in order to freeze the defect in that configuration. In a p-type material a hole trap lies in the lower half of the energy gap. The application of a reverse bias shifts the Fermi level above the defect level. Therefore, the trap becomes empty and the corresponding configuration is formed. On the other hand, if no bias is applied, the defect level lies above the Fermi level; the trap captures holes, and then the second configuration is favored. A thorough study of configurationally bistable defects in semiconductors has been reported recently by M. Levinson.<sup>5</sup>

G. D. Watkins was the first who identified an EPR spectrum labeled Si-G10 as arising from a lattice vacancy trapped by a substitutional boron in float-zone silicon.<sup>6</sup> He did not trace any hyperfine structure caused by boron. However, he concluded indirectly the presence of a boron atom as the next-nearest neighbor to the lattice vacancy. Later electron-nuclear double resonance (ENDOR) measurements proved the presence of a boron atom in the defect center.<sup>7</sup> Recent deep-level transient capacitance spectroscopy (DLTS) measurements have shown that this center reveals two metastable configurations and displays at least three levels in the DLTS spectrum: (a)  $E_{\nu} + 0.31$  eV, (b)  $E_{\nu} + 0.37$  eV, and (c) another one with energy E, smaller than 0.13 eV, above the valence band.<sup>8</sup>

## EXPERIMENT

The samples used were Schottky diodes fabricated by evaporation of very pure aluminum on boron-doped floatzone silicon wafers with nominal resistivities of (0.85-1.15), 1.45, (6.4-7.4), and 9  $\Omega$  cm. C(V) analysis revealed uniform acceptor concentrations with corresponding values of  $2.1 \times 10^{16}$ ,  $1.4 \times 10^{16}$ ,  $2.1 \times 10^{15}$ , and  $1.3 \times 10^{15}$ cm<sup>-3</sup>. The larger part of the aluminum electrode was transparent in laser illumination to make feasible minoritycarrier trap spectroscopy (MCTS) measurements, but a small part of the electrode was thick enough to allow electrical contact needed for DLTS.

1.5 MeV electrons from the Van der Graaf accelerator of Reading University (England) irradiated the specimens at a beam current of 0.33  $\mu$ A, with a dose of  $3.5 \times 10^{16} e^{-}/cm^{2}$ , at 80 K. A liquid-nitrogen flow cryostat with provision for *in situ* irradiation, DLTS and MCTS measurements, was used. For the MCTS measurements a GaAs laser was mounted on the quartz window of the cryostat. During DLTS and MCTS measurements a reverse bias voltage  $V_R = 5$  V was applied. Allowing for the built-in potential (about 0.7 V for our specimens), a filling pulse with an amplitude of 5.8 V was used to fill all the traps.

Our pulse generator was unable to give square pulses with widths below  $0.5 \,\mu$ s. Thus, there was a limit regarding the capture cross-section measurements with the pulse width variation method. The reported capture cross sections are for the temperature where the peaks appeared in the spectrum. No temperature correction was made. The error in the reported values of the activation energies is about  $\pm 0.02 \,\text{eV}$ .

## **RESULTS AND DISCUSSION**

DLTS scans were taken at first on a Schottky diode with a 9  $\Omega$  cm resistivity, in the temperature range of 80-150 K and revealed four peaks:  $H_1$ ,  $H_2$  ( $E_v + 0.19$  eV),  $H_3$  ( $E_v + 0.29$  eV), and a low-concentration peak  $H_9$  ( $E_v + 0.16$  eV).  $H_1$  has been previously identified as the vacancy level with energy  $E_v + 0.13$  eV,  $H_2$  as the divacancy, and  $H_3$  as the carbon interstitial.<sup>8</sup>

Afterwards, we extended the temperature range to 220 K. There was hardly any change in the spectrum in the first scan. Then an annealing (with bias off) was performed for

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FIG. 1. The production rate of  $H_4$  vs boron concentration.

30 min at 220 K to facilitate the migration of the vacancy. After that the specimen was cooled quickly at 80 K and the DLTS measurement began. A scan with a rate window (RW) operating at 5  $s^{-1}$  revealed the following transformations in the spectrum:  $H_1$  has disappeared,  $H_2$  has increased its height by  $\sim 15\%$ , and two new peaks  $H_4$  and  $H_5$ have appeared. The vacancy-dependence of  $H_2$ ,  $H_4$ , and  $H_5$ is obvious. The peak amplitude of  $H_4$  is slightly larger than  $H_5$  which seems to decay during scanning. Afterwards, any DLTS scan that was made with the temperature increasing or decreasing in the range 80-220 K has shown that the peak amplitudes of  $H_4$  and  $H_5$  are very low in comparison with the amplitudes which they exhibited in the first scan. This reduction of the amplitudes did not happen if the measurements were restricted below 180 K. The energy levels for  $H_4$  and  $H_5$  were calculated as  $E_v + 0.31$  eV and  $E_v + 0.38$ eV, respectively. A scan with the fastest available rate window operating at 2500  $s^{-1}$  partially revealed another peak



FIG. 2. The percentage of vacancy conversion to  $H_4$  and  $H_5$  vs boron concentration.

 $H_8$  in the range of 80 K.  $H_8$  also appears when the specimen undergoes an annealing at 220 K with the bias on, and it is always present at scanning either with increasing or decreasing temperature.  $H_8$  disappears after annealing at 220 K with bias off, which results in the regeneration of  $H_4$  and  $H_5$ . From the previous analysis it becomes evident that  $H_4$ ,  $H_5$ , and  $H_8$  belong to the same defect center. However, due to the lack of any information for the spectrum below 80 K, we do not know if another level exists.

The proposed model of a bistable defect<sup>8</sup> with two charge-state related metastable configurations (configuration A, with levels  $H_4$  and  $H_5$  established after annealing with bias off, and configuration B, with at least one level  $H_8$  es-



FIG. 3. The DLTS and MCTS spectrum of boron-doped, float-zone silicon,  $\rho = 9 \Omega$  cm, after 1.5 MeV electron irradiation at 80 K. Solid curve: after annealing at 220 K with bias off (RW=5 s<sup>-1</sup>); Dashed curve: after annealing with bias on (RW=5 s<sup>-1</sup> for peaks  $H_4$  and  $H_5$  and RW=2500 s<sup>-1</sup> for peak  $H_8$ ). The arbitrary unit on MCTS axis is four times larger than on DLTS axis.

tablished after annealing with bias on) fits very well the above results. The transformation, A to B, is thermally activated at a temperature  $T_{A \rightarrow B}$  around 180 K. Consistent with this, peak  $H_4$  is slightly higher than  $H_5$ . This happens because with the used rate windows we either have  $T_4 < T_{A \rightarrow B} < T_5$ , which means that  $H_4$  is stable and  $H_5$  decays, or  $T_{A \rightarrow B} < T_4 < T_5$ , which means that  $H_5$  decays faster than  $H_4$ .

The measurements were repeated with samples of different resistivities irradiated under the same conditions. Figure 1 shows that the production rate of  $H_4$  increases with boron concentration. Figure 2 shows that the percentage of vacancy conversion to  $H_4$  and  $H_5$  also increases with boron concentration. The boron dependence of  $H_4$  and  $H_5$  is obvious. We extend this boron dependence to boron association. This is consistent with the fact that  $H_4$ ,  $H_5$ , and  $H_8$ are not present in pulled silicon<sup>9</sup> where the oxygen concentration is higher; in the competition with boron for trapping the vacancy the oxygen prevails. The whole analysis strongly suggests that the defect center with levels  $H_4$ ,  $H_5$ , and  $H_8$ is the boron substitutional-vacancy pair  $(B_s - V)$  in accordance with previous results.<sup>6,8</sup> Hall coefficient and conductivity measurements<sup>10</sup> after low-temperature electron irradiation are also consistent with the above results in borondoped, but not in aluminium or galium-doped, float-zone silicon. However, we know that the aluminium-vacancy pair has quite different properties.11,12

In the course of this investigation the minority-carrier trap spectrum measurement has been taken in order to find out any complementary behavior between the features of the latter and those of the metastable defect. Four minority traps were traced:  $E_1$  ( $E_c - 0.17 \text{ eV}$ ),  $E_2$  ( $E_c - 0.24 \text{ eV}$ ),  $E_3$  ( $E_c - 0.36 \text{ eV}$ ), and  $E_4$  ( $E_c - 0.45 \text{ eV}$ ). The application of the standard procedure of quenching under zero or 5 V reverse bias did not show any changes in the features of these defects or any other relation to the metastable properties of ( $B_s - V$ ). Figure 3 gives the DLTS and MCTS spectrum



FIG. 4. Capture cross-section analysis for  $H_{4}$ .

measurements after annealing of the vacancy for the sample with resistivity  $\rho = 9 \Omega$  cm.

A capture cross-section analysis of  $H_4$  was done by using the slowest available RW of  $0.4 \text{ s}^{-1}$ , which gives a trace of  $H_4$  at a temperature around 145 K. This temperature is clearly lower than that of the transformation of the configurations. By using the pulse width variation method we drew the plot of  $\log_{10}(S_0 - S)$  vs  $t_p$ . S is the height of DLTS peak for a filling pulse width  $t_p$ , and  $S_0$  the saturated DLTS peak height when all the traps are full. Figure 4 shows that two straight lines can be fitted with the data indicating two capture rates for  $H_4$ . The corresponding capture cross sections are  $1.94 \times 10^{-19}$  cm<sup>2</sup> and  $1.30 \times 10^{-19}$  cm<sup>2</sup>.  $H_4$ lies on the right-hand side of  $H_3$  which has been attributed to the carbon interstitial. However, it is rather difficult to



FIG. 5. 10 min isochronal annealings under zero-bias conditions for  $H_4$ .

associate either one of the above centers with the carbon interstitial which has a capture cross-section value around  $7 \times 10^{-18}$  cm<sup>2,12</sup> Clearly this method cannot be used to measure the capture cross section of  $H_5$ . We have seen that  $T_5 \ge T_{A \to B}$ . Since we know that the conversion  $A \to B$ takes place during the trap filling pulse, and the conversion  $B \to A$  tends to occur during the time intervals between the pulses, it is evident that the capture rate of  $H_4$  is affected from these transformations. Thus, the corresponding DLTS signal is too complex to be analyzed in a simple manner.<sup>5</sup> An Arrhenius analysis showed the value for the capture cross section of  $H_5$  to be about  $5 \times 10^{-17}$  cm<sup>2</sup>.

An attempt to study the regeneration of  $H_4$  versus temperature by zero bias annealings has shown (Fig. 5) that  $H_4$  becomes unstable around 270 K, and it disappears after a few hours at room temperature. The above results are consistent with those in Ref. 6, where EPR measurements were performed on samples with the Fermi level pinned to the boron acceptors so that the defect was in configuration A.

Finally, we should notice that  $H_6$  ( $E_v + 0.60$  eV,  $\sigma = 6$ 

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 $\times 10^{-20}$  cm<sup>2</sup>) was observed to increase its height as  $H_4$  and  $H_5$  vanish. Since it is not known if the  $(B_s - V)$  anneals out by dissociation or by migration as an entity, we cannot state that  $H_6$  involves the vacancy or the boron or if it is a more complicated center.

Evidently the study of defects exhibited metastable configurations, and the determination of their kinetics parameters will improve generally our understanding about defects in semiconductors. The microscopic identity of such defects is still unknown. To this end, a repetition of our experiment using EPR, or ENDOR, or both the techniques, could provide useful information.

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