Negative-*U* centers in 4*H* silicon carbide

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Characterization of two negative-*U* centers in *4H* SiC has been performed using various capacitance transient techniques. Each center gives rise to one acceptor level (−/0) and one donor level (0/+), where the electron ionization energy of the acceptor level is larger than that of the donor level. The two-electron emissions from the two acceptor levels give rise to the previously reported deep level transient spectroscopy peak associated with the so-called Z_1 center. Direct evidence for the inverted ordering and temperature dependence studies of the electron-capture cross sections of the acceptor levels will be presented.
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A defect that has the possibility to be occupied by more than one charge carrier has negative-*U* properties if the binding energy of the second charge carrier is larger than that of the first one.[1] This phenomenon is observed when the gain of total energy of the defect system overcomes the Coulombic repulsion of the two charge carriers. The gain in net attraction is supplied by a local rearrangement of the lattice. These phenomena have previously been reported in several semiconductors and the most famous example is the *DX* center in GaAs and $Al_xGa_{1-x}As$ alloys.[2] The dominant feature in a deep level transient spectroscopy (DLTS) spectrum measured on electron irradiated or ion implanted *4H* SiC is the peak associated to the center named Z_1.[3–5] The Z_1 center is sometimes present also in as-grown material. It has previously been extensively studied and it has been discussed in terms of a divacancy.[3]

We will in this paper show that the DLTS peak associated to the Z_1 center consists of two peaks, where each peak corresponds to the emission of two electrons from the negative-*U* centers U_1 and U_2, respectively. Each one of the two negative-*U* centers gives rise to two levels in the band gap, one acceptor level (Z_1^-) and one shallower donor level (Z_1^0). The subscript *i* corresponds to the level associated to the center U_1 where $i=1,2$ and the superscript to the charge of the level when it is occupied by an electron. Unambiguous evidence of the inverted order of the acceptor and donor levels will be presented by direct detection of the one electron emission from the shallower donor levels Z_1^0 and Z_2^0.

For the capacitance transient studies, both p^+n and *n*-type Schottky diodes were used. The *n*-type layers used for the diodes were grown with chemical vapor deposition[6] (CVD) or high-temperature chemical vapor deposition (HTCVD).[7] The net donor concentration in these layers was in the range $2\times10^{14}-5\times10^{15}\,cm^{-3}$. To increase the concentration of the Z_1 center, some of the diodes were irradiated by 2.5 MeV electrons at room temperature with a dose of $2.5\times10^{14}\,cm^{-2}$. Electron irradiation and ion implantation create another peak overlapping with that of the Z_1 center.[4,5] This peak was annealed out at 900 °C in order to get a pure signal from the Z_1 center. Capacitance transient measurements were made by using a homemade setup described elsewhere.[5] In order to improve the selectivity in the DLTS measurements, three-point correlation windows were used.[8]

Figure 1(a) shows a conventional DLTS spectrum with a filling pulse width of 100 μs measured on an as-grown sample with a high concentration of the Z_1 center. As can be seen, only the strong peak labeled $Z_{1,2}^{-/+}$, associated with the previously reported Z_1 center, is observed. However, if the sample was illuminated with a GaN light-emitting diode (LED) with a peak wavelength of 470 nm before each filling pulse and a short filling pulse ($t_p=50$ ns) was used, two new peaks, labeled $Z_1^{0/+}$ and $Z_2^{0/+}$, appeared, as can be seen in

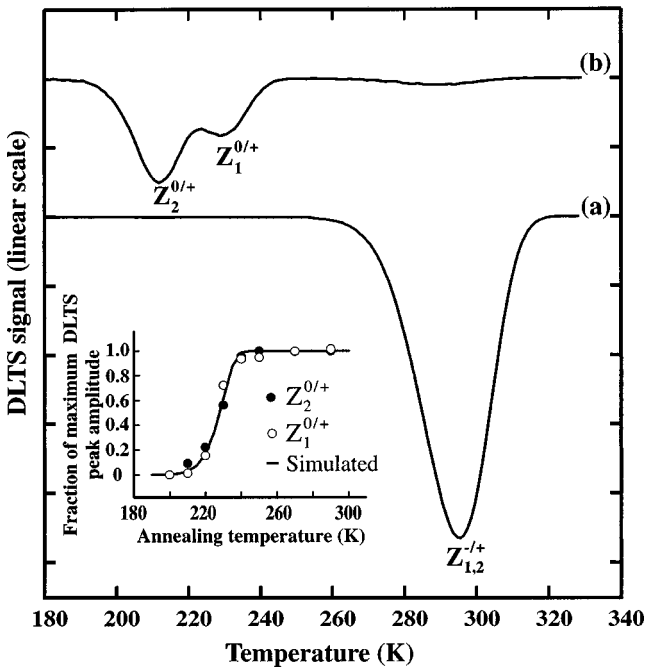

FIG. 1. Two DLTS spectra observed in a 4*H* SiC diode. The measurements were performed (a) with a pulse width of 100 μs and (b) with a pulse width of 50 ns and illumination with light ($\lambda\sim470$ nm) from a GaN LED before each filling pulse. The pulse height was 9.9 V and the reverse bias −9.9 V in both cases. The reappearing of the levels Z_1^0 (○) and Z_2^0 (●) due to annealing with bias is shown as an inset. The solid curve shows a simulation, assuming that thermal ionization of the levels $Z_{1,2}^-$ is responsible for the reappearing of peaks $Z_1^{0/+}$ and $Z_2^{0/+}$.

Fig. 1(b). These two peaks are associated to the two shallower donor levels Z_1^0 and Z_2^0. The relation in amplitudes of the peaks $Z_1^{0/+}$ and $Z_2^{0/+}$ in the as-grown samples follows approximately the relation 1:2. However, in electron irradiated material, the amplitudes of the two peaks are in close 1:1 correspondence.

The failure to observe the donor levels Z_1^0 and Z_2^0 in a conventional DLTS measurement can be explained as follows: in a conventional DLTS measurement, some of the centers will capture two electrons during each filling pulse and since the binding of the electrons are strengthened when two electrons are captured, these centers are frozen out from the experiment. Consequently, with the respective pulses required by DLTS, the one-electron emission from the donor levels will not be observed.

The freeze-out of the donor levels was avoided in the measurement shown in Fig. 1(b) by optically emptying the centers before each filling pulse and using a short filling pulse. The illumination before each pulse ionizes the small fraction of the centers, which had captured two electrons during the preceding pulse, by the reactions,

$$Z_1^- \xrightarrow{h\nu} Z_1^0 + e^- \xrightarrow{h\nu} Z_1^+ + 2e^-,$$

and (1)

$$Z_2^- \xrightarrow{h\nu} Z_2^0 + e^- \xrightarrow{h\nu} Z_2^+ + 2e^-,$$

respectively.

The entire optical ionization of the defects (i.e., $Z_i^- \xrightarrow{h\nu} Z_i^+ + 2e^-$) was confirmed by observing the amplitude of the photoinduced capacitance transient at temperatures below the freeze-out of the one-electron emission. The optical ionization of the two acceptor levels Z_1^- and Z_2^-, in conjunction with a short filling pulse, short enough to prevent capturing of two electrons to the centers, reveals the two peaks $Z_1^{0/+}$ and $Z_2^{0/+}$, which correspond to the electron emission from the two donor states Z_1^0 and Z_2^0. In a negative-U system, when two electrons have been captured, the electron emission requires higher thermal energy than when only one electron is captured. Consequently, the electron emission associated to peak $Z_{1,2}^{-/+}$ corresponds to a two-stage ionization event where the first ionization event is immediately followed by the second event. A strong indication of negative-U ordering is therefore the relation of the DLTS peak amplitudes since they correspond to the change of the net charge of the defects. The sum of the amplitudes of peaks $Z_1^{0/+}$ and $Z_2^{0/+}$ follows closely the relation 1:2 to the amplitude of peak $Z_{1,2}^{-/+}$. It suggests that the peak $Z_{1,2}^{-/+}$ consists of two components, each component corresponds to emission of two electrons from the centers associated to the peaks $Z_1^{0/+}$ and $Z_2^{0/+}$, respectively.

In order to confirm the relation between peak $Z_{1,2}^{-/+}$ and the centers U_1 and U_2, the reappearing of the peaks $Z_1^{0/+}$ and $Z_2^{0/+}$ by ''annealing'' at low temperatures (200–300 K) was investigated. The inset of Fig. 1 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 eV was applied for 5 min and the sample was thereafter cooled down to 200 K with bias where the concentrations of the levels Z_1^0 and Z_2^0 were measured by recording the capacitance transient following a single 50-ns filling pulse and fitting two exponential transients to the biexponential transient using multiple linear regression. The levels Z_1^0 and Z_2^0 reappear at $\sim$230 K and a simulation, assuming thermal ionization of the levels $Z_{1,2}^-$ is responsible for the reappearance, gives a good agreement, as depicted with the solid curve.

TABLE I. The thermal activation energies ΔE, electron binding energy E_i, and measured capture cross sections σ_{meas} for the different electron-capturing processes. The energy range comes from the assumptions $\sigma \propto T^{-1}$ and $\sigma \propto T^{-3}$, respectively. The temperature-dependent capture cross sections correspond to the capture of the second electron to the centers.

Process	ΔE (eV)	E_i (eV)	σ_{meas} (cm^2)
$Z_1^0 \leftrightarrow Z_1^+ + e^-$	0.45	0.50–0.54	$>1\times10^{-14}$
$Z_2^0 \leftrightarrow Z_2^+ + e^-$	0.52	0.43–0.46	$>1\times10^{-14}$
$Z_1^- \leftrightarrow Z_1^0 + e^-$	0.76	0.67	$1.71\times10^{-15}\times\exp(-0.065/k_sT)$
$Z_2^- \leftrightarrow Z_2^0 + e^-$	0.72	0.71	$1.31\times10^{-15}\times\exp(-0.080/k_sT)$

The thermal electron emission rates (e_n) from the levels Z_1^0 and Z_2^0 were obtained from DLTS measurements. However, the two components, labeled $Z_1^{-/+}$ and $Z_2^{-/+}$, of peak $Z_{1,2}^{-/+}$, which correspond to thermal electron emission from the levels Z_1^- and Z_2^-, respectively, were not possible to resolve from the DLTS spectra. Although the overlapping of the $Z_1^{-/+}$ and $Z_2^{-/+}$ was severe, it was possible to resolve them by fitting two exponential transients directly to the biexponential capacitance transients $Z_{1,2}^{-/+}$ by keeping the relation in amplitudes between the two components fixed. The fixed relation was determined from the peak amplitudes of $Z_1^{0/+}$ and $Z_2^{0/+}$. The thermal activation energies of the electron emission processes from the defects were obtained from Arrhenius plots $[\log(e_n) - 1/T]$ and are presented in Table I.

The decay process of the peaks $Z_1^{0/+}$ and $Z_2^{0/+}$ (i.e., $Z_{1,2}^0 + e^- \rightarrow Z_{1,2}^-$) was monitored by observing the amplitudes of the capacitance transients and the capacitance baseline as a function of number n of applied 1-μs filling pulses. The result is shown in Fig. 2. 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, directly to the capture rate of the second electron (providing that the capture rate of the first electron is much faster) since the capacitance transient amplitude is proportional to the remaining concentration of levels Z_1^0 and Z_2^0, respectively. The solid curve in Fig. 2 indicates twice the sum of the transient amplitudes $Z_1^{0/+}$ and $Z_2^{0/+}$. The 2:1 correspondence between the sum of the transients amplitudes and the change of baseline shows that the defects keep two electrons each when they are frozen-out. From these experiments the capture cross sections of the second electron to the U_1 and U_2 centers were obtained, as depicted in Fig. 3 (empty symbols). The capturing process of the first electron to the centers seems to be very efficient since we could not observe any decrease of the transient

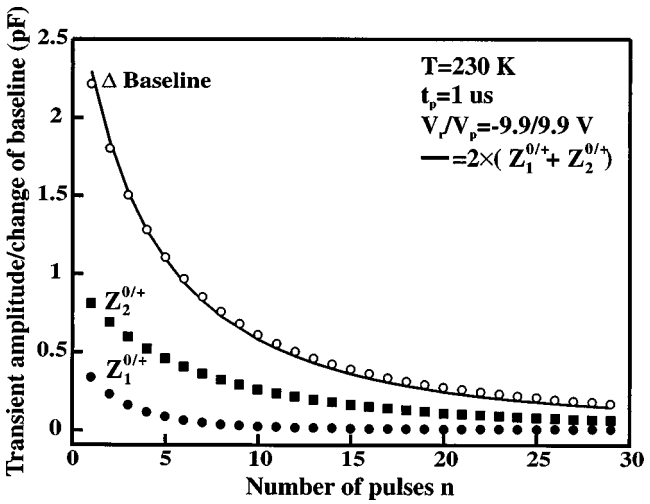

FIG. 2. The decay of the capacitance transients $Z_1^{0/+}$ (●) and $Z_2^{0/+}$ (■), respectively, and the change of the capacitance baseline (○) as a function of the number n of 1-μs filling pulses at 230 K. The solid curve indicates twice the sum of the capacitance transient amplitudes $Z_1^{0/+}$ and $Z_2^{0/+}$.

amplitudes when we decreased the filling pulse width further, not even when the filling pulse width was 50 ns, which is the limit of our system. It indicates a very large capture cross section and we estimate them to be larger than $1\times10^{-14}\,\mathrm{cm}^2$. The filled symbols in Fig. 3 show the electron capture cross section for the second electron measured by observing the capacitance transient amplitudes $Z_1^{-/+}$ and $Z_2^{-/+}$ in the biexponential transient $Z_{1,2}^{-/+}$ as a function of the filling pulse width. Each capacitance transient amplitude was obtained by fitting two exponential transients to the biexponential transient using multiple linear regression. Although two electrons are captured to the defects in the measured electron capture processes, the obtained capture cross sections correspond to the capture of the second electron since the capture of the first electron is very fast. The capture cross sections for the capturing to the acceptor levels (i.e., of the second electron) show a weak exponential temperature dependence. Assuming a multiphonon capturing process,[9] the temperature dependent capture cross sections can be fitted, as shown in Fig. 3 with the solid lines. The obtained temperature-dependent capture cross sections are presented in Table I.

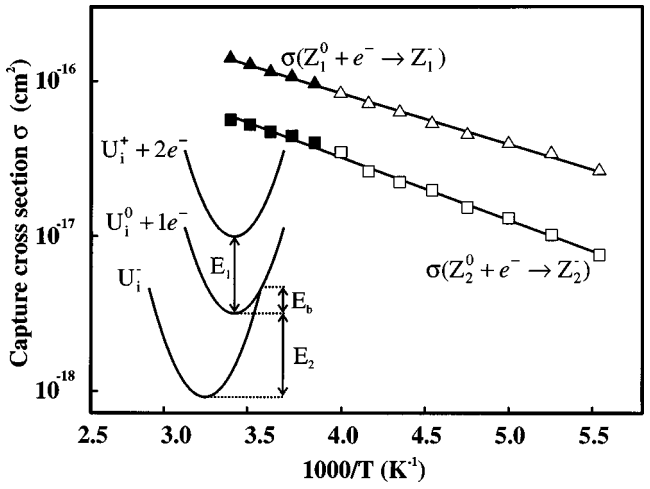

FIG. 3. Temperature dependence of the electron capture cross sections for the acceptor levels Z_1^0 and Z_2^0: (△) and (□) represent the capture cross sections measured by observing the decay of the capacitance transient amplitudes $Z_1^{0/+}$ and $Z_2^{0/+}$, respectively, as a function of the number of filling pulses. (▲) and (■) represent the capture cross sections measured by observing the two capacitance transient amplitudes in the biexponential transient associated to peak $Z_{1,2}^{-/+}$ as a function of the filling pulse width. The solid lines indicate the fitted temperature-dependent capture cross sections. Shown as an inset is the configuration-coordinate diagram for the center U_i where $i=1,2$.

The large capture cross section for the first electron suggests donorlike centers. The $Z_{1,2}^{-/+}$ peak has previously been investigated by double correlated DLTS and it was shown to be acceptorlike[4] in agreement with our results. Consequently, the DLTS peaks $Z_1^{0/+}$ and $Z_2^{0/+}$ correspond to the electron emission processes,

$$Z_1^0 \rightarrow Z_1^+ + e^-,$$

and (2)

$$Z_2^0 \rightarrow Z_2^+ + e^-,$$

respectively.

Based on the relation of the peak amplitudes, annealing behavior, capture cross sections, and the acceptorlike nature of peak $Z_{1,2}^{-/+}$, we suggest that the two electron emission processes,

$$Z_1^- \rightarrow Z_1^0 + e^- \rightarrow Z_1^+ + 2e^-,$$

and (3)

$$Z_2^- \rightarrow Z_2^0 + e^- \rightarrow Z_2^+ + 2e^-,$$

are associated to the peak $Z_{1,2}^{-/+}$.

The inset of Fig. 3 shows a configuration-coordinate diagram of the defect system U_i $(i=1,2)$ where E_1 and E_2 correspond to the binding energy of the first electron and second electron, respectively. The energy E_b is the barrier for capturing of the second electron. The actual location in the band gap of the U_1 and U_2 centers in different charge states can now be obtained. The fast capturing of the first electron to the positively charged center suggests a cascade capturing process,[10] while the slower capturing process of the second electron is described by a multiphonon process. Refitting the previously obtained thermal emission rates, assuming a cascade and multiphonon capturing process of the first and second electron, respectively, gives the electron binding energies, as presented in Table I. The given energy range is caused by the assumptions $\sigma\propto T^{-1}$ and $\sigma\propto T^{-3}$ for the temperature dependence of the cascade capturing process. The obtained electron binding energies give the energy positions $E_c-(1.10-1.14)$ and $E_c-(1.06-1.09)$ eV eV for the two acceptor states U_1^- and U_2^-, respectively, and $E_c-(0.50-0.54)$ and $E_c-(0.43-0.46)$ eV eV for the two donor states U_1^0 and U_2^0, respectively.

The close resemblance of the electronic properties of the U_1 and U_2 centers and the 1:1 correspondence in concentrations after electron irradiation suggests that the centers may

be associated to a defect residing at the two crystallographically inequivalent lattice sites in 4*H* SiC, i.e., the hexagonal and cubic lattice sites. However, the origin of the discrepancy in the 1:1 relation of the concentrations in the as-grown samples is not yet clear.

In summary, we have presented evidence of two negative-*U* centers in 4*H* SiC. These two centers have one donor level and one acceptor level each. The levels at $E_c-(0.50-0.54)$ and $E_c-(0.43-0.46)$ eV eV correspond to the donor levels Z_1^0 and Z_2^0, respectively, and the levels at $E_c-0.67$ and $E_c-0.71$ eV correspond to the acceptor levels Z_1^- and Z_2^-, respectively.

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