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External electric field effect on the hydrogenic donor impurity in zinc-blende GaN/AlGaN cylindrical quantum dot
High-Al-content Al\textsubscript{x}Ga\textsubscript{1-x}N (x > 0.7) is the principal alloy system for the development of deep ultraviolet light emitting diodes (LEDs)\textsuperscript{1-5} with contemplated enormous social impact if considering their intended implementation in portable units for water/air purification and sterilization.\textsuperscript{6} Electrical pumping of LEDs requires both n- and p-type doping. Silicon (Si) is the only technologically important n-type dopant in the Al\textsubscript{x}Ga\textsubscript{1-x}N alloy system (0 < x < 1). Achieving high n-type conductivity in high-Al-content Al\textsubscript{x}Ga\textsubscript{1-x}N is proven difficult. The presence of readily incorporated oxygen (O) impurity, especially in high-Al-content Al\textsubscript{x}Ga\textsubscript{1-x}N, complicates the doping study even further. It is known that both Si and O are shallow donors in GaN but their electronic structure in high-Al-content Al\textsubscript{x}Ga\textsubscript{1-x}N is still much debated.\textsuperscript{2,7}

Theoretical studies by Park and Chadi\textsuperscript{2} suggested that O and Si undergo a transition from a shallow donor in GaN to a deep DX center in Al\textsubscript{x}Ga\textsubscript{1-x}N when x \sim 0.20 for O and x \sim 0.26 for Si. The DX behavior has also been found by other calculations for Si (at x ≥ 0.6)\textsuperscript{8} and O (at x ≥ 0.4).\textsuperscript{9,10} In these DX (or negative-U) centers, the donor in its neutral charged state d\textsuperscript{0} prefers to capture another electron and relaxes to a deeper negatively charged state DX\textsuperscript{−}, forming an ionized donor state d\textsuperscript{+} according to the process: 2d\textsuperscript{0} \rightarrow d\textsuperscript{+} + DX\textsuperscript{−}.\textsuperscript{7} The DX behavior occurs in connection with a large lattice relaxation caused by a Coulomb attraction between the impurity and third nearest neighbors.\textsuperscript{10} This is relevant for O occupying the anion site, which is negatively charged in the DX\textsuperscript{−} state, interacting with the third neighbor cation (Ga or Al), but not for Si substituting for the cation site. It was, therefore, suggested that Si should remain to be a shallow donor even in AlN.\textsuperscript{10} The conclusion was supported by a Raman scattering study of Si and O in GaN under hydrostatic pressure\textsuperscript{11} which increases the band gap similar to increasing the Al content in Al\textsubscript{x}Ga\textsubscript{1-x}N. This study predicted the transition from a shallow donor to a DX center to occur at x \sim 0.40 for O, but no DX formation for Si up to x \sim 0.56 (corresponding to the highest pressure used in their experiments).\textsuperscript{11} Hall-effect and persistent photoconductivity measurements suggested that O becomes a DX center for x \sim 0.27, whereas no DX behavior has been detected for Si up to x \sim 0.44.\textsuperscript{12} In a later transport study of Si-doped Al\textsubscript{x}Ga\textsubscript{1-x}N with higher Al content (0.5 < x < 0.6), O and Si were suggested to become DX centers for x exceeding \sim 0.3 and \sim 0.5, respectively.\textsuperscript{13}

Concerning O, previous studies seem to agree that O becomes a DX center in Al\textsubscript{x}Ga\textsubscript{1-x}N with x exceeding \sim 0.3–0.4, and hence, is a carrier compensating defect, hindering the n-type doping in the material. For Si, reported results are controversial. More recently, several groups have obtained n-type conductivity in Al\textsubscript{x}Ga\textsubscript{1-x}N:Si with x \sim 0.5–1.0 and concluded that Si is a shallow donor even in AlN.\textsuperscript{14–19} However, in transport measurements, it is not possible to know if free carriers come from the neutral d\textsuperscript{0} or negative DX\textsuperscript{−} states of the donor. In electron paramagnetic resonance (EPR) studies of Si-doped AlN, the EPR signal of the shallow donor could only be observed under or after illumination at temperatures below 60 K.\textsuperscript{20} The behavior was explained by the negative-U properties of the Si donor with the DX\textsuperscript{−} level at \sim 0.32 eV below the conduction band E\textsubscript{C}.\textsuperscript{20} Similar DX behaviors were observed for the donor in Al\textsubscript{x}Ga\textsubscript{1-x}N:Si with x \sim 0.75 or larger, but the location of the DX\textsuperscript{−} level was not determined.\textsuperscript{21} In EPR studies of undoped AlN, O was also suggested to be a DX center.\textsuperscript{22,23} However, in the EPR study of AlN:Si by Irmscher et al.,\textsuperscript{24} Si was suggested to be a shallow donor and the failure of detecting the signal in darkness was explained as due to carrier compensation by other lower-lying defect levels. In a more recent EPR study of unintentionally Si-doped AlN, the EPR spectrum of the Si shallow donor could be detected in darkness at temperature above \sim 95 K and from the temperature dependent study of the donor concentration it was suggested that Si is a DX center with the DX\textsuperscript{−} level at \sim 78 meV below the neutral d\textsuperscript{0} state.\textsuperscript{25} More recent hybrid functional calculations suggest that both Si and O are DX centers in AlN.\textsuperscript{26}

In this letter, we report EPR study of Al\textsubscript{x}Ga\textsubscript{1-x}N:Si with x \sim 0.77. By monitoring the change of the concentration of the neutral state d\textsuperscript{0} with temperature in darkness, we show that Si already becomes a DX center as previously suggested by Bayerl and co-workers,\textsuperscript{21} but behaves as a shallow donor due to a small separation of only \sim 3 meV between the DX\textsuperscript{−} and d\textsuperscript{0} states, and its shallow states follow the effective mass theory (EMT).

The Al\textsubscript{x}Ga\textsubscript{1-x}N:Si epitaxy was performed by metal-organic chemical vapor deposition (MOCVD) on semi-insulating 4H-SiC substrates following an in situ template
growth. Typical performance of the MOCVD system as to the AlN growth, and Si-doped high-Al-content AlGaN layers can be found elsewhere. The dopant gas silane (SiH₄) was delivered with a gas-flow-rate ratio to the total metal-organic precursor flow in the range of ~1.8–3.3 × 10⁻⁴. The Al content, the thickness of the AlₓGa₁₋ₓN:Si layer, and the atomic concentration of Si, [Si], and O, [O], were determined by secondary ion mass spectrometry (SIMS) by Evans Analytical Group (the notation [ ] is used in this paper to denote the concentration obtained from SIMS). The deposition parameters were tuned to obtain [Si] in the range of low 10¹⁷ cm⁻³, which gives good EPR signals while the conductivity is still not too high so that EPR measurements with high Q-factors can be performed at high temperatures. The typical thickness of the layers is ~400 nm and the Al content is x ~ 0.77. The energy of the near band edge (NBE) emission in the studied AlₓGa₁₋ₓN structures as measured by cathodoluminescence at room temperature is ~5.37 eV. EPR measurements were performed on an X-band (~9.4 GHz) E500 Bruker spectrometer equipped with a continuous He-flow cryostat, allowing the regulation of the sample temperature from 4 to 295 K. For illumination, halogen (200 W) or xenon (150 W) lamp was used as excitation source. The donor concentration or the number of spins were determined from double integration and measurement conditions with the spin counting application provided and calibrated by Bruker.

In the Alₓ₋₀.₇₇Ga₀.₂₃N:Si layers with the free carrier concentration, n, in the range of low 10¹⁷ cm⁻³ as determined by either capacitance-voltage or microwave-based contactless measurements, an EPR line was observed in darkness at low temperatures. Fig. 1 shows the EPR spectra measured in darkness at different temperatures for an Al₀.₇₇Ga₀.₂₃N:Si sample grown by MOCVD on 4H-SiC substrates. As has also been observed in many samples, the change of the signal intensity induced by illumination in this Si-rich sample is n ~ 1.6 × 10¹⁸ cm⁻³ (i.e., ~80% of Si shallow donors activated). In this sample, [Si] is about an order of magnitude higher than [O] and should be the principal source of free carriers. The observation of the EPR signal of the shallow donor in darkness at low temperatures indicates that Si behaves as shallow donor in the material.

From the temperature dependence of the donor concentration on the neutral state d⁰, it is possible to estimate the energy distance between the shallow state and the first excited state as previously shown for the P shallow donor in SiC. If a donor transforms into a DX center, the Fermi level E_F is expected to move close to the DX⁻ state, E_DX⁻, at low temperatures. Monitoring the temperature dependence of the population on d⁰ (or E_d) also allows determining the energy distance between d⁰ and E_DX⁻. The population on d⁰ can be described by the Boltzmann distribution.

![FIG. 1. EPR spectra measured in darkness at different temperatures for B|c in a Si-doped Al₀.₇₇Ga₀.₂₃N layer with [Si] ~ 2 × 10¹⁸ cm⁻³, [O] ~ 3 × 10¹⁷ cm⁻³, and n ~ 1.6 × 10¹⁸ cm⁻³. The inset shows the integrated EPR spectra with their intensity being corrected for the Boltzmann distribution between the two spin levels M₅ = ±1/2 and the Q-factors at different temperatures so that the area under the curve is directly proportional to the number of spins.](image1)

![FIG. 2. EPR spectra measured at 5 K for B|c in darkness and under illumination with white light in an O-rich Si-doped Al₀.₇₇Ga₀.₂₃N layer with [Si] ~ 2 × 10¹⁸ cm⁻³, [O] ~ 2 × 10¹⁸ cm⁻³, and n ~ 2.3 × 10¹⁸ cm⁻³.](image2)
Here, $N$ is the total concentration of the donor, $k_B$ is the Boltzmann factor, the degenerate factor $G = 2$ for $E_d$ (taking into account the two spin levels $M_S = \pm 1/2$) and $E_i$ are the excited states. The energy is taken to be zero at the conduction band ($E_C = 0$), and hence, $E_d - E_F > 0$, and $E_i - E_d > 0$. The transition from $d^0$ to the first excited state ($2p$ or $2s$) is the most important for the process of removing electrons from the level since once electrons reach the first excited state, they can move up to higher-lying states within $k_BT$. Considering only the first excited state, Eq. (1) can be rewritten as

$$n(T) \propto \frac{N2e^{-(E_d-E_F)/k_BT} + \sum G_i e^{-(E_i-E_d)/k_BT}}{1 + 2e^{-(E_d-E_F)/k_BT} + \sum G_i e^{-(E_i-E_d)/k_BT}}.$$  

(2)

Here, $\Delta E$ is the energy distance between $d^0$ ($E_d$ or $E_i$) and the first excited state, and $C$ is a factor taking into account the thermal excitation from the first excited state to higher-lying excited states (including their degeneration factors). At low temperatures, $E_F$ is close to $E_d$ for a shallow donor and to $E_{DX}$ for a DX center.

Figs. 3(a) and 3(b) show the temperature dependence of the number of spins on $d^0$ determined by EPR for two representative Si-rich and O-rich $Al_{0.77}Ga_{0.23}N$ layers whose EPR spectra were shown in Figs. 1 and 2. Unlike a shallow donor in semiconductors, which has higher concentrations on the neutral state at lower temperatures, $n(T)$ in these $Al_{0.77}Ga_{0.23}N$ layers is smallest at lowest temperatures and increases with increasing temperature (Fig. 3). Such behaviors at low temperature are typical for a DX center since the Fermi level $E_F$ lies close to $E_{DX}$ and below $d^0$. As long as the process of thermal excitation of electrons from $E_{DX}$ to $E_d$ is dominating, $n(T)$ increases with increasing temperature. When the thermal energy can excite electrons from $E_d$ to the first excited state, $n(T)$ will be governed by two competing processes. At higher temperatures, the removal of electrons from $d^0$ to the excited states by the latter process becomes dominant, leading to the decrease of $n(T)$.

From the best fits to the experimental data using Eq. (2), we obtained the energy distances $(E_d-E_F)$ and $\Delta E$: $(E_d-E_F) \sim 2.8–3.2$ meV and $\Delta E \sim 39–44$ meV for several $Al_{0.77}Ga_{0.23}N$:Si samples including thick (1.2 and 2.1 $\mu m$) Si-doped layers which show a similar linewidth narrowing effect as reported in Refs. 21 and 29. In this case, the Fermi level is expected to locate close to the DX state and we can approximate $E_d - E_F \sim E_d - E_{DX}$. Locating only few meV above the DX- level, the shallow $d^0$ state can be populated even at low temperatures, giving rise to the observed EPR signal in darkness similar to the behavior of a normal shallow donor. The main source of errors in determination of the donor concentration comes from the temperature measurements. In a He-flow cryostat, at very low temperatures ($<10$ K), the sample temperature can be $\sim 1–1.5$ K higher than the reading from the temperature sensor which is placed separately 1.5–2 cm below the sample. (According to Boltzmann distribution and for an energy separation of 2.8 meV, $n(T)$ at 6 K is three times larger than that at 5 K.) This leads to higher $n(T)$ values than predicted as can be seen in the low temperature range in Fig. 3 (three data points at T $< 15$ K). Since the errors from temperature measurements and the linewidth narrowing effect are pronounced only at very low temperatures, their influence on the obtained results is small.

With the thickness of Si-doped layer obtained from SIMS and the number of spins measured by EPR, the spin density or the concentration of the donor on the $d^0$ state can be determined. The highest spin densities in both O-rich and Si-rich samples are about $\sim 1.5–1.8 \times 10^{18} \text{cm}^{-3}$ at 70–80 K and the larger number of spins in the Si-rich sample in Fig. 3 was due to a larger volume of Si-doped layers. In the Si-rich sample, $|S|_i$ is significantly higher than $|O|$, and thus, the obtained energy separations should be related to Si.

Assuming that the neutral state and excited states of the donor follow the EMT, i.e., the $E_d/S^2$ rule ($i = 1, 2, \ldots, n$) or $E_{2p} \sim E_d/4$ and $|\Delta E| = |E_{2p} - E_d| = |E_d/4 - E_d| = 3E_d/4$, we can estimate the energy of the neutral state $E_d$ from the observed $\Delta E$ value: $E_d = 4\Delta E/3 \sim 52–59$ meV for the studied $Al_{0.77}Ga_{0.23}N$ samples. Taking into account the formation of the $DX$ state at $\sim 3$ meV below the shallow $d^0$ state, the activation energy $E_a$ of Si is estimated to be: $E_a \sim E_{DX} \sim 55–62$ meV, which is considerably higher than the value of $\sim 41$ meV determined from the temperature dependence of the resistivity for Si in heavy Si-doped $Al_{0.77}Ga_{0.23}N$ (the Si concentration $\sim 4 \times 10^{19} \text{cm}^{-3}$). 16 (The observed activation energy of the donor in $Al_{x}Ga_{1-x}N$ measured by transport measurements was...
found to depend strongly on the Si concentration in heavy Si-doped samples. 32)

In order to compare the obtained results with the EMT, we calculate the corresponding EMT values for an effective mass shallow donor in $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ with $x = 0.77$. The electron effective masses and dielectric constants for $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ were obtained by linear interpolation from the corresponding values in $\text{GaN}$ (Refs. 33 and 34) and $\text{AlN}$ (Refs. 33 and 35) and we followed the calculation used in Ref. 36. The EMT values obtained from calculations are: $\Delta E = 40.5 \text{ meV}$ and $E_d = 54.6 \text{ meV}$. These EMT values are within the range of the corresponding energies determined by EPR ($\Delta E \sim 39–44 \text{ meV}$ and $E_d \sim 52–59 \text{ meV}$), suggesting that in $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ with $x$ up to 0.77, although Si becomes a DX center, its neutral state follows the EMT.

In summary, we have observed an EPR signal of a shallow donor in Si-doped $\text{Al}_{0.77}\text{Ga}_{0.23}\text{N}$ layers grown on 4H-SiC substrates in darkness at low temperatures. The temperature dependence of the donor concentration on the neutral state shows that Si already becomes DX center when $x \sim 0.77$ but behaves as a shallow donor due to a small separation ($\sim 3 \text{ meV}$) between the DX$^-$ and $d^0$ states. The neutral donor state is determined to be $E_d \sim 52–59 \text{ meV}$, which follows the EMT. Taking into account the DX formation, the activation energy of Si is estimated to be in the range of $E_a \sim 55–62 \text{ meV}$. The energy separation between $E_d$ and $E_{\text{DX}}$ is much smaller than the accuracy of calculations and a slight difference in the charge correction between calculations would put the DX$^-$ level above or below $d^0$ corresponding to a positive-U (shallow donor) or negative-U (DX) Si center. This explains the controversial results in calculations as well as the shallow donor behavior of Si in high-Al-content $\text{AlGaN}$ as indicated in transport measurements.

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