Observation of negative-*U* centers in 6H silicon carbide

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Two negative-*U* centers in 6H SiC have been observed and characterized using capacitance transient techniques. These two defects give rise to one acceptor level $(-/0)$ and one donor level $(+/0)$ each in the band gap. The donor and the acceptor level have inverted ordering, i.e., the thermal ionization energy of the acceptor level is larger than that of the donor level. Direct evidence for the inverted ordering of the acceptor and donor levels and temperature dependence studies of the electron capture cross sections of the acceptor levels are presented. © *1999 American Institute of Physics.* [S0003-6951(99)02606-6]

A defect which possesses the properties of the strengthening the binding energy of the carriers when capturing additional carriers has a so-called negative-*U* property.[1] This phenomena occurs when the gain of total energy of the defect system overcomes the Coulombic repulsion of the additional carriers. The gain in net attraction is supplied by a local rearrangement of the lattice or/and by the defect itself. These phenomena have previously been reported in several semiconductors and recently in 4H SiC.[2] Electron irradiance and ion implantation create two strong deep level transient spectroscopy (DLTS) peaks of 6H SiC, the so-called E_1 and E_2 peaks.[3–6] These peaks have also been observed with lower concentration in as-grown materials and double-correlated DLTS investigations indicates that they are associated to two acceptorlike levels.[4] However, their identities are still not known.

In this letter, we present studies of two negative-*U* centers, U_1 and U_2, in electron irradiated 6H SiC. Each of these centers gives rise to two levels in the band gap, one donor level (E_i^0) and one acceptor level (E_i^-). The subscript i corresponds to the center U_i where $i=1,2$ and the superscript denotes the charge state of the level when it is occupied by an electron. In this investigation, we will show that the DLTS peaks E_1 and E_2 corresponds to a two-stage ionization event from the two acceptor levels E_1^- and E_2^-, respectively. From our capacitance transient experiments, direct detection of the one electron emission from the shallower donor levels E_1^0 and E_2^0 will be presented, providing a clear evidence of the inverted ordering of the levels.

For the capacitance transient studies, electron irradiated Schottky diodes were used. The *n*-type layers used for the diodes were grown with chemical vapor deposition (CVD).[7] The net donor concentration in these layers was in the range of 2×10^{14}–$2\times10^{16}\,\mathrm{cm}^{-3}$. To increase the concentration of the U_1 and U_2 centers, the diodes were irradiated by 2.5 MeV electrons at room temperature with doses varying between 1×10^{14} and 1×10^{15} cm^{-2}. Capacitance transient measurements were made by using a homemade setup described elsewhere[8] where the capacitance transients are recorded and stored in a computer. Three-point correlation windows[9] were used for the DLTS analysis. When the thermal electron emission rates were known from the DLTS analysis, multiple linear regression was used to determine the capacitance transient amplitudes and the capacitance baselines of the recorded transients.

The majority DLTS spectra observed in an electron irradiated Schottky diode in the temperature range of 80–230 K with a filling pulse width of 100 μs is characterized by three peaks, labeled E_0, $E_1^{-/+}$, and $E_2^{-/+}$, as depicted in Fig. 1(a), where the peaks $E_1^{-/+}$ and $E_2^{-/+}$ corresponds to the previous reported peaks E_1 and E_2, respectively. If the sample was illuminated during 3 s with a GaN light emitting diode (LED) with a peak wavelength of 470 nm before each filling pulse and a short filling pulse ($t_p=300$ ns) was used, two new peaks, labeled $E_1^{0/+}$ and $E_2^{0/+}$, appeared, as can be seen in Fig. 1(b). The E_0 peak in Fig. 1(a), which is slightly shifted to higher temperatures compared to peak $E_2^{0/+}$, has completely disappeared. The absence of peak E_0 in Fig. 1(b) is explained by the inset of Fig. 1, which shows the E_0 peak measured with various filling pulse widths. For filling pulses less then 1 μs, the peak has completely disappeared.

The two shallower donor levels E_1^0 and E_2^0 are not observed in Fig. 1(a) since the centers captures two electrons during the filling pulses. When two electrons are captured to

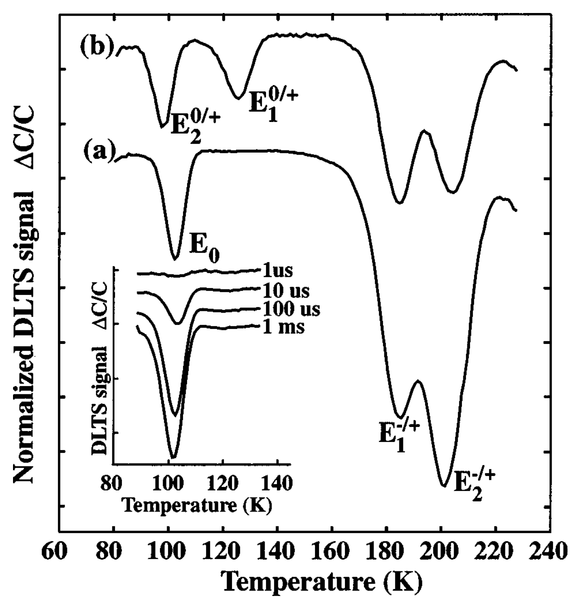

FIG. 1. Two DLTS spectra observed in a 6H SiC diode in the temperature range of 80–230 K. The measurements were performed with: (a) filling pulse width of 100 μs and (b) with a filling pulse width of 300 ns and illumination before the filling pulse. Shown as an inset, the peak E_0 measured with four different filling pulse widths. The pulse height and the reverse bias were 9.9 and -9.9 V, respectively. The spectra are shown with a 50 s^{-1} rate window.

TABLE I. The thermal activation energies ΔE, thermal activation energies ΔE_t corrected for the temperature dependence of the pre-exponential factor of the electron emission rate, measured capture cross sections σ_{meas}, and concentration of traps N_T. The range of energies comes from the assumptions that the electron capturing process is governed by a cascade capturing process, i.e. $\sigma \propto (T^{-1} \ldots T^{-3})$.

Peak	ΔE (eV)	ΔE_t (eV)	σ_{meas} (cm^2)	N_T (cm^{-3})
$E_1^{0/+}$	0.28	0.27 . . . 0.29	$>2.4\times10^{-15}$	4.9×10^{13}
$E_2^{0/+}$	0.20	0.19 . . . 0.21	$>5.5\times10^{-15}$	6.4×10^{13}
$E_1^{-/+}$	0.42	0.38	$1.11\times10^{-15}\times\exp(-0.048/k_BT)$	4.7×10^{13}
$E_2^{-/+}$	0.47	0.44	$7.70\times10^{-16}\times\exp(-0.070/k_BT)$	6.0×10^{13}
E_0	0.20		1.2×10^{-18}	5.6×10^{13}

the centers, the binding of the electrons is strengthened and, consequently, these centers are frozen out and not observed in the measurement. The peaks $E_1^{-/+}$ and $E_2^{-/+}$ are associated to a two-stage ionization event of the two acceptor levels E_1^- and E_2^-, respectively, since at temperatures when the deeper acceptor level is ionized, the second electron should follow immediately.

The peaks $E_1^{0/+}$ and $E_2^{0/+}$ in Fig. 1(b) corresponds to thermal electron emission from the two shallower donor levels E_1^0 and E_2^0, respectively. The freeze out was avoided by using a short filling pulse (300 ns), fast enough to prevent capturing of two electrons to the centers. Although a short filling pulse was used, a small fraction of the centers captured two electrons during the filling pulse and with the repetitive pulses required by DLTS, the signal from the levels E_1^0 and E_2^0 was decreasing to zero during the measurement. By applying a light pulse from a GaN LED before each filling pulse, the small fraction of defects, which had captured two electrons during the preceding pulse, is optically ionized, preventing the decrease of the signals during the measurement.

From the DLTS measurements, the electron emission rates (e_n) were determined and the thermal activation energies (ΔE) of the electron emission processes were obtained from Arrhenius plots [$\log(e_n)$ versus $1/T$]. These parameters for different levels are presented in Table I.

In order to confirm the relation between the peaks $E_1^{-/+}$ and $E_2^{-/+}$ and the centers U_1 and U_2, respectively, the reappearing of the peaks $E_1^{0/+}$ and $E_2^{0/+}$ by ''annealing'' at low temperatures (110–200 K) was investigated. The inset of Fig. 2 shows a 5 min isochronal anneal with a reverse bias applied to the diode. To assure that two electrons were captured to the defects before the annealing commenced, the diode was heated without bias to the annealing temperature. A reverse bias of −9.9 V was applied for 5 min and the sample was thereafter cooled down to 110 K with bias where the amplitudes of the capacitance transients $E_1^{0/+}$ and $E_2^{0/+}$ were measured following a single 500 ns filling pulse. The transients $E_1^{0/+}$ and $E_2^{0/+}$ reappear at ~130 and ~150 K, respectively, and a simulation, assuming the thermal ionization of the levels E_1^- and E_2^- responsible for the reappearing, gives a good agreement, as depicted with the solid curve.

In order to study the decay process of the DLTS peaks associated to the donor levels, the capacitance transients $E_1^{0/+}$ and $E_2^{0/+}$ as a function of number n of applied 500 ns filling pulses was recorded in the temperature range of 105–135 and 85–110 K, respectively. During each filling pulse, a fraction of the defects will capture two electrons and, consequently, be frozen out from the experiment. The decay rate of the amplitudes corresponds therefore to the capture rate of the second electron (providing that the capture process of the first electron is much faster). The result at 110 K is shown in Fig. 2. The one-to-one correspondence between twice the sum of the transients amplitudes $E_1^{0/+}$ and $E_2^{0/+}$ (○) and the change of the capacitance baseline (●) shows that the levels keep two electrons each when they are frozen out from the experiment.

The electron capturing process to the donor levels E_1^0 and E_2^0 is fast since no decrease of the peaks $E_1^{0/+}$ and $E_2^{0/+}$ was observed when using 50 ns filling pulses, which is the limit of our system. This supports the assumption that the decay rates of $E_1^{0/+}$ and $E_2^{0/+}$ correspond to the capture rate of the second electron. The electron capture rates to the acceptor levels E_1^- and E_2^-, i.e., capture rates of the second electron, were measured in the temperature range of 155–205 and 175–225 K, respectively, by observing the variation of the capacitance transient amplitudes of the peaks $E_1^{-/+}$ and $E_2^{-/+}$ as a function of the filling pulse width.

In order to determine the capture cross sections from the obtained capture rates, the free electron concentration has to be known. However, at temperatures when the measurements were performed, the free electron concentration is strongly affected by the freeze-out of free electrons since the n-type doping impurities, which is nitrogen in SiC, are relatively deep. We have therefore calculated the free electron concentrations by solving the neutrality equation of a nondegener-

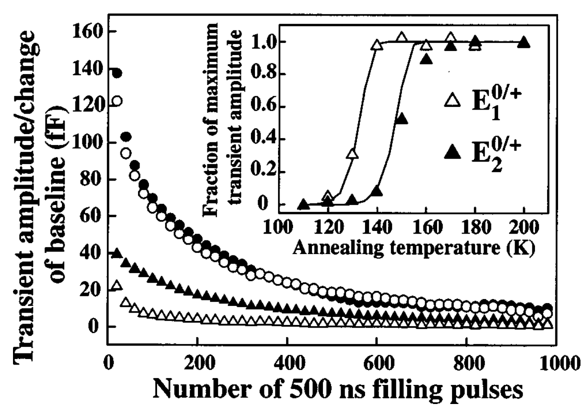

FIG. 2. The decay of the capacitance transients $E_1^{0/+}$ (△) and $E_2^{0/+}$ (▲) and the change of the capacitance baseline (●) as a function of the number n of 500 ns filling pulses at 110 K. The symbols (○) represents two times the sum of the capacitance transient amplitudes $E_1^{0/+}$ and $E_2^{0/+}$. Shown as an inset, the reappearance of the peaks $E_1^{0/+}$ (△) and $E_2^{0/+}$ (▲) due to annealing with bias. The solid curves shows a simulation, assuming that the thermal ionization of levels E_1^- and E_2^- are responsible for the reappearance.

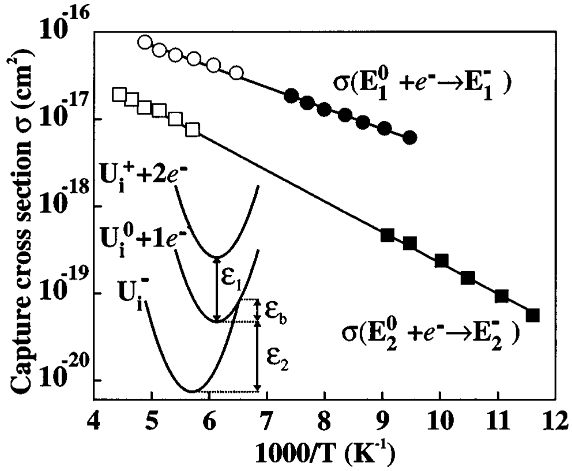

FIG. 3. Temperature dependence of the electron capture cross sections for the acceptor levels E_1^- and E_2^-: (●) and (■) represent the capture cross sections measured by observing the decay of the capacitance transient amplitudes of $E_1^{0/+}$ and $E_2^{0/+}$, respectively, as a function of the number of filling pulses. (○) and (□) represent the capture cross sections measured by observing the capacitance transient amplitudes $E_1^{-/+}$ and $E_2^{-/+}$, respectively, as a function of the filling pulse width. The solid lines indicate the fitted capture cross sections. Shown as an inset, the configuration-coordinate diagram for the centers U_i, where $i=1,2$.

ated, n-type semiconductor, with nitrogen residing the three inequivalent lattice sites in 6H SiC as a donor. For these calculations, the ionization energies of the nitrogen donor levels in Ref. 10 were used. The capture cross section of the first electron to the donor levels E_1^0 and E_2^0 is estimated to be larger than 2.4×10^{-15} and $5.5\times10^{-15}\,\mathrm{cm}^2$, respectively. The obtained capture cross sections for the capturing of the second electron to the U_1 and U_2 centers shows an exponential temperature dependence, as depicted in Fig. 3. Assuming a multiphonon capturing process,[11] the temperature dependent capture cross section can be fitted, as shown in Fig. 3 by the solid line. The electron capture cross section of E_0 was estimated from the variation of the DLTS peak amplitude as a function of the filling pulse width, as depicted in the inset of Fig. 1. The obtained capture cross sections are given in Table I.

A strong indication of negative-U ordering is the 1:2 relation of the capacitance transient amplitudes between the donor and the acceptor level due to the two-stage ionization process of the acceptor level. However, the amplitudes of the $E_1^{0/+}$ and $E_2^{0/+}$ are suppressed by the capturing of a second electron during the filling pulse. Compensating for this, using the obtained electron capturing rates of the second electron, the amplitudes of $E_1^{0/+}$ and $E_2^{0/+}$ follows the expected 1:2 relation to the amplitudes of $E_1^{-/+}$ and $E_2^{-/+}$, respectively. The corresponding concentrations of the centers are presented in Table I.

Judging from the relation of the peak amplitudes, the annealing behavior and capture cross sections, we suggest the electron emission processes

$$E_i^0 \rightarrow E_i^+ + e^-,$$

are associated to the DLTS peak $E_i^{0/+}$ and the two stage electron emission processes,

$$E_i^- \rightarrow E_i^0 + e^- \rightarrow E_i^+ + 2e^-,$$

are associated to the peak $E_i^{-/+}$, where $i=1,2$.

The thermal activation energies corrected for the temperature dependence of the pre-exponential factor of the electron emission rate (e_n) can now be obtained from Arrhenius plots [$\log(e_n/T^{n+2})$ versus $1/T$]. Here T^{n+2} is the temperature dependence of the pre-exponential factor of e_n and n is the contribution from the temperature dependence of the electron capture cross section (σ). The factor 2 comes from the temperature dependence of the effective density of states in the conduction band ($N_c \propto T^{1.5}$) and of the thermal velocity of electrons ($V_{\mathrm{th}} \propto T^{0.5}$). Assuming a fast cascade capturing process[12] ($n=-1\ldots-3$) to the donor levels E_1^0 and E_2^0, and a multiphonon process ($n=0$) to the acceptor levels E_1^- and E_2^- gives the corrected thermal activation energies (ΔE_t) as presented in Table I. The inset of Fig. 3 shows a configuration-coordinate diagram of the defect system U_i ($i=1,2$) where ε_1 and ε_2 correspond to the binding energy of the first electron and second electron, respectively. The energy ε_b is the thermal barrier for capturing of the second electron. The corrected thermal activation energies ΔE_t for the acceptor levels corresponds to the total energy barrier $\varepsilon_2+\varepsilon_b$. Correcting for the thermal barrier ε_b, i.e., $\Delta E_t-\varepsilon_b$, gives the energy positions $E_c-0.33$ eV and $E_c-0.37$ eV for the acceptor states of the U_1 and U_2 centers, respectively.

The two negative-U centers, observed in 4H and 6H SiC have many properties in common. Both are annealed out at approximately the same temperature ($\sim$1400 °C)[3,6,13] and they have very similar electronic properties. It suggests that the two negative-U defect systems in 4H and 6H SiC have a similar structure.

In conclusion, we have characterized two negative-U centers in 6H SiC. These two centers, U_1 and U_2, have one acceptor state ($-/0$) and one shallower donor state ($0/+$) each. The levels at $E_c-(0.27\ldots0.29)$ eV and $E_c-(0.19\ldots0.21)$ eV corresponds to the donor levels E_1^0 and E_2^0, respectively, and the levels at $E_c-0.38$ eV and $E_c-0.44$ eV correspond to the acceptor levels E_1^- and E_2^-, respectively.

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