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Electron paramagnetic resonance studies of Si-doped Al\(_{0.77}\)Ga\(_{0.23}\)N (0.79 ≤ x ≤ 1.0) reveal two Si negative-U (or DX) centers, which can be separately observed for x > 0.84. We found that for the stable DX center, the energy \(E_{\text{DX}}\) of the negatively charged state DX\(^{-}\), which is also considered as the donor activation energy, abruptly increases with AI content for x ~ 0.83–1.0 approaching ~240 meV in AlN, whereas \(E_{\text{DX}}\) remains to be close to the neutral charge state \(E_{\text{d}}\) for the metastable DX center (~11 meV below \(E_{\text{d}}\) in AlN). © 2014 AIP Publishing LLC.

High-efficiency compact deep-ultraviolet (UV) light sources such as light-emitting diodes and laser diodes for replacing low-efficiency and toxic gas lasers and mercury lamps used in water/air purification and disinfection or high-resolution photolithography have so far been developed based on AlN\(^2\) and high-Al-content AlGaN.\(^3\) In such devices, high n-type conductivity is required. Silicon (Si) is used for the n-type doping but achieving highly conductive n-type Al\(_{1-x}\)Ga\(_{1+x}\)N for x ≥ 0.70 is proven difficult. A shallow increase in the donor activation energy \(E_{\text{d}}\) and resistivity\(^7\) was reported for Si-doped Al\(_{1-x}\)Ga\(_{1+x}\)N with x in the range of ~0.8–1.0. Carrier compensation by deep level defects, including deep Si DX (or negative-U) centers, has often been speculated.

Different calculations\(^8,9\) suggested Si to be a deep DX center in AlN. In the neutral charge state d\(^0\), a Si donor prefers to capture another electron and undergoes a large lattice relaxation, relaxing to its lower-lying negatively charged state DX\(^{-}\) according to the process: 2d\(^0\) → DX\(^{-}\) + d\(^+\) (here d\(^+\) is the positive charge state of the donor). Depending on the energy separation between the d\(^0\) and DX\(^{-}\) states, \(E_{\text{d}} - E_{\text{DX}}\) is small or large compared to \(E_{\text{d}}\); such a DX donor may behave as a shallow donor or a self-compensation center. Some hybrid functional calculations in AlN\(^10,11\) have found two configurations of Si DX donors: a stable DX\(_1\) center in Al\(_{1-x}\)Ga\(_{1+x}\)N with x in the range of ~0.8–1.0. Carrier compensation by deep level defects, including deep Si DX (or negative-U) centers, has often been speculated.

In a Raman spectroscopy study of GaN:Si under hydrostatic pressure, where the results can be transferred to Al\(_{1-x}\)Ga\(_{1+x}\)N, no DX behavior was detected for x up to ~0.56.\(^13\) A later transport study\(^14\) suggested Si to be a DX center in Al\(_{1-x}\)Ga\(_{1+x}\)N for x ≥ 0.5. In electron paramagnetic resonance (EPR) studies of Si-doped Al\(_{1-x}\)Ga\(_{1+x}\)N (x ≥ 0.75)\(^15\) and AlN,\(^16\) the requirement of illumination at low temperatures (T < 60 K) for detecting the signal of the shallow donor was explained by the DX-like nature of Si. However, a later EPR study suggested that Si is a shallow donor in AlN and explained the failure of detecting its EPR signal in darkness to be due to carrier compensation by deeper electron traps.\(^17\) The DX behavior was also reported for donors in undoped AlN\(^18\) which was later suggested to be related to the oxygen donor O\(_{\text{en}}\).\(^19\) A recent EPR study of Si-doped Al\(_{0.77}\)Ga\(_{0.23}\)N\(^20\) suggested that Si forms a stable DX\(^{-}\) state already for x ~ 0.77 but its influence on the n-type conductivity is not essential since the neutral state \(E_{\text{d}}\) lies only ~3 meV above the Fermi level \(E_{\text{F}}\). In AlN, the energy separation \(E_{\text{d}} - E_{\text{F}}\) increases to ~78 meV.\(^21\) A recent hybrid functional calculation\(^22\) suggested that Si transforms to a DX center in AlGaN when the AI content reaches ~94%.

In this letter, EPR was used to study Si-doped Al\(_{1-x}\)Ga\(_{1+x}\)N epitaxial layers, 0.79 ≤ x ≤ 1.0, grown by metalorganic chemical vapor deposition (MOCVD). The energy levels of DX\(^{-}\) and d\(^0\) states were determined from the temperature dependence of the Si concentration in the neutral state d\(^0\). From EPR experiments, we found the existence of two DX configurations of the Si donor for x ≥ 0.84: one with EDX remaining close to Ed and the other with EDX increasing linearly and drastically with the Al content. The drastic deepening of the stable DX center explains the sharp decrease of the conductivity often observed in transport measurements.

Si-doped Al\(_{0.77}\)Ga\(_{0.23}\)N (0.79 ≤ x ≤ 1.0) layers with typical thickness of ~400–600 nm were grown by MOCVD on semi-insulating 4H-SiC substrates using silane (SiH\(_4\)) as dopant gas. Further details about the growth processes can be found elsewhere.\(^23,24\) The AI content, the thickness of the Al\(_{1-x}\)Ga\(_{1+x}\)N:Si layers, and the atomic concentration of Si, O, and C 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). In all studied samples, the concentration of Si was kept at [Si] ~ 2 × 10\(^{18}\) cm\(^{-3}\) while the concentrations of O and C were reduced to the detection limit of SIMS ([O] ~ [C] ~ 2 × 10\(^{17}\) cm\(^{-3}\)) so that the influence of these impurities on the free-carrier concentration and EPR results can be neglected. At such a moderate Si doping level, layers usually have good morphology and conductivity, which are important factors to guarantee the observation of good EPR signal of the shallow donor in darkness (It is known from our previous study\(^23\) that in layers with high Si doping and pit-populated morphology, neither conductivity nor EPR signal can be detected). For the studied samples, XRD
Here, \( N \) is the total donor concentration, \( k_B \) is the Boltzmann constant, \( E_i \) and \( G_i \) are the energy level of excited states and their degenerate factors, respectively. It has been shown that in a negative-U center, the Fermi level is pinned at the middle of \( E_d \) and \( E_{\text{DX}} \) levels (i.e., \( E_F = E_{\text{DX}} = E_d \)) almost independently of the electron density on the levels.\(^{27,29}\) A recent calculation of Si DX center in AlGaN and AlN\(^{22}\) also showed that the Fermi level is located at the middle between \( E_d \) and \( E_{\text{DX}} \) levels. Thus, with considering only the first excited state 2p, Eq. (1) can be rewritten as

\[
n(T) \propto \frac{N_2e^{-\left(E_d-E_F\right)/k_BT}}{1 + 2e^{-\left(E_d-E_F\right)/k_BT} + e^{-\left(2E_d-(E_{\text{DX}}-2E_F)\right)/k_BT} + \sum G_i e^{-\left(E_i-E_F\right)/k_BT}}.
\]
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Here, $E_{2p}-E_d$ is the energy distance from $d^0$ ($E_d$ or $E_{1s}$) to first excited state $2p$, 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). From the best fits to experimental data using Eq. (2), $E_{2p}-E_F$ was found to increase drastically from $\sim 3–5$ meV for $x = 0.79–0.83$ to $\sim 28$ meV for $x = 0.85$. The value $E_{2p}-E_d$ determined to be $\sim 42.3$ meV for $x = 0.79$ and $\sim 47$ meV for $x = 0.85$. Assuming that the neutral state $E_d$ and excited states of the Si donor follow the effective mass theory (EMT), we obtained the EMT values for different Al contents $E_{d,\text{EMT}}$. The calculated $E_{d,\text{EMT}}$ values and the $|E_d|$ values obtained from experiments are shown in Fig. 3. Extrapolation from the linear fit to the obtained $|E_d|$ values gives $|E_d| \sim 84$ meV for AlN with a deviation of $\sim 19$ meV from the corresponding EMT value (65.2 meV).

The energy separation $E_d-E_F$ was determined to be: $\sim 3.2$, $\sim 4.5$, $\sim 28.8$ and $28.1$ meV for Al$_x$Ga$_{1-x}$N layers with $x \sim 0.79$, $\sim 0.83$, $\sim 0.84$ and $\sim 0.85$, respectively. In our previous studies, $20,21$ the term related to the DX$^-$ state in the partition function, i.e., the third term in the denominator of Eq. (1), was neglected. Using Eq. (2), we analyzed the data in Refs. 20 and 21 and obtained small changes, e.g., $E_d-E_F \sim 2.3$ and $\sim 77$ meV compared to the values of $\sim 2.8$ and $\sim 78$ meV for Si in Al$_{0.77}$Ga$_{0.23}$N and AlN, respectively. $20,21$ The $E_{DX}$ levels of Si in Al$_x$Ga$_{1-x}$N with $x \sim 0.79$, $\sim 0.83$, $\sim 0.84$, $\sim 0.85$ and in AlN were estimated to be $|E_{DX}| \sim |E_d| + 2|E_d-E_F| \sim 63$, $\sim 71$, $\sim 123$, $\sim 119$ and $\sim 238$ meV, respectively. The obtained $|E_d-E_F|$ and $|E_{DX}|$ values are shown in Fig. 3. The best fit to $|E_{DX}|$ values for $x \geq 0.83$ gave the dependence of $|E_{DX}(x)|$ on the Al content as

$$|E_{DX}(x)| = 851.27x - 611.35 \text{ (meV)}. \quad (3)$$

For $x \geq 0.83$, the observation of strong EPR signals of the Si donor at low temperatures required illumination. After illumination, the EPR signals of the Si donor were persistent for hours in darkness for $T \leq 50$ K. We found that $n(T)$ measured

![FIG. 3. The linear dependence on the Al content of the ionization energy of the neutral charge state $d^0$ ($E_d$), the DX$^-$ state ($E_{DX}$ = $E_d$), and the energy separation $E_d-E_F$ in Al$_x$Ga$_{1-x}$N:Si with 0.79 $\leq x \leq 1$. The dependence of the ionization energy $E_{d,\text{EMT}}$ on the Al content obtained from EMT calculations is also plotted for comparison. The $|E_{DX}|$ value for AlN was measured in an unintentionally Si-doped AlN bulk sample similar to the one previously used in Ref. 21.](image)

![FIG. 4. Temperature dependence of the donor concentration in the $d^0$ state in darkness after illumination at 10 K in Si-doped Al$_x$Ga$_{1-x}$N with (a) $x \sim 0.83$, (b) $x \sim 0.85$ (c) $x \sim 0.91$ and (d) in Si-doped AlN. The solid curves represent the fits. The insets show the temperature dependences of the donor concentration in darkness and in dark after illumination at 10 K in Al$_{0.77}$Ga$_{0.23}$N:Si in the same scale for comparison.](image)
in darkness after illumination increased with increasing temperature and reached its maximum at $T \sim 60 - 70 \text{K}$, which was close to the SIMS value [Si] for all samples, and then rapidly decreased, approaching the values measured in darkness without prior illumination (see the inset of Fig. 4).

The increase of $n(T)$ in darkness after illumination is typical for a DX center. Thus, the EPR signal measured at low temperatures ($T < 60 \text{K}$) after illumination should be from another DX configuration whose DX$^-$ level lies higher than that of the center detected in darkness at higher temperatures. At $T < 60 \text{K}$, electrons are confined in this higher-lying (or metastable) DX configuration. When temperature exceeds 60 K, thermal energy is enough to help electrons to overcome the barrier between the two DX configurations and to relax to the lower-lying (or stable) DX configuration, leading to the sharp drop of $n(T)$ (Fig. 4). We label the stable and metastable DX configurations as DX1 and DX2, respectively. For DX2, the temperature dependence of $n(T)$ in the temperature range below 60 K can be described by Eq. (2) but without the third term in the denominator since the thermal energy is not enough to excite electrons to the excited states. In this case, electrons are confined within the metastable DX2 configuration, and the Fermi level $E_F$ is local. For all samples with $x \geq 0.84$, the energy separation $E_d - E_F$ obtained from the best fit is in the range of ~3.9–5.3 meV (Fig. 4). These values are much smaller than the corresponding values determined in darkness (~28 meV or larger), indicating that in this metastable DX2 configuration, the DX$^-$ state is much closer to the $d^0$ state ($E_d - E_{DX} \sim 8–11 \text{meV}$ for $x \sim 0.83–1.0$, respectively). Our observation of two distinguishable DX configurations of the Si donor in Al$_x$Ga$_{1-x}$N for $x \geq 0.84$ supports the theoretical prediction by Silvestri et al. for Si in AlN. 10,11

In darkness, transport measurements would probe the stable DX1 center. For AlN, our value $|E_{DX}| \sim 240 \text{meV}$ is close to the activation energy determined from transport measurements for Si: $E_a \sim 238–254 \text{meV}$ 30 and $E_a \sim 250 \text{meV}$ 5,6. The Fermi level found in our experiments for AlN of ~160 meV below the conduction band minimum is also close to the (+) level of Si ($E_a \sim 150 \text{meV}$), where the Fermi level is pinned, determined recently from calculations by Gordon et al. 22 From Eq. (3), the $|E_{DX}|$ value for Si in Al$_x$Ga$_{1-x}$N with $x$ in the range of ~0.83–1.0 can be interpolated, for example $|E_{DX}| \sim 189 \text{meV}$ for $x \sim 0.94$ which is close to the corresponding $E_d$ value of ~200 meV determined by Borisov et al. 5

In summary, our EPR characterization of Si-doped Al$_x$Ga$_{1-x}$N, $0.79 \leq x \leq 1.0$, showed that up to $x \sim 0.83$, the DX$^-$ state is close to the neutral state $E_a$ ($E_a - E_{DX} \sim 9 \text{meV}$) and Si behaves rather similar to a shallow effective-mass donor. For $x \geq 0.84$, two DX centers could be separately observed. For the stable DX1 center, the activation energy $E_a \sim |E_{DX}|$ increases drastically and linearly from ~71 meV in Al$_{0.83}$Ga$_{0.17}$N to ~240 meV in AlN. For the metastable DX2 center, the $E_{DX}$ level remains to be close to the neutral charge state $d^0$ (~11 meV below $E_a$ in AlN). The dependence of the $E_{DX}$ level of the stable DX1 center on the Al content explains well the sudden increase of the resistivity in high-Al-content AlGaN reported by transport measurements.
