Electron Paramagnetic Resonance studies of negative-U centers in AlGaN and SiC

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ABSTRACT

Silicon (Si) is the most commonly used n-type dopant in AlGaN, but the conductivity of Si-doped Al$_x$Ga$_{1-x}$N was often reported to drop abruptly at high Al content (x>0.7) and the reason was often speculated to be due to either compensation by deep levels or self-compensation of the so-called DX (or negative-U) center. Understanding the electronic structure of Si and carrier compensation processes is the essential for improving the n-type doping of high-Al-content Al$_x$Ga$_{1-x}$N. In our studies of Si-doped AlGaN layers grown by metal-organic chemical vapor deposition, Electron Paramagnetic Resonance (EPR) was used to study the electronic structure of Si in high-Al-content Al$_x$Ga$_{1-x}$N.

From the temperature dependence of the concentration of the Si donor on the neutral charge state $E_d$ determined by EPR, we showed that Si already forms a stable DX center in Al$_x$Ga$_{1-x}$N with x ~0.77. However, with the Fermi level locating only ~3 meV below $E_d$, Si still behaves as a shallow donor and high conductivity at room temperature could be achieved in Al$_{0.77}$Ga$_{0.23}$N:Si layers. In samples with the concentration of the residual oxygen (O) impurity larger than that of Si, we observed no carrier compensation by O in Al$_{0.77}$Ga$_{0.23}$N:Si layers, suggesting that at such Al content, O does not seem to hinder the n-type doping in the material. The result is presented in paper 1.

In paper 2, we determined the dependence of the $E_{DX}$ level of Si on the Al content in Al$_x$Ga$_{1-x}$N:Si layers (0.79≤x≤1) with the Si concentration of ~2×10$^{18}$ cm$^{-3}$ and the concentrations of residual O and C impurities of about an order of magnitude lower (~1÷2×10$^{17}$ cm$^{-3}$). We found the coexistence of two DX centers (stable and metastable ones) of Si in Al$_x$Ga$_{1-x}$N for x≥0.84. For the stable DX center, abruptly deepening of $E_{DX}$ with increasing of the Al content for x≥0.83 was observed, explaining the drastic decrease of the conductivity as often reported in previous transport studies. For the metastable DX center, the $E_{DX}$ level remains close to $E_d$ for x=0.84÷1 (~11 meV for AlN).

The $Z_1/Z_2$ defect is the most common deep level revealed by Deep Level Transient Spectroscopy (DLTS) in 4H-SiC epitaxial layers grown by chemical vapor deposition (CVD). It has previously been shown by DLTS to be a negative-U system which is more stable with capturing two electrons. The center is also known to be the lifetime killer in as-
grown CVD material and, therefore, attracts much attention. Despite nearly two decades of intensive studies, including theoretical calculations and different experimental techniques, the origin of the $Z_1/Z_2$ center remains unclear. EPR is known to be a powerful method for defect identification, but a direct correlation between EPR and DLTS is difficult due to different requirements on samples for each technique. Using high n-type 4H-SiC CVD free-standing layers irradiated with low-energy (250 keV) electrons, which mainly displace carbon atoms creating C vacancies, C interstitials and their associated defects, it was possible to increase the irradiation dose, allowing the application of EPR and DLTS on the same samples. Combining EPR, DLTS and supercell calculations, we identified the negatively charged carbon vacancy at the quasi-cubic ($k$) site and observed clear negative-U behaviors of the negative carbon vacancies at both hexagonal ($h$) and $k$ sites. Our results showed that the $Z_1/Z_2$ center is related to the $(2\rightarrow 0)$ level of $V_C$ and its higher-lying levels $Z_1$ and $Z_2$ are related to the $(-\rightarrow 0)$ levels of $V_C$ at the $h$ and $k$ sites, respectively. The result is presented in paper 3.
Included papers

1. Negative-U behavior of the Si donor in Al$_{0.77}$Ga$_{0.23}$N

2. Stable and metastable Si negative-U centers in AlGaN and AlN

3. Negative-U carbon vacancy in 4H-SiC: Assessment of charge correction schemes and identification of the negative carbon vacancy at the quasicubic site
   X. T. Trinh, K. Szász, T. Hornos, K. Kawahara, J. Suda, T. Kimoto, A. Gali, E. Janzén, and N. T. Son

Publications not included in the thesis

1. Electron paramagnetic resonance and theoretical studies of Nb in 4H- and 6H-SiC

2. Negative-U System of Carbon Vacancy in 4H-SiC

3. Investigation on origin of $Z_{1/2}$ center in SiC by deep level transient spectroscopy and electron paramagnetic resonance
4. The complex impact of silicon and oxygen on the n-type conductivity of high-Al-content AlGaN

5. Theoretical and electron paramagnetic resonance studies of hyperfine interaction in nitrogen doped 4H and 6H SiC
K. Szász, X. T. Trinh, N. T. Son, E. Janzén and A. Gali.

6. Quantitative comparison between $Z_{1/2}$ center and carbon vacancy in 4H-SiC

7. Characterization of the nitrogen split interstitial defect in wurtzite aluminum nitride using density functional theory
A. Szállás, K. Szász, X. T. Trinh, N. T. Son, E. Janzén and A. Gali.

8. Electron paramagnetic resonance studies of Nb in 6H-SiC.
X. T. Trinh, A. Gällström, N. T. Son, S. Leone, O. Kordina, and E. Janzén.
Materials Science Forum 740-742, 385 (2013)

9. Silicon and oxygen in high-Al-content AlGaN: incorporation kinetics and electron paramagnetic resonance study
Solid State Phenomena 205-206, 441 (2014)

10. Identification of the negative carbon vacancy at quasi-cubic site in 4H-SiC by EPR and theoretical calculations
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1. High-Al-content Al$_x$Ga$_{1-x}$N

The wurtzite AlGaN alloys are the promising materials for the development of light emitters in ultraviolet (UV) and deep-UV spectral region thanks to their direct and wide band gap. The band gap of AlGaN increases with increasing of the Al content varying from 3.4 eV for GaN to 6.2 eV for AlN, which corresponds to the changing of wavelength from 365 nm to 200 nm. It was known that light emitting diodes (LEDs) emitting light in the deep-UV spectral region of ~270 nm can be efficiently used for water/air purification and sterilization [1,2]. Therefore, the successful fabrication of high-efficiency deep-UV LEDs and laser diodes (LDs) based on high-Al-content Al$_x$Ga$_{1-x}$N (x≥70%) [3–5] for replacing low-efficiency and toxic gas lasers and mercury lamps has enormous social impact and attracted much attention. Achieving of high n-type and p-type conductivity Al$_x$Ga$_{1-x}$N is the technological key for electrical pumping LEDs and LDs. Although considerable progress has been made, dopants, doping and carrier compensation in high-Al-content Al$_x$Ga$_{1-x}$N still remain unclear.

1.1. N-type conductivity of high-Al-content Al$_x$Ga$_{1-x}$N

For n-type conductivity, silicon (Si) is the most commonly used dopant while oxygen (O) and carbon (C) are among the most common residual impurities in the entire range of the AlGaN alloys. Achieving high n-type conductivity in high-Al-content Al$_x$Ga$_{1-x}$N:Si is proven difficult [6–8]. Generally, it is expected that higher doping concentration leads to higher conductivity. However, the conductivity was found to increase to maximal value at a certain Si doping concentration and then to decrease with further increasing of the Si concentration in high-Al-content AlGaN [8–10]. It was suggested that Si did not only replace group-III atoms (Ga or Al) to form isolated donors, but might also introduce other Si-related deep energy level defects such as Si antisite, Si$_N$, at high doping level and caused the self-compensation effect [9]. In addition, other studies reported several problems due to heavily Si doping such as the reduction of material quality, the stress-induced band gap shift, the near band-gap cathodoluminescence shift and Raman shift [11], and the formation of pits on the surface [12].
High resistivity observed in Si-doped high-Al-content AlGaN was often speculated to be due to either the formation of the so-called DX center or the presences of deep defects, including cation (Ga and Al) vacancies and/or other impurities such as O and C, which act as carrier compensation centers. For O, it was suggested that the substitutional \( \text{ON} \) is a DX center [13–16] and can also form complexes with cation vacancies which play as deep acceptors [17,18]. The substitutional \( \text{C}_{\text{Ga}} \) was suggested to be a shallow donor in GaN [19,20] but the substitutional \( \text{C}_{\text{Al}}, \text{C}_{\text{N}} \) and interstitial \( \text{C}_{\text{i}} \) [20] and a cluster of three carbon atoms [21] were suggested to introduce deep acceptor levels in AlN. The complex effects of the lattice mismatch between the AlGaN epilayer and foreign substrate [22] further complicated the Si doping study.

1.2. Si-doped \( \text{Al}_{x}\text{Ga}_{1-x}\text{N} \)

Metal-organic chemical vapor deposition (MOCVD) was used to grow Si-doped \( \text{Al}_{x}\text{Ga}_{1-x}\text{N} \) epilayers. The precursor gases were \( \text{TMAl}, \text{TMGa} \) and \( \text{NH}_3 \) while the dopant gas was silane (\( \text{SiH}_4 \)). The small lattice mismatch between 4H-SiC and high-Al-content \( \text{Al}_{x}\text{Ga}_{1-x}\text{N} \) allows
obtaining layers with less strain and better crystal quality. In our studied samples, a buffer AlN layer of ~500-600 nm was initially grown on 4H-SiC substrate and a grade Al$_x$Ga$_{1-x}$N layer with the total thickness of ~400 nm was grown subsequently. Finally, the Si doped Al$_x$Ga$_{1-x}$N epilayers was deposited on the top of the template as can be seen in the Secondary Ion Mass Spectroscopy (SIMS) profile shown in Fig. 1. In our studies of Si in AlGaN [12,23,24], the concentrations of residual C and O were often kept at ~ 1-2×10$^{17}$ cm$^{-3}$, which is about one order of magnitude below the Si concentration ( [Si]~ 2×10$^{18}$ cm$^{-3}$), in order to reduce their complex impact on the n-type doping (Fig. 1). More details on MOCVD growth and Si doping of high-Al-content AlGaN can be found elsewhere [12,25,26].
2. Silicon carbide

The formation of chemical bond between silicon and carbon was first suggested by Swedish chemist Jöns Jakob Berzelius in 1824. He was considered as the first person who discovered silicon carbide (SiC) [27]. The first synthesized SiC powder carried out by Edward Goodrich Acheson was patterned in 1893. At that time, SiC was used as an abrasive material and was called “carbonrundum” by its author. The nature mineral of SiC was found much later in 1905 due to its extremely rare naturally occurring and was named as moissanite in honor of Henri Mosan, who discovered it [27]. Since 1955, several growth methods [28–30] have been developed and the crystal quality of SiC has constantly been improved, allowing electronic device applications.

One of the most important applications of SiC is in the field of high-voltage and high-power devices. These devices have long been developed based on Si due to its superior properties compared to germanium [31]. For such high-voltage and high-power devices, it is required high blocking voltage, fast response (high switching frequency) and is able to operate at high temperatures [32]. However, Si has small band gap (~1.1 eV) and other disadvantages causing the limitation of Si-based high-voltage, high-power devices [32]. In this case, larger band gap semiconductor such as SiC becomes promising material [32–34]. Compare to Si, SiC has superior properties such as lower intrinsic carrier concentration, higher thermal conductivity, higher breakdown field, and large saturated electron drift velocity [31,32,35–38]. Therefore, high-voltage and high-power devices based on SiC have an ability to overcome the theoretical limitation of the high-voltage, high-power Si-based devices.

2.1. Common polytypes of SiC

Silicon carbide can exist in more than 250 types of polytypes in which the most common and technologically important ones are 3C-, 4H- and 6H-SiC. In all polytypes, each C atom has chemical bonding with four surrounding Si atoms and vice versa. However, the arrangement of the outer neighbor atoms is different for each polytype. The polytypes can be viewed as the different stacking sequence of bi-layers.
of Si and C atoms along the c-axis. The notation of each polytype consists of a minimal number of bi-layers along the c-axis required for the periodicity of crystal structure and a letter describing the crystal system (C-cubic, H-hexagonal and R-rhombohedral). For example, the 3C-SiC polytype has the cubic crystal structure with 3 bi-layers periodicity of Si and C atoms along the [111] direction (equivalent to the c-axis in other SiC polytypes) (Fig. 2).

There are different inequivalent sites in the crystal structure of SiC polytypes. In 3C-SiC, the crystal has zinc blende structure with all atoms having similar environment of cubic crystal, while in the hexagonal polytypes, there are different inequivalent sites for atoms: h-site or hexagonal site and k-site or quasi-cubic site in 4H-SiC and h, k₁ and k₂-sites in 6H-SiC. The arrangement of the second nearest neighbor of the h and k-sites in 4H-SiC is similar to that in 2H-SiC and 3C-SiC, respectively (Fig. 3). It is expected that a defect occupying different inequivalent sites can have different properties. In 6H-SiC, nitrogen (N) substitutes C atoms at three inequivalent sites (h, k₁ and k₂-sites) were detected by EPR as three N shallow donor centers having different g-values [39]. For another example, the EPR signals of the carbon vacancies at inequivalent sites in 4H-SiC (h and k-sites) were also distinguishably observed [40–43].

Figure 2. The (11 \( \overline{2} \) 0) plane of 2H-, 4H-, 6H-SiC, and the (110) plane (the vertical axis is the [111] direction) of the 3C-SiC polytype. The Si atoms at k, h, k₁, k₂ sites are indicated. The solid lines are used to guide for the eyes of the arrangement of the second nearest neighbors of a Si atom at the h and k sites. The figure is adapted from Ref. [38].
2.2. Carrier lifetime in SiC

In semiconductor materials, the carrier lifetime is influenced by four recombination processes of electrons and holes [44] which include radiative recombination, Auger recombination, recombination at surfaces or at interfaces, and the Shockley-Read-Hall (SRH) recombination [45,46]. The radiative recombination is the band-to-band recombination, resulting in a photon emission. In indirect-band-gap semiconductors, such as SiC, the radiative recombination is insignificant since it requires the participation of extra phonons. The Auger recombination also requires the participation of three particles and only becomes significant under high injection levels. The surface recombination is due to defects present at the surface or interface and this process can play an important role to the carrier lifetime. Finally, the SRH process is the process in which a deep level defect first captures an electron from the conduction band and subsequently captures a hole from the valence band (or vice versa). The SRH process is enhanced with deeper defect level as well as its concentration and electron and hole capture cross sections [45,46]. At high temperatures, the thermal emission of electrons and/or holes from the deep level reduces the probability of the recombination process, leading to the increase of the carrier lifetime [44–46].

The carrier lifetime is an important factor for high-voltage, high-frequency devices. For high-voltage bipolar devices such as PiN diodes, bipolar junction transistor and thyristors operate under high injection condition, the lower on-resistance due to the so-called conductivity modulation effect leads to the reduction of conductivity losses. In such devices, the increase of exceed carrier concentration during the avalanche and injection processes results in the increase of the conductivity of particular region and this effect is defined as the conductivity modulation [47]. The presence of high exceeding carrier concentration which contributes to conductivity is governed by carrier lifetime. Long carrier lifetime under high injection condition is required to obtain effective conductivity modulation that helps to reduce the on-state resistance [44,48,49]. However, a very long carrier lifetime could increase the recovery time, leading to the decrease of the switching frequency and the increase of thewitching loss. Thus, shorter carrier lifetime under low injection condition is preferred for energy-saving [50,51].
3. Negative-U and DX centers in semiconductors

3.1. Concepts of the negative-U behavior and DX centers

The concept of negative-U defects in semiconductors was initially introduced by Anderson [52]. The Coulomb repulsion between two electrons is positive and causes the energy level of two electrons occupied state higher than that of a single electron occupied state. However, in certain cases, the energy of a two electrons occupied state is reduced by electron pairing saturating dangling bonds and the defect undergoes a large lattice relaxation [52]. If the energy reduction of these attractive interactions is smaller than energy of the Coulomb repulsion, the effective change of energy after capturing the second electron, $U$, is positive (positive-U behavior). If the energy earned from the attractive interaction overcomes the energy of the Coulomb repulsion, the energy $U$ is negative (negative-U behavior). In darkness at low temperatures, the paired electron state (electron spin $S=0$ and, hence, is EPR inactive) of a negative-U defect has lower energy and is the stable state of the defect, while the unpaired electron state ($S=1/2$ and EPR active) of the defect is metastable. When the energy separation between the two levels is large, the thermal induced population on the unpaired electron state at low temperatures in darkness may be below the detection limit of EPR. In such case, the observation of the EPR signal of the negative-U center requires thermal energy at elevated temperatures or illumination to increase the population on the unpaired electron state. When the paired electron state lies only a few meV below the unpaired electron state, the population of the unpaired electron state at low temperatures in darkness can be detectable by EPR [23,24].

The term DX was first used by Lang et al. [53,54] for a dominant deep level defect which was suggested as a complex between the Te donor and unidentified component in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. Later studies showed that DX centers could be formed in GaAs under hydrostatic pressure which increased the band gap in similar way as increasing the Al content in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and suggested that DX centers are can be isolated donors [55]. The term DX becomes common for a donor that has negative-U properties with its negatively charged state $\text{DX}^-$ lying deeper
than the neutral state. Therefore, in equilibrium the donor in its neutral charge state \( d^0 \) tends to capture another electron to lower its energy. This process forms a deeper negatively charged state \( \text{DX}^- \) and an ionized donor state \( d^+ \) according to the reaction \( 2d^0 \rightarrow \text{DX}^- + d^+ \) and, thus, the donor acts as an electron trap, leading to self-compensation of carriers [56].

It was known that several configurations of a DX center can be coexistent. The large lattice relaxation model of DX was firstly suggested by several studies [53, 54, 56]. There were also suggestion of DX models with small lattice relaxation in which the position of the DX center is close to the substitutional site [57–60]. Chadi [61] suggested the existences of the different negative charge states [62] and neutral charge states [63] of DX centers corresponding to different distortions around the impurities. Other studies suggested different DX configurations of Si in Al\(_x\)Ga\(_{1-x}\)As to be related to different numbers of Al atoms surrounding the isolated Si donor [64–66]. In addition, the negative charge state of a DX center and the positively charged donor were theoretically suggested to form a complex (denoted DDX) at high doping concentration due to Coulomb interaction [67]. In that case, the DDX center is more stable than the single DX center and its formation increases further self-compensation effect. The above issues make the study of DX centers more complicate but also of great fundamental defect physics and technological interests.

3.2. Statistical analysis of DX center

The population on the \( d^+ \), \( d^0 \), and \( \text{DX}^- \) states [denoted as \( N^+_d \), \( n(T) \) and \( N_{DX} \), respectively] can be described by using the statistical model of amphoteric impurities with three electronic charge states: \( d^+ \) the conduction band minimum (with degeneration factor of 1 and spin polarization \( M_S=0 \)), \( d^0 \) at \( E_d \) (with a degeneration factor of 2 corresponding to two spin states with \( M_S=\pm1/2 \)), and \( \text{DX}^- \) at \( E_{DX} \) (with a degeneration factor of 1, \( M_S=0 \)) [68]

\[
\frac{N^+_d}{n(T)} = \frac{1}{2} \exp \left( \frac{E_d - E_F}{k_BT} \right)
\]

\[
\frac{n(T)}{N_{DX}} = 2 \exp \left( \frac{E_{DX} - E_F}{k_BT} \right)
\]
From above equations, one can obtain

\[
N_{DX} = \frac{0.5N_d \exp \left( \frac{E_F - E_{DX}}{k_BT} \right)}{1 + 0.5 \exp \left( \frac{E_d - E_F}{k_BT} \right) + 0.5 \exp \left( \frac{E_F - E_{DX}}{k_BT} \right)}
\]

\[
n(T) = \frac{N_d}{1 + 0.5 \exp \left( \frac{E_d - E_F}{k_BT} \right) + 0.5 \exp \left( \frac{E_F - E_{DX}}{k_BT} \right)} \tag{1}
\]

Here \(N_d = N_d^+ + n(T) + N_{DX}\) is the total concentration of the donor, \(k_B\) is the Boltzmann constant. The Eq. (1) can also be obtained by using the statistics of multi-charge center [69–71]. In this case, there are three states for a DX center: \(d^+\) state without occupied electron and neutral charge state (degeneration factor is 2 corresponding to two states with \(M_S = \pm 1/2\)) with one occupied electron and one DX state with two occupied electrons. The total energy of electrons on the \(d^+\), \(d^0\) and DX states are 0, \(E_d\) and \(2E_d - (E_d - E_{DX})\), respectively (the negative correlation energy \(U = E_d - E_{DX}\) is the energy that the negative-U center can reduce by capture the second electron). The detail of the interpretation can be found elsewhere [69–71].

It has also been shown that in a negative-U center, the Fermi level varies only very slowly with electronic density and temperature and is effectively pinned at the middle of the two populated levels (i.e. \(E_d\) and \(E_{DX}\) levels for DX center) [69,71]. These studies showed that the Fermi level is almost constant when the average number of electrons per DX center [\(n_{av} = (2N_{DX} + n(T))/N_d\)] varies from close to 0 to 2. Within the error of determination of energy level, the Fermi level can be approximately at the middle of \(E_d\) and \(E_{DX}\) levels (i.e. \(E_F - E_{DX} \approx E_d - E_F\)) and Eq. (1) is rewritten as

\[
n(T) = \frac{N_d}{1 + \exp \left( \frac{E_d - E_F}{k_BT} \right)} \tag{2}
\]

With including the excited states of donors [68,70,71], the temperature dependence of the population on the \(d^0\) state of a DX center can be described as
Here, $G_i$ is the degenerate factor of corresponding excited states. With considering only the first excited state $2p$, Eq. (3) can be rewritten as

$$n(T) = \frac{N_d}{1 + \exp \left( \frac{E_d - E_F}{k_B T} \right) + 0.5 \sum_i G_i \exp \left( \frac{E_d - E_i}{k_B T} \right)}$$

(3)

Here, $G_i$ is the degenerate factor of corresponding excited states. With considering only the first excited state $2p$, Eq. (3) can be rewritten as

$$n(T) = \frac{N_d}{1 + \exp \left( \frac{E_d - E_F}{k_B T} \right) + C \exp \left( \frac{E_d - E_{2p}}{k_B T} \right)}$$

(4)

Here, $E_{2p} - E_d$ is the energy distance from $d^0$ ($E_d$ or $E_{1s}$) to the first excited state $2p$ and $C$ is the total degenerate factor of excited states within $k_B T$ from the first excited state. The number of spins or the net donor concentration obtained from EPR experiments with considering the temperature effect and measurement conditions is directly proportional with $n(T)$ determined from Eq. (4). Thus, the energy distance $E_d - E_F$ and $E_{2p} - E_d$ can be obtained from the fits of experiment data using Eq. (4). The $E_d$ can be obtained as $|E_d| = 4|E_{2p} - E_d|/3$ when the energy levels of excited states of the donor is assumed to follow the effective mass theory [i.e. the $E_d/i^2$ rule ($i = 1, 2, ..., n$) or $E_{2p} = E_d/4$ and $|E_{2p} - E_d| = |(E_d/4) - E_d| = 3|E_d|/4$. Since the Fermi level is approximated at the middle of $E_d$ and $E_{DX}$, the $E_{DX}$ level is estimated to be $|E_{DX}| = |E_d| + 2|E_d - E_F|$. 

3.3. Negative-U center $Z_1/Z_2$ in 4H-SiC

The $Z_1/Z_2$ center in 4H-SiC ($\sim$0.65 eV below the conduction band minimum $E_C$) detected by deep level transient spectroscopy (DLTS) [72,73] is known to be a negative-U system having two higher-lying excited levels $Z_1$ (at $E_C - 0.52$ eV) and $Z_2$ (at $E_C - 0.45$ eV) [74]. This center is the lifetime killing defect in SiC grown by chemical vapour deposition (CVD) [50,51,75–77]. The $Z_1/Z_2$ is one of the most common deep levels in as-grown material [73] and very thermally stable [72]. Since this center governs the carrier lifetime in as-grown CVD epitaxial layers [50,51,75–77], it had been intensively studied. Different defect models such as the divacancy [72], nitrogen-related defect [78] or N-dicarbon interstitial complex [79] had been suggested for $Z_1/Z_2$. 

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The Z$_1$/Z$_2$ center could be created by irradiation with electrons of energy as low as ~100 keV which only displace carbon atoms [50,51,80–82]. Therefore, the origin of Z$_1$/Z$_2$ should be related to intrinsic defect at C sites (carbon vacancy-V$_C$, carbon interstitial or their associated complexes) [80,81]. In later studies [83,84], the reduction of the concentration of Z$_1$/Z$_2$ by C implantation and subsequent annealing was observed, supporting the suggestion that these centers are V$_C$-related defects. In EPR studies, the C vacancies in the single positive charge state (V$_C^+$) at both the k and h sites [40] and in the single negative charge state (V$_C^-$) at the h site [41] have been identified. The carbon vacancies are very thermally stable and have similar annealing behaviors as the Z$_1$/Z$_2$ center [85]. However, no clear evidence indicating the negative-U properties of V$_C^-$ has been observed and the missing EPR signal of V$_C^-$ at the k site, V$_C^-(k)$, is believed to be due to overlapping with EPR signals of other defects introduced during high-energy (2 MeV) electrons irradiation at 850°C [41]. Due to the lack of direct correlation in concentration between Z$_1$/Z$_2$ determined by DLTS and the carbon vacancies determined by EPR, the origin of Z$_1$/Z$_2$ had not been conclusively identified.

In our present studies [42,43,86,87], we used low-energy (250 keV) electrons to irradiate free-standing 4H-SiC CVD layers at room temperature to displace mainly carbon atoms. Combining EPR experiments and the supercell calculations, the V$_C^-(k)$ was identified [43]. We show that the negative carbon vacancies are negative-U systems with the double negative charge state lying below the single negative charge state [42,43]. Using high n-type doping 4H-SiC irradiated with high electron fluences it was possible to apply EPR and DLTS on the same samples, allowing direct correlation between Z$_1$/Z$_2$ concentration determined by DLTS and the V$_C^-$ concentration determined by EPR. Combining DLTS, EPR and supercell calculations, we show that the Z$_1$/Z$_2$ deep level is related to the (2|-0) level of V$_C$ [42,86,87] and the higher-lying levels Z$_1$ and Z$_2$ are the (-|-0) levels of V$_C$ at h and k sites, respectively [42,43].
4. Electron paramagnetic resonance

The first successful experiments of EPR (also known as Electron Spin Resonance or ESR) were performed by Zavoisky [88] in 1944. The detail about early history of magnetic resonance techniques was given by Ramsey [89]. Since its discovery, EPR has been developed and become a powerful method for researchers in various fields (Ref. [90], pages 7 and 8).

4.1. Electronic Zeeman interaction

Under external magnetic field, the energy level of the unpaired electrons is separated to multi levels due to the interaction between magnetic field and their total angular momentum and this effect is called Zeeman effect [91]. The total angular momentum of an electron ($\mathbf{J}$) has two components: spin angular momentum ($\mathbf{S}$) and orbital angular momentum ($\mathbf{L}$). The magnetic moment caused by the total angular momentum $\mathbf{M}$ is given by $\mathbf{M}=-g\mu_B\mathbf{J}$ (the negative sign is due to negative electronic charge of electron). Thus, the Hamiltonian of the interaction between an external magnetic field $\mathbf{B}$ and the total angular momentum is described as

$$H = -M_B = \mu_B B \cdot g \cdot \mathbf{J} \quad (5)$$

Here, $\mu_B=9.27400968\times10^{-24}$ J T$^{-1}$ is the Bohr magneton and $g$ is the splitting factor of the energy levels. In the classical theory, the $g$ factor was given by Landé formula in which the electron spin $g_e$ factor and the electron orbital $g_L$ factor are equal to 2 and 1, respectively (Ref. [92], page 141).

$$g = \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)} \quad (6)$$

In many cases, the orbital angular momentum of the unpaired electron center in crystal solid is quenched ($L=0$) and thus, the total angular momentum $J$ in Eq. (5) is often replaced by electron spin $S$. In this case, the $g$ factor in Eq. (6) is equal 2. It was found that the electron spin $g_e$ factor for a free electron is ~ $2.002319$ [93]. The deviation from the value from 2 (obtained from classic Dirac equation) can be calculated in
terms of the anomalous magnetic dipole moment of electron which is
due to the interaction between electrons and virtue photons [94].

4.2. The basic principle of EPR

The principle of EPR is based on the interactions between an ex-
ternal magnetic field and unpaired electron center such as electronic
Zeeman interaction. The energy splits of energy levels caused by those
interactions are often equal the energy of photon of a microwave. There-
fore, transitions between the splitting energy levels can be induced by
absorption or emission of photons of microwave. The resonance absor-
tion of the microwave occurs when the energy separation between two
levels is equal to the photon energy of microwave. For a simplest case
when the electron spin \( S = 1/2 \) and without the presence of angular mo-

![Figure 3](image)

Figure 3. (a) The separated energy level of an unpaired electron \( (S=1/2, 
L=0, \ g \ \text{factor is 2}) \), (b) the absorption of microwave occurs at
\( B=339.377 \ \text{mT} \) with the microwave frequency of 9.5 GHz) and (c) the
corresponding EPR signal obtained from the derivation of the absorp-
tion.
momentum (L=0), the energy level is split into two sublevels under external magnetic field and there is only one resonance absorption corresponding to the transition between the two levels. The observed EPR signal is often obtained from the derivation of the absorption (Fig. 3).

In practice, the applied magnetic field is swept and controlled by the magnetic-field controller. The typical components of an EPR spectrometer are shown in Fig. 4. The generation of a constant frequency microwave and the detection of the absorption signal are processed by the microwave bridge. The sample is kept inside a cavity which acts as a resonator of the microwave, creating standing waves. For angular dependence measurements, either the sample or the magnet is rotated. The cavity can be equipped with a cryostat allowing the regulation of the sample temperature in the range of 4-295 K. The quality factor Q of the cavity is defined as the ratio between the energy stored and the energy lost during a period of microwave. Higher Q factor improves the sensitivity of the EPR spectrometer. The signal-to-noise ratio of the absorption of the microwave is enhanced using a lock-in amplifier. Finally, the

![Figure 4. The typical block diagram of an EPR system (adapted from Ref. [95]).](image)
dependence of the recorded EPR intensity on the applied magnetic field, i.e. the EPR spectrum, is recorded.

4.3. Hyperfine interaction

When the wave function of unpaired electron overlaps with an impurity which has a nuclear spin $I \neq 0$, there will be an interaction between the electron spin and the nuclear spin. This interaction is called hyperfine interaction since the split of the energy levels caused by this interaction is often much smaller than that of the electronic Zeeman interaction. If both the unpaired electron and the nuclear spin are belonged to the same atom, the hyperfine interaction is called self-hyperfine interaction. In the case the hyperfine interactions are caused by the unpaired electron and the nuclear spins of its neighbor atoms, these interactions are called ligand-hyperfine interaction.

![Figure 5. (a) The scheme of energy levels and (b) corresponding EPR spectrum of an impurity with an electron spin $S=1/2$ and a nuclear spin $I=1/2$ (with 100% natural abundance). The vertical lines in figure (a) indicate the allowed transitions which give rise to the EPR lines observed in figure (b).](image-url)
The interaction between the electron spin \( S \) and the nuclear spin \( I \) splits further each energy level of the electronic Zeeman interaction into \( 2I+1 \) levels corresponding to \( 2I+1 \) values of the magnetic quantum number \( M_I (\pm I, \pm I+1, \ldots, I-1, I) \). The allowed transitions between two levels have to follow the selection rules in which \( \Delta M_S = \pm 1 \) and \( \Delta M_I = 0 \). The forbidden transitions with \( \Delta M_I = \pm 1 \) might become partly allowed in some particular cases [96,97]. For a spin center which has \( S=1/2 \) and a hyperfine interaction with an impurity having a nuclear spin \( I=1/2 \) and 100% natural abundance, the level will split into four levels under an external magnetic field \( B \). The hyperfine interaction is independent of the magnitude of \( B \) and occurs at zero field (\( B=0 \)), i.e. the energy level already splits off even for \( B=0 \) [Fig. 5(a)]. The dependence of these energy levels on \( B \) [92] (pages 30-31) is shown in Fig. 5(a). In this EPR center, there are only two allowed transitions and, therefore, only two EPR lines can be observed (for the case of the electronic Zeeman and hyperfine interactions being isotropic) [Figs. 5].

In nature, many elements have several stable isotopes with different natural abundances and different nuclear spins and nuclear \( g_n \) factors. Thus, the hyperfine interactions involving these isotopes are different and can be distinguishable in the EPR spectrum. For an example, in SiC, Si has three stable isotopes, \( ^{28}\text{Si} \) (\( I=0, 92.2\% \) natural abundance), \( ^{29}\text{Si} \) (\( I=1/2, 4.7\% \) natural abundance) and \( ^{30}\text{Si} \) (\( I=0, 3.1\% \) natural abundance) while C has two isotopes, \( ^{12}\text{C} \) (\( I=0, 98.9\% \) natural abundance) and \( ^{13}\text{C} \) (\( I=1/2, 1.1\% \) natural abundance). For carbon vacancies in 4H-SiC [40,43] with the magnetic field along the \( c \)-axis, the hyperfine interactions between an electron spin \( S=1/2 \) and nuclear spins \( I=1/2 \) of a \( ^{29}\text{Si} \) atom occupying at one of three nearest-neighbor sites in the basal plane become equivalent, giving rise to a pair of hyperfine lines with the same splitting. There is 86.55\% (=95.3\%×95.3\%×95.3\%) in probability that all three Si atoms has \( I=0 \) and, hence, no hyperfine interaction and only the Zeeman interaction responses for the observed EPR spectrum (it is often called the central line or main line since no splitting occurred and the intensity is strongest compare to the others). There is 12.81\% (=3×4.7\%×95.3\%×95.3\%) in probability that one of the three atoms is \( ^{29}\text{Si} \) and the hyperfine interaction gives rise to two hyperfine lines. The probabilities that two and three atoms among three Si in the basal plane are \( ^{29}\text{Si} \) are 0.63\% (=3×4.7\%×4.7\%×95.3\%) and 0.01\%
The equivalent hyperfine interactions of S and I of two or three $^{29}$Si atoms give rise to three (intensity ratio is 1:2:1) or four (intensity ratio is 1:3:3:1) EPR lines, respectively. Due to their small probabilities, the hyperfine interactions of the electron spin S=1/2 and nuclear spins of two or three $^{29}$Si occupying three equivalent sites in basal plane could not be observed in EPR spectra. The ratio of the intensity between the total intensity of the two hyperfine lines due to hyperfine interaction of electron spin S=1/2 and a nuclear spin of $^{29}$Si occupying one of three equivalent sites in the basal plane and the central line is estimated to be 14.8% ($=12.81%/86.55%$) (Fig. 6). For C, only the $^{13}$C isotope has non-zero nuclear spin (I=1/2 and 1.1% natural abundance), thus, the total intensity of its two hyperfine lines is $\sim$1.1% the intensity of the main line. From the number of hyper-

![EPR spectrum](image)

**Figure 6.** Typical EPR spectrum of the carbon vacancy in SiC having electron spin S=1/2 and ligand hyperfine interaction with nuclear spins I=1/2 of $^{29}$Si atoms occupying three equivalent sites in the basal plane. Two lines at ~335.8 mT and 342.9 mT are the hyperfine lines due to the hyperfine interaction between S and I of a $^{29}$Si occupying one of three equivalent sites. The inset shows two hyperfine lines (at ~332.2 mT and 348.5 mT) due to the hyperfine interactions between S and I of two $^{29}$Si atoms occupying two of three equivalent sites in the basal plane. The hyperfine lines in the inset are often undetectable in EPR measurements due to their small intensities.
fine lines and the intensity ratio between hyperfine lines and the main line, we can determine the nuclear spins and the number of atoms involved in the hyperfine interaction and estimate the natural abundance of the isotopes, respectively. The information is very useful for identification of the involved atoms at the defect site and/or surrounding and, hence, the microscopic model of the defect.

4.4. Spin-Hamiltonian and angular dependence

The spin-Hamiltonian describing an electronic Zeeman interaction and hyperfine interactions has the following form

\[ H = \mu_B B \cdot g \cdot S + \sum_i S \cdot A_i \cdot I_i \]  \hspace{1cm} (7)

Here, \( S \) and \( I_i \) are the spins of unpaired electrons and nucleus spins, respectively. In general cases, \( g \) and \( A_i \) are the tensors describing the anisotropic of electronic the Zeeman and hyperfine interactions. In the following sections, the physical principle of the angular dependence of EPR line positions caused by the anisotropy of those tensors is given.

4.4.1. The \( g \) tensor

Generally, the \( g \) factor of an unpaired electron (\( S=1/2 \) and \( L=0 \)) in semiconductors is not a constant and depends on the orientation of the external magnetic field. The origin of the anisotropy is mainly due to the spin-orbit correction, spin-other-orbit correction and the electronic Zeeman kinetic energy correction [98]. The unpaired electron moves relatively with the electric field caused by the ions and other electrons. This movement results in the appearance of a magnetic field following the Joules-Bernoulli equation. The physical meaning of the spin-orbit correction is the interaction of the unpaired electron spin and this magnetic field [98]. The spin-other-orbit correction can be considered as the interaction between the external magnetic field \( B \) and the induced electronic currents of unpaired electron [98]. The calculation of the \( g \) factor and its anisotropic property is recently available [98,99] and it could be used to identify the origin of the unpaired electron center.

In a single crystal, there are equivalent orientations and one defect is expected to exist in all orientations with a similar probability. We can
also consider the defect existing in only one orientation and the observed EPR spectrum is the results of all the equivalent orientations of the magnetic field $\mathbf{B}$. For a low symmetry $g$ tensor, these equivalent orientations of $\mathbf{B}$ can have different effectual values of $g$ for an arbitrary direction. The inequivalent effectual values of $g$ result in different field positions of EPR lines.

![Figure 7. Angular dependence of EPR line positions of a center with $C_{1h}$ symmetry $g$ tensor in a single crystal with hexagonal lattice when the magnetic field rotates in (a) (1 1 00) (b) (0001) and (c) (1 1 2 0) planes. The $g$ tensor used for simulation has components $g_{xx}=2$, $g_{xy}=g_{xz}=0$, $g_{yy}=1.9$, $g_{yz}=0.1$, $g_{zz}=2.1$ (the axes $x$, $y$, $z$ are parallel to [1 1 2 0], [1 1 0 0] and $c$ directions, respectively) and the frequency of microwave is 9.5 GHz.](image)

The number of EPR splitting lines is determined by the symmetry of both the symmetry of the crystal lattice and the $g$ tensor of the defect. In the hexagonal lattice such as 4H-SiC, 6H-SiC and wurtzite III-Nitrides, there are six equivalent orientations of an arbitrary $\mathbf{B}$ having the same angle $\theta$ (the angle between the $c$-axis and $\mathbf{B}$) but with $\varphi$ differing from each other by 60° ($\varphi$ is the angle between the [1 1 2 0] direction and the projection of $\mathbf{B}$ on the (0001) plane). When $\mathbf{B}||c$, the six
orientations of $\mathbf{B}$ are equivalent and their six EPR lines coincide, giving rise to a single EPR line with six times in intensity. At an arbitrary direction of the magnetic field, the line splits into six lines if the $\mathbf{g}$ tensor has $C_1$ symmetry. For higher symmetry of the $\mathbf{g}$ tensor, some orientations of $\mathbf{B}$ becomes equivalent, giving rise to the same effectual values of $\mathbf{g}$ and, thus, reducing the number of observed EPR lines and increasing the intensity of the coincident lines. If the $\mathbf{g}$ tensor has $C_{1h}$ symmetry in which $g_X$ is parallel to the crystal axis [1120], there will be 4 or 3 distinguished EPR lines when rotating the magnetic field in the (1120) or (1T00) planes, respectively (Fig. 7). In the case of $C_{3v}$ symmetry with $g_Y \parallel c$ and $g_X = g_Y$, all six $\mathbf{B}$ orientations become equivalent with respect to the $\mathbf{g}$ and all EPR lines coincide. In EPR experiments, the $\mathbf{g}$ tensor of the defect can be determined from the least-square fits of the obtained angular dependence using the first term of Eq. (7) with the magnetic field rotating in a high symmetric plane, such as (1120) or (1T00) or equivalent planes.

4.4.2. The $A$ tensor

In solid crystals, the hyperfine interaction is often anisotropic and described by the $A$ tensor. The symmetry of the $A$ tensor can be lower than that of the $\mathbf{g}$ tensor and, therefore, the number of the hyperfine lines can be more than expected for the electronic Zeeman interaction (Fig. 8). From the fits of the angular dependence of the EPR line positions with the magnetic field $\mathbf{B}$ rotating in a certain high symmetric plane using Eq. (7), the hyperfine tensor $A$ can be determined. From the obtained hyperfine data, possible defect models can be suggested and compared to the corresponding values obtained from theoretical calculations. The correlation between EPR experiments and theoretical calculations allows a conclusive identification of the defect.

In semiconductors, intrinsic defects or impurities have strong influence on the properties of the materials. The obtained $\mathbf{g}$ tensor provides information about the symmetry of the defect. If the impurities have a nuclear spin $I \neq 0$, the involved impurities can be directly and chemically identified from the observed self-hyperfine structure. The information on neighboring atoms of a defect or an impurity can be obtained from the ligand-hyperfine structure. Such information is essential
for identification of the defect and understanding its electronic structure. In many cases, identification of point defects in semiconductors needs additional help from theoretical modeling of the defect. In some cases, the position of the energy level of a point defect can be determined by photoexcitation EPR (photo-EPR) [42,100] or temperature dependence of the EPR signal [23,24,96]. To this end, EPR is a powerful method for identification and characterization of point defects in semiconductors.

Figure 8. Angular dependence of EPR line positions (upper and lower lines) of a spin center with $S=1/2$ having a hyperfine interaction with a nuclear spin $I=1/2$ in a single crystal with the hexagonal lattice for the magnetic field rotating in (a) (1 1 0 0), (b) (0 0 0 1) and (c) (1 1 2 0) planes. The $g$ tensor has $C_{1h}$ symmetry while the $A$ tensor has $C_1$ symmetry. The central curves show the angular dependence of the EPR line positions determined by the $g$ tensor.
References

[95] www.bruker.com
Papers
Summary of the papers

In paper 1, we showed that Si already forms a stable DX center in Al$_x$Ga$_{1-x}$N with x ~0.77. However, with the Fermi level locating only ~3 meV below E$_d$, Si still behaves as a shallow donor and high conductivity at room temperature could be achieved in Al$_{0.77}$Ga$_{0.23}$N:Si layers. In samples with the concentration of the residual oxygen (O) impurity larger than that of Si, we observed no carrier compensation by O in Al$_{0.77}$Ga$_{0.23}$N:Si layers, suggesting that at such Al content, O does not seem to hinder the n-type doping in the material.

In paper 2, we determined the dependence of the E$_{DX}$ level of Si on the Al content in Al$_x$Ga$_{1-x}$N:Si layers (0.79≤x≤1) with the Si concentration of ~2×10$^{18}$ cm$^{-3}$ and the concentrations of residual O and C impurities of about an order of magnitude lower (~1÷2×10$^{17}$ cm$^{-3}$). We found the coexistence of two DX centers (stable and metastable ones) of Si in Al$_x$Ga$_{1-x}$N for x≥0.84. For the stable DX center, abruptly deepening of E$_{DX}$ with increasing of the Al content for x≥0.83 was observed, explaining the drastic decrease of the conductivity as often reported in previous transport studies. For the metastable DX center, the E$_{DX}$ level remains close to E$_d$ for x=0.84÷1 (~11 meV for AlN).

In paper 3, we identified the negatively charged carbon vacancy at the quasi-cubic (k) site in 4H-SiC and observed clear negative-U behaviors of the negative carbon vacancies at both hexagonal (h) and k sites. Combining EPR, DLTS and supercell calculations, we showed that the Z$_1$/Z$_2$ center is related to the (2-|0) level of V$_C$ and its higher-lying levels Z$_1$ and Z$_2$ are related to the (-|0) levels of V$_C$ at the h and k sites, respectively.
Papers

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