

# The Electronic Properties of Chlorine in GaN: An Ab Initio Study

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Chlorine-based reactive ion etching (RIE) is a fundamental processing step for the manufacturing of GaN semiconductor devices. As impurities can be unintentionally incorporated in the crystal during processing, the electronic properties of chlorine in GaN are investigated. Density functional theory calculations of substitutional Cl and related complexes (with a vacancy or a dopant) are carried out. It is found that Cl and its complexes explain the reported effects of Cl RIE-treated GaN on hole density and ohmic contact resistivity.

#### 1. Introduction

Gallium nitride (GaN) has a wide bandgap ( $E_{gap}$ ) and a high electron saturation velocity that make it the ideal candidate for high-voltage and high-frequency applications.<sup>[1]</sup> In addition, GaN has also a direct  $E_{gap}$  that allows the production of light-emitting diodes (LEDs). Furthermore, even if homoepitaxial GaN is still expensive, heteroepitaxial (Si, SiC, or Al<sub>2</sub>O<sub>3</sub>) GaN is a valid alternative for the realization of cost-competitive power electronics.<sup>[1]</sup>

Yet, the development of GaN optoelectronic devices cannot leave out of consideration the study of electrically active point defects. These are known to alter the functionality of devices; therefore, it is important to study defects to be able to control and/or limit their presence. Apart from intrinsic defects like the nitrogen vacancy  $(V_N)$ , which hinders the formation of p-type GaN,<sup>[2-4]</sup> impurities can also be detrimental for applications. This is the case of carbon and oxygen which are unintentionally incorporated during growth. The electronic properties of carbon, which sits at an N-site ( $C_N$ ), and its related complexes<sup>[5–7]</sup> have been thoroughly studied in the past. C<sub>N</sub> was found to be responsible for current collapse<sup>[8]</sup> and for the yellow luminescence (YL).<sup>[9]</sup> Oxygen (O<sub>N</sub>), which behaves as a shallow donor, is known to decorate dislocations<sup>[10]</sup> and diffuse in the epilayer from a sapphire substrate.<sup>[11]</sup> In the latter case, it leads to p-type doping passivation due to the formation of neutral complexes with  $Mg_{Ga}$ .<sup>[12]</sup>

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Impurities can also be unintentionally incorporated during processing steps like etching. Dry etching is a fundamental step for the realization of semiconductor devices and, in the case of GaN, it is typically favored over wet etching for its selectivity.<sup>[13]</sup> In particular, Cl-based reactive ion etching (RIE) and inductive coupled plasma (ICP) RIE are chosen because they yield higher etching rates than H-based RIE.<sup>[13]</sup>

Despite Cl-based dry etching being useful for mesa and termination etching,

this process was found to have an impact on the electronic properties of GaN. Deep levels in  $E_{\rm gap}$ , affecting the leakage current and the breakdown voltage, were observed in both dry-etched n- and p-GaN.<sup>[14–16]</sup> A decrease by two orders of magnitude of carrier concentration was found in Cl-based treated p-type GaN.<sup>[17]</sup> In addition, controversial reports on how Cl-RIE affects n-GaN ohmic contact resistivity ( $\rho_c$ ) are present in the literature: while some authors have shown that Cl-RIE decreases  $\rho_c$ ,<sup>[18,19]</sup> some other studies have shown that the presence of gallium vacancies<sup>[20,21]</sup> and the formation of oxides on the surface<sup>[22,23]</sup> increase  $\rho_c$ . Due to these effects, it is straightforward to ask what the role of Cl, which is used in the RIE plasma, is on the electronic properties or GaN.

To answer this question, we conducted a theoretical investigation, by means of density functional theory, of the electronic properties of substitutional chlorine, both isolated and complexed with a vacancy or a dopant, in wurtzite GaN.

#### 2. Theoretical Methodology

The siesta code<sup>[24]</sup> was used for conducting density functional theory calculations, using Troullier-Martins' norm-conserving pseudopotentials<sup>[25]</sup> to account for the effect of core electrons and the Ceperley-Alder form of local density approximation (LDA) for the exchange correlation potential.<sup>[26]</sup> A double-C plus polarization was used as atomic orbitals basis set throughout the calculations. For the Ga atoms the d-orbital electrons were treated as valence electrons. The equilibrium configurations of the pristine and defected 96-atom GaN supercells  $(2\sqrt{3}a \times 3a \times 2c, a = 3.184 \text{ Å}, c = 5.184 \text{ Å})$  were obtained by relaxing the atomic coordinates with a conjugate gradient algorithm, until the maximum atomic forces were less than  $0.025 \text{ eV} \text{ Å}^{-1}$  and the stress tensor less than 0.5 GPa. The charge density was projected onto a real space grid with an equivalent cutoff of 375 Ry and eight Monkhorst-Pack special k-points<sup>[27]</sup> were used. The a = b and c lattice constants were both 1% larger than the experimental value with a direct bandgap of 2 eV.



The formation energy ( $E_{\text{form}}$ ) of a defect with charge state q was calculated using the followng equation

$$E_{\rm form}^{q} = E_{\rm tot}^{q} - E_{\rm tot}^{\rm bulk} - \sum_{i} n_{i} \mu_{i} + q(E_{F} + E_{V} + \Delta \nu_{0/b}) + E_{\rm corr}(q)$$
 (1)

 $E_{\text{tot}}^q$ ,  $n_i$ ,  $\mu_i$ ,  $E_F$ ,  $E_V$ ,  $\Delta \nu_{0/b}$ , and  $E_{\text{corr}}$  are the total energy (for the defective or pristine supercell), the number of added ( $n_i > 0$ ) or removed ( $n_i < 0$ ) *i*-atoms, the chemical potential of the *i*-atom, the Fermi energy, the top of the valence band, the electrostatic potential alignment term (between the bulk and defective supercells), and the finite-size correction term, respectively. This last one ( $E_{\text{corr}}$ ) was calculated following both the Makov–Payne method<sup>[28]</sup> (hereafter MP) and the one reported by Freysoldt et al.<sup>[29]</sup> (hereafter FNV), as implemented in a previous study.<sup>[30]</sup>

As it is known that variations of  $E_{\rm form}$  (and thus of charge transition levels) depend on the choice of the functional, we applied a correction scheme based on the alignment of electrons and chemical potential of the atomic species, as in a previous study.<sup>[31]</sup> This correction is applied to the FNV results and will be labeled as FNV\*.

Calculation of  $\mu_i$  was conducted as described in a previous study.<sup>[32]</sup>  $\mu_{Ga}$  and  $\mu_N$  were calculated using a Ga supercell and N<sub>2</sub> molecule, respectively. For the FNV\* scheme,  $\mu_i$  was corrected using Equation (14) of a previous study<sup>[31]</sup> and using the hybrid functional (HSE) value of the formation enthalpy (-1.34 eV). For  $\mu_{Cl}$ , we used the LDA value. However, the optimized geometry of the Cl<sub>2</sub> molecule, as obtained by siesta, was also used to calculate  $\mu_{Cl}$  with a B3LYP functional (kinetic energy cutoff of 180 Ry).<sup>[33]</sup>

#### 3. Validation of the Methodology

To begin with, we conducted the calculation of the electronic properties of two intrinsic defects, the  $V_{\rm N}$  and  $V_{\rm Ga}$ . This was done to evaluate the corrections to  $\mu_{\rm N}$ ,  $\mu_{\rm Ga}$ , and  $E_{\rm V}$ . Once these corrections were obtained, we tested the FNV\* scheme on two defect complexes, one related to  $V_{\rm N}$  and another to  $V_{\rm Ga}$ .

Figure 1 shows the results of the LDA calculations carried out on V<sub>N</sub>. Our LDA calculations predict the negative-U behavior of  $V_{\rm N}$ .<sup>[3,4]</sup> The negative-U behavior (with U being the electronelectron repulsion) occurs when the (q - 1/q) charge state of a defect lies closer to  $E_V$  than the (q/q + 1) one.<sup>[34,35]</sup> As a consequence, only a (q - 1/q + 1) charge state is found in  $E_{gap}$ . The MP correction (Figure 1a) does not show  $V_N$  (+/3+) in the Kohn-Sham  $E_{gap}$ . As a matter of fact, this level is resonant in the valence band ( $E_V$ -0.30 eV) and so are the singly positive and negative charge states, which are resonant in the conduction band (shadowed in Figure 1a). When the FNV correction was used, we obtained similar results to MP with  $V_{\rm N}(+/3+)$  predicted at  $E_V - 0.52 \,\text{eV}$ . Figure 1b shows the results of  $E_{\text{form}}$ calculated using the FNV\* correction. By lowering  $E_V$  relative to  $V_{\rm N}(+/3+)$ , we adjust the charge transition level position in  $E_{\text{gap}}$ .  $\mu_{\text{N}}$  is corrected to match the  $E_{\text{form}}$  of  $V_{\text{N}}(+/3+)$  reported by Diallo et al.<sup>[36]</sup> The corrected values of  $\mu_{\rm N}$  are  $-270.8 \le \mu_{\rm N} \le$  $-269.5 \text{ eV} \text{ atom}^{-1}$  (from  $-271.2 \le \mu_{\text{N}} \le -269.8 \text{ eV} \text{ atom}^{-1}$ ). We point out that, by using a bigger supercell (144 atoms), the variation of  $E_{\text{form}}$  is  $\leq 0.1 \text{ eV}$ .





**Figure 1.** Formation energy plot of the  $V_N$  calculated with the a) MP and b) FNV\* correction schemes. Red (black) line is for the N (Ga)-rich case. The shadowed area represents the limit of the Kohn-Sham  $E_{gap}$ .

We repeat analogous calculations for  $V_{\text{Ga}}$  (Figure 2). The MP correction (Figure 2a) does not show any donor level in the Kohn-Sham  $E_{\text{gap}}$  ( $E_{\text{V}} - 0.14 \text{ eV}$ ) and leads to the single, double, and triple negative charge state transition levels at  $E_{\text{V}} + 0.33 \text{ eV}$ ,  $E_{\text{V}} + 1.06 \text{ eV}$ , and  $E_{\text{V}} + 2.08 \text{ eV}$ , respectively. Using the FNV correction, the single donor level of  $V_{\text{Ga}}$  is located at  $E_{\text{V}} - 0.31 \text{ eV}$  and the single, double, and triple acceptors at  $E_{\text{V}} + 0.25 \text{ eV}$ ,  $E_{\text{V}} + 0.88 \text{ eV}$ , and  $E_{\text{V}} + 0.186 \text{ eV}$ , respectively. By lowering  $E_{\text{V}}$  relative to  $V_{\text{Ga}}(0/+)$ ,<sup>[36]</sup> we found that the acceptor levels agree well with HSE results<sup>[3,36]</sup> to within 0.2 eV (Figure 2b). The same occurs for  $E_{\text{form}}$  ( $-1808.5 \le \mu_{\text{Ga}} \le -1807.2 \text{ eV}$  atom<sup>-1</sup>).<sup>[36]</sup>

Having obtained the corrected values of  $\mu_N$ ,  $\mu_{Ga}$ , and  $E_V$ , we then proceed to validate the FNV\* scheme used in this study. To do this, we calculated the charge transition levels of the Mg<sub>Ga</sub> $V_N$  and O<sub>N</sub>V<sub>Ga</sub> complexes.



**Figure 2.** Formation energy plot of the  $V_{Ga}$  calculated with the a) MP and b) FNV\* correction schemes. Red (black) line is for Ga (N)-rich case.



The (0/2+) charge transition level of  $Mg_{Ga}V_N^{[2]}$  is found resonant in the valence band at  $E_V - 0.19$  and  $E_V - 0.39$ for the MP and FNV correction scheme, respectively. To correct the charge state transition level position in  $E_{gap}$ , we employed the value of  $E_V$  used to adjust the  $V_N(+/3+)$  transition level.  $\mu_{Mg}$  is calculated using a Mg<sub>3</sub>N<sub>2</sub> supercell<sup>[2]</sup> and used to compute the  $E_{form}$  of Mg(-/0).  $\mu_{Mg}$  was corrected so that  $E_{form}$  of Mg(-/0) matched the HSE value reported in the literature.<sup>[2,3]</sup> With  $E_V$  and  $\mu_{Mg}$ , we find that Mg<sub>Ga</sub> $V_N$  (0/2+) is located at  $E_V + 0.64$  eV, 0.2 eV lower than the value reported in a previous study<sup>[2]</sup>, and the  $E_{form}$ is in good agreement with a previous study.<sup>[2]</sup>

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The FNV (MP) correction scheme shows that  $O_N V_{Ga}(0/+)$ ,  $O_N V_{Ga}(-/0)$ , and  $O_N V_{Ga}(2-/-)$  are found at  $E_V - 0.30(-20)$  eV,  $E_V + 0.48(0.52)$  eV, and  $E_V + 1.32(1.68)$  eV, respectively. The adjusted electron chemical potential for  $V_{Ga}$  and the adjusted value of  $\mu_0^{[37]}$  were used to calculate the charge state transition level positions and their  $E_{\text{form}}$ . The single donor, single, and double acceptors are found at  $E_V + 0.96$  eV,  $E_V + 1.74$  eV, and  $E_V + 2.5$  eV, respectively. These levels are in agreement up to <0.20 eV with those obtained by HSEs, with the exception of

**Table 1.** Charge state transition levels of the  $V_N$ ,  $V_{Ga}$ , and  $O_N V_{Ga}$ , calculated using the MP, FNV, and FNV\* schemes. For  $O_N V_{Ga}$ , the correction to  $E_V$  is the one taken from  $V_{Ga}$ . Numerical values indicate  $E_V + E_t$  and units are in eV. In brackets, the difference between the values obtained by HSE calculations and those of the present study is shown.

Defect	MP	FNV	FNV*
V <sub>N</sub> (+/3+)	-0.30	-0.52	0.48 (0)
V <sub>N</sub> (0/+)	2.06	2.42	3.13 (-0.03)
V <sub>Ga</sub> (0/+)	-0.14	-0.31	0.97 (0)
$V_{Ga}(-/0)$	0.32	0.25	1.51 (-0.17)
V <sub>Ga</sub> (2-/-)	1.07	0.88	2.14 (-0.16)
V <sub>Ga</sub> (3-/2-)	2.08	1.86	2.95 (0.15)
$Mg_{Ga}V_{N}(0/2+)$	-0.19	-0.39	0.64 (-0.20)
$O_N V_{Ga}(0/+)$	-0.20	-0.30	0.96 (-0.14)
$O_N V_{Ga}(-/0)$	0.52	0.48	1.74 (-0.06)
O <sub>N</sub> V <sub>Ga</sub> (2-/-)	1.68	1.32	2.58 (0.28)

the double donor level, which is 0.28 eV higher than the hybrid counterpart.<sup>[37,38]</sup> Their  $E_{\rm form}$  also agrees reasonably well with the literature.<sup>[37]</sup>

A summary of the above results is shown in Table 1.

#### 4. Results and Discussion

To find out whether Cl sits at a N–(Cl<sub>N</sub>) or at a Ga-site (Cl<sub>Ga</sub>), we calculated the  $E_{\text{form}}$  of Cl<sub>N</sub> and Cl<sub>Ga</sub>. First, we focused on Cl<sub>N</sub>, as shown in **Figure 3**. After geometry optimization, the Cl–N bond length ranges between 2.3 and 2.4 Å and Cl<sub>N</sub> has a tetrahedral symmetry. The ten electrons (three from  $V_N$  and seven from Cl) occupy two singlets and one triplet state. Inspection of the highest occupied molecular orbital (HOMO) reveals a fully occupied  $a_1$  state (Figure 3a), meaning that Cl<sub>N</sub> is a double donor.

Analysis of  $E_{\rm form}$ , with the MP correction (Figure 3b), shows that  $\rm Cl_N$  is a double donor for each value of  $E_{\rm F}$  in the Kohn-Sham  $E_{\rm gap}$ . Two transition levels (doubly and singly positive charge states) are found resonant in the conduction band. The same occurs after application of the FNV correction.<sup>[39]</sup> Using the  $E_{\rm V}$  corrected for  $V_{\rm N}(+/3+)$ , the  $E_{\rm form}$  of  $\rm Cl_N$  shows only one charge state transition level in  $E_{\rm gap}$  (Figure 3c), at  $E_{\rm V} + 3.0$  eV. The use of  $\mu_{\rm Cl}$  calculated using a HSE<sup>[33]</sup> results in a higher  $E_{\rm form}$  of 0.4 eV. This applies also to the results shown in the remainder of this study.

Analogous calculations were also conducted on  $Cl_{Ga}$ . Geometry optimization results in a severe change of the Cl–N bond length, with the shortest being 1.6 Å and the longest 2.6 Å. As a result,  $Cl_{Ga}$  has a  $C_s$  symmetry (**Figure 4**a), meaning that the 12 electrons found in the defect molecule model are accommodated in singlet levels. The analysis of the  $E_{form}$  with the MP correction reveals the presence of two charge states in the Kohn-Sham  $E_{gap}$  (Figure 4b). The singly and doubly negative are found at  $E_V + 0.60 \text{ eV}$  and  $E_V + 1.22 \text{ eV}$ , respectively. To conduct FNV\* correction (Figure 4c), we use the value of  $E_V$ corrected for  $V_{Ga}(0/+)$ . This leads to the presence of four charge transition levels in  $E_{gap}$  at  $E_V+0.76 \text{ eV}$ ,  $E_V+1.56 \text{ eV}$ ,  $E_V+2.01 \text{ eV}$ , and  $E_V+2.70 \text{ eV}$  for  $Cl_{Ga}(+/2+)$ ,  $Cl_{Ga}(0/+)$ ,  $Cl_{Ga}(-/0)$ , and  $Cl_{Ga}(2-/-)$ , respectively.



**Figure 3.** a) Isosurfaces of the calculated wave function for  $Cl_N$  (0.09 e bohr<sup>-3</sup>). The red (green) isosurface represents the positive (negative) values of the wave function. Formation energy plot of  $Cl_N$  calculated with the b) MP and c) FNV\* correction schemes. Red (black) line is for N (Ga)-rich case. Ga (N) atoms are yellow (blue), whereas Cl is light green.







**Figure 4.** a) Isosurfaces of the calculated wave function for  $Cl_{Ga}$  (0.03 e bohr<sup>-3</sup>). The red (green) isosurface represents the positive (negative) values of the wave function. Ga (N) atoms are yellow (blue), whereas Cl is light green. Formation energy plot of  $Cl_{Ga}$  calculated with the b) MP and c) FNV\* correction schemes. Red (black) line is for N (Ga)-rich case.

As shown in Figure 3c and 4c, the most stable configuration, for most of the  $E_{\rm F}$ -level values, is  ${\rm Cl}_{\rm N}$ .  ${\rm Cl}_{\rm Ga}$  has a lower  $E_{\rm form}$  than  ${\rm Cl}_{\rm N}$  ( $\approx 0.5 \,{\rm eV}$ ) only when 3.2 eV $< E_{\rm V} + E_{\rm F} \leq$  3.4 eV, that is, when GaN is heavily n-type doped.

As Cl preferably occupies N-site for a wider range of  $E_{\rm F}$  values, it is straightforward to analyze the Cl<sub>N</sub>V<sub>Ga</sub> complex (**Figure 5**). We considered the parallel configuration, that is, the defect is parallel to the *c*-axis. This is because it was seen that for the C<sub>N</sub>V<sub>Ga</sub>, no significant difference of  $E_{\rm form}$  was present between the parallel and perpendicular configurations.<sup>[6]</sup> Geometry optimization results in a  $C_{3v}$  symmetry, meaning that the seven electrons (five of  $V_{\rm Ga}$  and two of Cl<sub>N</sub>) can be found in two singlets (*a*<sub>1</sub>) and one doublet (*e*). We find that the spare electron occupies one doublet as the HOMO is an *e* state (Figure 5a). As Lyons et al.<sup>[38]</sup> have shown, the higher the number of donors binding to  $V_{\rm Ga}$ , the lower the number of acceptors of the resulting complex. This means that if the analogy with the O<sub>N</sub>V<sub>Ga</sub>H complex is correct,<sup>[38]</sup> the Cl<sub>N</sub>V<sub>Ga</sub> complex will give rise to one donor or one acceptor level (or both) in  $E_{\rm gap}$ .

Figure 5b shows the results of our calculations for the  $Cl_N V_{Ga}$  complex, with the MP scheme. We find a donor level at  $E_V + 0.21 \text{ eV}$  and an acceptor level at  $E_V + 1.28 \text{ eV}$ . Another

acceptor level, doubly negative, is resonant in the conduction band, at  $E_V$  + 2.8 eV. The FNV shows the singly and doubly acceptor levels at  $E_V$  + 0.58 eV and  $E_V$  + 1.16 eV, respectively. We also find a donor level at  $E_V$  + 0.11 eV. To apply the FNV\* scheme, similarly to what we have done for the O<sub>N</sub>V<sub>Ga</sub> complex, we consider the corrected  $E_V$  of  $V_{Ga}(0/+)$ . By doing so, we obtain  $Cl_N V_{Ga}(0/+)$  at  $E_V$  + 1.61 eV, whereas the negative one is at  $E_V$  + 2.70 eV (Figure 5c).

As the  $Cl_{Ga}$  is more stable than  $Cl_N$ , in heavily doped n-GaN, we also examined the  $Cl_{Ga}V_N$  complex. Similarly to  $Cl_NV_{Ga}$ , this complex was also studied in the parallel configuration. Geometry optimization, of the neutral and charged defects, shows that the Cl atom leaves the Ga-site and moves into the N-site, that is.  $Cl_{Ga}V_N$  transforms into  $Cl_NV_{Ga}$ . An analogous transformation was reported also in rare-earth-doped  $GaN^{[40]}$  and demonstrates that, although  $Cl_{Ga}$  might be stable for a limited range of  $E_F$ values, it does not form complexes with native defects.

Next, we evaluate the effects of Cl on GaN dopant species. To do this, we consider how  $Cl_N$  affects Mg, which is the p-type dopant of choice for GaN and sits at a Ga-site.<sup>[41]</sup> The same cannot be done for  $Cl_{Ga}$ , as the n-type dopant is Si and also sits at a Ga-site. We investigated the  $Cl_NMg_{Ga}$  complex (Figure 6) in the



**Figure 5.** a) Isosurfaces of the calculated wave function for  $CI_NV_{Ga}$  (0.09 e bohr<sup>-3</sup>). The red (green) isosurface represents the positive (negative) values of the wave function. Red translucent sphere represents  $V_{Ga}$ . Formation energy plot of  $CI_N$  calculated with the b) MP and c) FNV\* correction schemes. Red (black) line is for the N (Ga)-rich case.







Figure 6. a) Isosurfaces of the calculated wave function for  $Cl_NMgGa$  (0.09 e bohr<sup>-3</sup>). The red (green) isosurface represents the positive (negative) values of the wave function. Mg atom is red. Formation energy plot of  $Cl_N$  calculated with the b) MP and c) FNV\* correction schemes. Red (black) line is for the N (Ga)-rich case.

perpendicular configuration (the Cl–Mg bond is perpendicular to the *c*-axis), because the Si<sub>Ga</sub>C<sub>N</sub> defect has a slightly lower  $E_{form}$  in such a configuration.<sup>[7]</sup> Based on the fact that O<sub>N</sub> is a single donor, it was found that the O<sub>N</sub>Mg<sub>Ga</sub> complex is neutral.<sup>[12]</sup> This suggests that Cl<sub>N</sub>Mg<sub>Ga</sub> could be a single donor. Geometry optimization reveals that the Cl<sub>N</sub>Mg<sub>Ga</sub> complex has a C<sub>1</sub> symmetry, meaning that of the seven electrons of this complex (five from Mg<sub>Ga</sub> and two from Cl<sub>N</sub>), there will be an unpaired electron in a singlet level (Figure 6a).

Using the MP correction scheme, we see that  $Cl_NMg_{Ga}$  is a single donor throughout the Kohn-Sham  $E_{gap}$  (Figure 6b). The same occurs after applying the FNV correction. To apply the FNV\* scheme, we point out that as  $V_{Ga}$  was used as a reference for  $Cl_NV_{Ga}$  complex, in the present case we will use the  $Mg_{Ga}$  defect as a reference. We adjust  $E_V$  and  $\mu_{Mg}$  to match the charge transition level and  $E_{form}$  of Mg(-/0) calculated by HSE.<sup>[2,3]</sup> Then, these values are used for the  $Cl_NMg_{Ga}$  complex (Figure 6c) which is found to be a single donor throughout the Kohn-Sham  $E_{gap}$ .

A summary of the Cl-related charge state levels calculated in this study is shown in **Table 2**.

As our results show that the electronic properties of Cl can have a significant impact on GaN electronic devices. The reported decrease by two orders of magnitude of the carrier concentration in Cl-based-treated p-type GaN was attributed to the formation of  $Mg_{Ga}V_N$  complexes.<sup>[17]</sup> However, this defect might already be present in the as-grown p-type material acting as a compensating center. As our results show,  $Cl_N$ ,  $Cl_NV_{Ga}$ , and  $Cl_NMg_{Ga}$  behave as donors in p-type GaN. Due to their low  $E_{form}$ ,  $Cl_N$  and  $Cl_NMg_{Ga}$ might also be quite abundant, meaning that their presence can significantly reduce the hole density.  $Cl_NV_{Ga}$  possesses the

**Table 2.** Charge state transition levels detected in the present study for the two substitutional (Cl<sub>N</sub> and Cl<sub>Ga</sub>) and complex Cl<sub>N</sub>V<sub>Ga</sub> defects, calculated using the FNV\* correction scheme.

	(2-/-)	(-/0)	(0/+)	(+/2+)
Cl <sub>N</sub>	_	_	3.0	_
$Cl_{Ga}$	0.76	1.56	2.01	2.70
$CI_NV_{Ga}$	_	1.61	2.70	-

highest  $E_{\text{form}}$  possibly due to the fact that  $V_{\text{Ga}}$  has a rather high  $E_{\text{form}}$  in as-grown p-type.<sup>[3]</sup> However, high ion fluxes and energies, used during RIE,<sup>[13]</sup> might contribute to the formation of  $V_{\text{Ga}}$  which, binding to Cl, can reduce the hole concentration, possibly causing type conversion.<sup>[13]</sup>

Regarding the controversy on the ohmic contact resistivity, its improvement was attributed to the formation of donors, like  $V_{\rm N}$  or divacancies  $(V_{\rm N}V_{\rm Ga}, V_{\rm Ga}(V_{\rm N})_2)$ .<sup>[18,19]</sup> However, in n-type GaN,  $V_{\rm N}$  is neutral and divacancies are acceptors.<sup>[2,42]</sup> In addition, our results support the reported increase of  $\rho_c$ , following Cl-RIE. As a matter of fact, if Cl is incorporated in GaN,  $Cl_{\rm Ga}$  and  $Cl_{\rm N}V_{\rm Ga}$  are acceptors in n-GaN and can lead to donor compensation, thus worsening the ohmic behavior.

Last, we comment on the electron and chemical reservoir method: as described in a previous study,<sup>[31]</sup> this is derived from the "marker method." Typically, the charge state transition level position in  $E_{\rm gap}$  of a well-localized defect A is corrected by shifting  $E_{\rm V}$ . This  $E_{\rm V}$  is then used to calculate the charge state transition levels of another defect B. No constraints are given on the geometry and/or symmetry of the defects. As the marker method performs best when the wavefunctions of A and B defects have the same symmetry,<sup>[43]</sup> the same should apply to a previous study.<sup>[31]</sup> The main obstacle to this approach is the difficulty in finding suitable defects calculated by HSE, whose symmetry matches the one under investigation. For instance, even if both  $O_{\rm N}V_{\rm Ga}^{[44]}$  and  $Cl_{\rm N}V_{\rm Ga}$  have  $C_{3\nu}$  symmetry after geometry optimization, the respective highest occupied orbitals do not, as it is  $a_1$  for  $O_{\rm N}V_{\rm Ga}^{[44]}$  and e for  $Cl_{\rm N}V_{\rm Ga}$ .

#### 5. Conclusions

Density functional theory calculations revealed that Cl sits at a N-site and  $Cl_N$  behaves as a double donor, in agreement with the fact that O is a single donor.  $Cl_N$ -related complexes, with  $V_{Ga}$  or  $Mg_{Ga}$ , were also found to behave as donors. The presence of these defects, due to possible unintentional incorporation during processing, might explain the observed increase (decrease) of the electron (hole) concentration, reported in dry etched n-(p-) type GaN.



## **Conflict of Interest**

The authors declare no conflict of interest.

### **Keywords**

chlorine, density functional theory, dry etching, point defects

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