

***E* Center in Silicon Has a Donor Level in the Band Gap**

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It has been an accepted fact for more than 40 years that the *E* center in Si (the group-V impurity—vacancy pair)—one of the most studied defects in semiconductors—has only one energy level in the band gap: namely, the acceptor level at about 0.45 eV below the conduction band. We now demonstrate that it has a second level, situated in the lower half of the band gap at 0.27 eV above the valence band. The existence of this level, having a donor character, is disclosed by a combination of different transient-capacitance techniques and electronic-structure calculations. The finding seriously questions some diffusion-modeling approaches performed in the past.

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The *E* center in silicon, consisting of a vacancy trapped next to a substitutional group-V atom (P, As, Sb) is not only one of the most studied defects in semiconductors, if not the most, but also one of the most important. Suffice it to mention that diffusion of the technologically important group-V dopants (P, As, Sb) takes place via this defect [1], and that electrical deactivation of donor atoms often is a result of the formation of this defect. A complete knowledge of the physical parameters of this defect, including its different charge states, is therefore a prerequisite for any modeling of dopant diffusion in silicon, and the more so as these parameters enter into all process simulators for the design of silicon-based integrated circuits [2]. The *E* center was first identified by Watkins and Corbett in 1964 [3] using electron paramagnetic resonance (EPR) measurements of electron irradiated silicon, and it was already established by Watkins and Corbett that it introduces an acceptor level at about 0.4 eV from the conduction-band edge  $E_C$ . The level position has later on been confirmed by numerous deep level transient spectroscopy (DLTS) investigations, and only small differences between the level positions of the PV ( $E_C - 0.45$  eV), AsV ( $E_C - 0.47$  eV), and SbV ( $E_C - 0.44$  eV) pairs have been established [4]. The center anneals at temperatures between  $\sim 350$  and  $\sim 450$  K, the exact temperature depending mainly on the charge state of the center [5,6]. It is not established whether the center anneals by dissociation or migration to sinks; there are experimental indications of both processes taking place [7,8].

The above have broadly been the accepted characteristics of the *E* center in silicon for 40 years. In this Letter we will present experimental and theoretical evidence pointing unambiguously towards the existence of a donor level of the PV pair in addition to the well-known acceptor level. The donor level is situated in the lower part of the

energy gap at an energy of 0.27 eV from the valence band edge  $E_V$ , and has probably lain hidden for 40 years because *p*-type Si, which is typically used for DLTS investigations of the lower half of the band gap, does not normally contain group-V impurities, and because the positive charge state of the *E* center is not paramagnetic and hence not visible with EPR. The possibility of a positive charge state of the PV pair was, however, included in some early models of dopant diffusion in silicon, but it was done so without any experimental justification [9]. Also first-principles local-density formalism cluster theory has previously suggested a donor level at  $E_V + 0.2$  eV with a precision of 0.2 eV [10], but it was questioned by the authors if it was a band-gap level with reference to the lack of experimental observation of a donor level.

Three different versions of space-charge capacitance transient spectroscopy have been used: standard deep level transient spectroscopy (DLTS) [11], in which the filling of the deep energy levels with charge carriers takes place by pulsing a reverse biased diode to zero bias, and where consequently only majority carriers are injected, Laplace DLTS [12] in which the emission-rate resolution is improved significantly, and minority-carrier transient spectroscopy (MCTS) [11] in which the filling with charge carriers is done optically and where both majority and minority carriers are injected. From an Arrhenius analysis of the carrier-emission rates versus reciprocal temperature the so-called “finger prints” can be extracted [11]: these are the energy-level positions relative to one of the band edges and the carrier-capture cross sections. In addition, from the heights of the DLTS peaks the concentration of the corresponding defects can be extracted.

Both  $n^+p$ - and  $p^+n$ -mesa diodes were used. The highly doped  $n^+$ - and  $p^+$ -top layers were made by molecular-beam epitaxy (MBE) on 4" silicon wafers which produces

very abrupt junctions. The thicknesses of the top layers were typically  $0.35 \mu\text{m}$ , and they were doped with arsenic or boron, respectively, to concentrations of  $\sim 10^{19} \text{ cm}^{-3}$ . The  $n$ -type Si wafer was a  $1 \Omega \text{ cm}$  ( $\sim 5 \times 10^{15} \text{ P/cm}^3$ ), (001) oriented, float-zone refined wafer. The  $p$ -type wafers were covered with  $\sim 5 \mu\text{m}$  thick chemical-vapor deposited (CVD)  $p$ -type layers of resistivities of  $\sim 2 \Omega \text{ cm}$  ( $\sim 8 \times 10^{15} \text{ B/cm}^3$ ). The experiments were performed within these CVD-deposited layers. The reason for using CVD deposited  $p$ -type layers was that the oxygen and carbon concentrations have been measured to be about a factor of 100 lower than in float-zone Si. It is well established that irradiation-induced defect complexes involving carbon and oxygen produce energy levels in the lower half of the band gap [4], the presence of which would have made the identification of the  $E$ -center donor level very difficult. The formation of the mesa diodes was done using photolithography and chemical etching.

Figure 1 shows DLTS and MCTS spectra of a  $p^+n$  diode after an irradiation at room temperature with 2-MeV electrons. The DLTS spectrum is a typical spectrum from  $n$ -type Si of resistivity around  $1 \Omega \text{ cm}$  having a dominant peak from the acceptor level of the PV center, and a small peak from the double-acceptor level of the di-vacancy ( $VV^{=/-}$ ). Within the PV peak there is a contribution from the single-acceptor state of the di-vacancy ( $VV^{-/0}$ ) of an intensity equal to that of the double-acceptor peak. The small shoulder at about 170 K has not been identified. The MCTS spectrum shows two minority-trap lines (the negative “peaks”) and one majority-trap peak (the positive). The majority peak stems from the  $E$ -center acceptor level. The reason for detecting both electron and hole traps in the same MCTS scan is due to the fact that when shining light from the front side, both types of carriers are injected in the depletion region although most of them are minority carriers (holes). As shown in Fig. 2, the minority-trap line

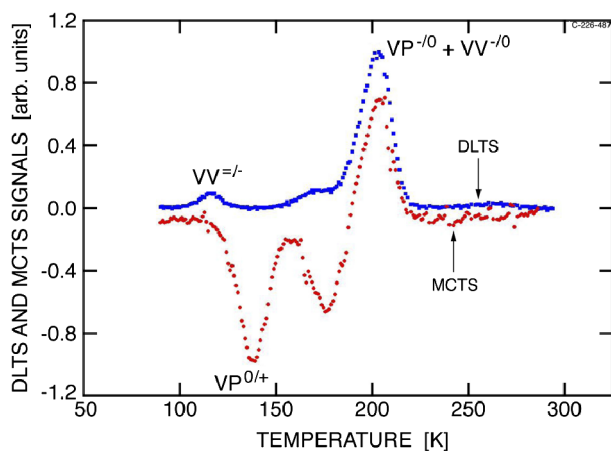


FIG. 1 (color online). DLTS and MCTS spectra of a silicon  $p^+n$ -mesa diode after electron irradiation at room temperature (2 MeV,  $\sim 1 \times 10^{15} \text{ cm}^{-2}$ ). The rate window was  $10 \text{ s}^{-1}$  and the voltage pulsing was done from  $-5$  to  $0 \text{ V}$ . A  $60 \mu\text{A}$  photocurrent was used for the MCTS measurement.

at the lower temperature anneals at exactly the same anneal temperature as does the peak from the acceptor state of the  $E$  center. The other minority line is stable at temperatures above 420 K. The level positions and capture-cross sections of the two minority traps have been determined from Arrhenius analyses of carrier emissivity versus reciprocal temperature. These “finger prints” are  $E_V + 0.277 \text{ eV}$  and  $\sigma_p = 5 \times 10^{-16} \text{ cm}^{-2}$  for the low-temperature line and  $E_V + 0.335 \text{ eV}$  and  $\sigma_p = 8 \times 10^{-16} \text{ cm}^{-2}$  for the high-temperature line. There is no indication of any electric-field dependence on the positions of the two lines which is indicative of donor characters of the two levels. Because of its annealing behavior, the trap level at  $E_V + 0.277 \text{ eV}$  is the most likely candidate for the donor level of the  $E$  center.

A critical test of this tentative assignment would be an investigation of irradiation-induced defects in  $p$ -type silicon counter doped with a small concentration of phosphorus. Thus phosphorus was ion implanted into  $n^+p$  structures at energies of either 1.3 or 2 MeV to a dose giving peak compensations of  $\sim 10\%$ . Mesa diodes were then produced followed by a heat treatment at  $850^\circ \text{C}$  for 30 min to anneal the radiation damage. This heat treatment also removed any hydrogen introduced in the diode structures during the chemical etch. DLTS investigations following electron irradiations at 2 MeV at room temperature did, however, not produce any significant trace of an energy level at  $E_V + 0.277 \text{ eV}$  as shown in Fig. 3. There is a weak trace of a line at  $\sim 175 \text{ K}$  in the spectrum but this was not taken as significant. Presumably, lack of Coulombic attraction between the positive  $P$  ions and the monovacancies, which are neutral or positive in  $p$ -type silicon [5], prevents the  $E$  centers from being formed. In order to change the charge states of the monovacancies to negative, the following scheme was devised: electron irradiation was performed at a temperature (20 K) where the monovacancies are immobile [they become mobile at  $\sim 80 \text{ K}$  [4]]. The charge state for the generated mono-

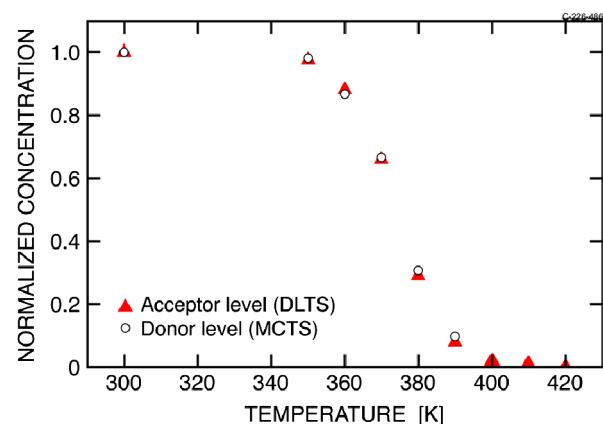


FIG. 2 (color online). Results from a 30 minutes isochronal annealing under  $-5 \text{ V}$  reverse bias of the same diode as used for the measurements shown in Fig. 1.

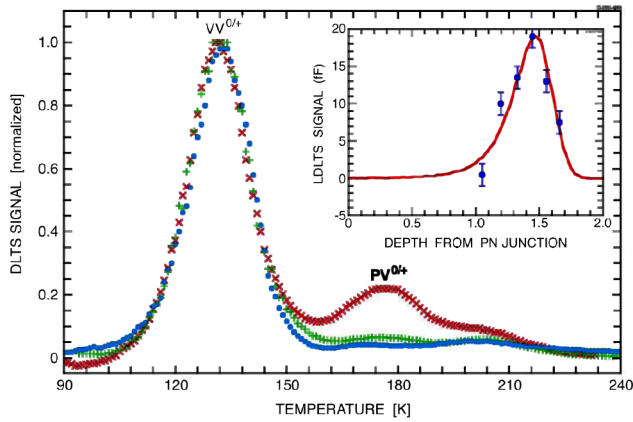


FIG. 3 (color online). DLTS spectra of electron irradiated Si- $n^+p$  mesa diode. Prior to mesa formation the structures were ion implanted with either P ( $\times$ ,  $+$ ) or Si ( $\bullet$ ) at an energy of 1.3 MeV to a dose of  $4 \times 10^{10} \text{ cm}^{-2}$  corresponding to a peak concentration of  $1 \times 10^{15} \text{ cm}^{-3}$  ( $\sim 10\%$  of the  $B$  concentration). After the mesa formation the structure was annealed at  $850^\circ\text{C}$  for 30 min. The electron irradiation was done at either 20 K ( $\times$ ,  $\bullet$ ) or 300 K ( $+$ ) with 2-MeV electrons to a dose of  $8 \times 10^{15} \text{ cm}^{-2}$ . The subsequent heating up to room temperature was done under light illumination. The shoulder at 200 K has not been identified nor has the small peak at 165 K in the spectrum of the Si implanted diode. The rate window was  $543 \text{ s}^{-1}$ , and the voltage pulsing was done from  $-5$  to  $-1$  V. The inset shows the depth profile of the  $E_V + 0.270$  eV peak extracted from Laplace DLTS measurements. The full-line curve is the result of a corresponding SRIM simulation [13] where the depth scale has been corrected for the  $0.35 \mu\text{m}$   $n$ -type top layer.

vacancies are then changed into the single or double negative state by continuous illumination of the diode with light of an energy of 1.46 eV during heating of the sample. As shown in Fig. 3, these experimental conditions resulted in the appearance of a new line situated at a temperature of  $\sim 180$  K in the DLTS spectrum. This line is not present when the P implantation is replaced by an equivalent Si implantation, and it is only weakly present when the heating up from 20 K to room temperature is done without light illumination (not shown in the figure).

The new line was studied further using Laplace DLTS [12], and an Arrhenius analysis of the emissivity versus reciprocal temperature gives a “finger print” of  $E_V + 0.270$  eV and  $\sigma_p = 5 \times 10^{-16} \text{ cm}^{-2}$ , which is in perfect agreement with the “finger print” of the  $E$ -center donor-

level candidate from the MCTS measurements shown in Fig. 1. With the Laplace DLTS setup a depth profiling of the signal from the  $E_V + 0.270$  eV center was performed; the results are shown in the inset of Fig. 3 together with the  $P$ -depth profile from a Monte Carlo simulation [SRIM [13]] of the ion-implantation process. The agreement between the experimental data and the simulation is striking. As the MeV electron irradiation produces vacancies uniformly distributed in depth, the depth profile of the  $E_V + 0.270$  eV center ties this defect closely to the implanted  $P$  ions.

At this stage of the investigation it can be concluded beyond any doubt that the  $E_V + 0.27$  eV level is the donor level of the  $E$  center.

The experimental observation of the donor level of the  $E$  center in Si presented above is in agreement with theoretical predictions. The acceptor and donor levels of the  $E$  center in Si were calculated using the density functional theory within the local-density approximation. Hartwigsen-Goedecker-Hutter pseudopotentials [14] were employed along with the Brillouin zone  $k$ -point sampling scheme of Monkhorst and Pack (MP) [15]. An MP sampling density of  $2 \times 2 \times 2$  was found to offer sufficient convergence. To ensure convergence with respect to supercell size, supercells of 216 atoms, the largest tractable supercell size, were used. The location of donor ( $0/+$ ) and acceptor ( $-/0$ ) levels was examined using the Marker Method, where inclusion of a similar, but well-known defect significantly increases the accuracy of the calculated position of the studied defect in the band gap. Here VOH was used as a marker defect since it has well-characterized levels [16–19] and is electrically similar to the  $E$  center.

The Marker Method has been proved to be a reliable technique in the calculation of electrical levels [20].

Calculations have been performed on phosphorus, arsenic, and antimony vacancy pairs, all of which are found to have similar properties. EPR studies [3,21] as well as density functional calculations [22] find that the neutral AsV center relaxes by a pairing of two of the Si atoms in the vacancy in the neutral charge state but stress measurements [23] show that they move apart in what has become known as a resonating bond configuration in the negative charge state. Our calculations find the pairing configuration is less stable than the resonating bond configuration in the negative charge state by 0.06 eV, degenerate in the neutral, while both configurations, along with the trigonal one, are

TABLE I. Comparison between density function theory (DFT) calculations and DLTS/MCTS measurements for the acceptor [ $E(-/0)$ ] and donor [ $E(0/+)$ ] levels. The experimental acceptor levels have been taken from Ref. [4].

	$E(-/0)$		$E(0/+)$	
	DFT	DLTS	DFT	DLTS and MCTS
PV	$E_C - 0.36$ eV	$E_C - 0.45$ eV	$E_V + 0.22$ eV	$E_V + 0.27$ eV
AsV	$E_C - 0.35$ eV	$E_C - 0.47$ eV	$E_V + 0.24$ eV	
SbV	$E_C - 0.31$ eV	$E_C - 0.44$ eV	$E_V + 0.27$ eV	

degenerate in the positive charge state. An important result of the calculations is that the energy surface experienced by the atoms forming the  $E$  center is rather flat. This is illustrated by the negligible change in energy with change in atomic positions of the silicon atoms neighboring the vacancy. Although this implies that it is difficult to determine the structure of the  $E$  center accurately it also implies that the calculated formation energy and hence calculated electrical levels are relatively insensitive to the precise details of the defect structure.

The calculated donor and acceptor levels of the phosphorus, arsenic, and antimony vacancy pairs are presented in Table I. The calculated and observed acceptor ( $-/0$ ) levels all agree to within 0.13 eV or better although we note that DFT predicts the acceptor level of PV to lie just above that of AsV while DLTS observes the opposite ordering. A change in level position of 0.01 eV is, however, far below the accuracy limit of the Marker Method. The agreement between calculated and observed acceptor levels gives confidence to the calculated positions of the donor levels. Thus, the calculated donor level of PV, placed at  $E_V + 0.22$  eV, provides compelling evidence that the level observed experimentally at  $E_V + 0.27$  eV is indeed the donor level of the  $E$ -center PV. Furthermore, it is predicted that the other  $E$  centers will also possess donor levels in this region of the band gap.

In conclusion, we have demonstrated that the phosphorus-vacancy pair in silicon (the  $E$  center) has, in addition to its well-established acceptor level at  $E_C - 0.45$  eV, also a donor level at  $E_V + 0.27$  eV. The existence of this level was disclosed by a combination of different transient-capacitance techniques using  $p^+n$  as well as  $n^+p$  mesa diodes with phosphorus implanted into the  $p$  layer of the  $n^+p$  diodes. The existence of the donor level is demonstrated to be in agreement with density functional theory calculations performed within the local-density approximation.

In addition to the important task of completing the level scheme of the  $E$  center in Si, the discovery of the donor level is also expected to have consequences for diffusion modeling of dopants in Si which diffuse using the  $E$  center as vehicle; it is, for example, expected that the simulation of codoping of boron and phosphorus might be strongly influenced as both the donor and acceptor levels are now active.

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