# Ab Initio Study of Substitutional Chlorine and Related Complexes in GaN

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## Introduction

Reactive ion etching (RIE) is typically employed in device processing, e.g., mesa etching. Cl-based RIE is known to:

- Decrease Ohmic contact resistivity in n-type GaN [1,2]
- Reduce carrier concentration in p-type GaN [3]

This was attributed to the formation of nitrogen vacancies ($V_N$) or $V_N$-complexes ($V_NV_{Ga}$). However, $V_N$ behaves as a donor in p-type GaN and not in n-type GaN (neutral). In addition, divacancies appear only after high temperature treatment.
For these reasons, we investigated the role of Cl in GaN. This is done by employing density functional theory (DFT).

## Results

We first analyzed the $Mg_{Ga}$ acceptor and $V_N$ donor, by employing the Makov-Payne [4] or the potential alignment [5] corrections to $E_{FORM}$. The latter gives better results and has been used throught the present work.

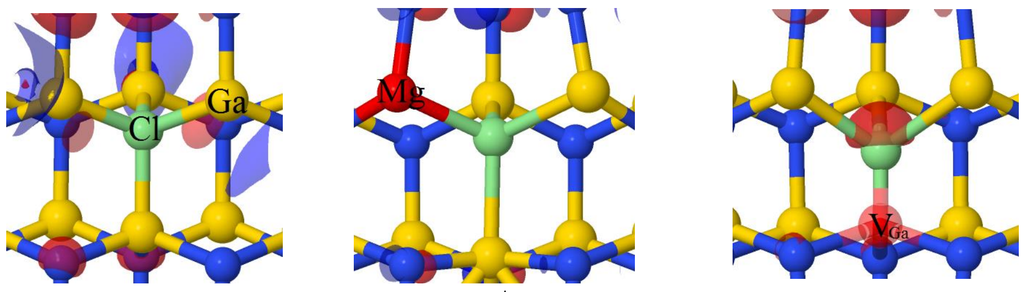
| Correction | $Mg_{Ga}$ | $V_N$ |
|---|---|---|
| Makov-Payne | $E_V$+0.35 eV | No Negative-U |
| Potential alignment | $E_V$+0.20 eV | Negative-U |

Substitutional Cl is more stable at N- ($Cl_N$) rather than Ga-site ($Cl_{Ga}$) by 2 eV.

**$Cl_N$**: after geometry relaxation, a $T_d$ symmetry is observed.
Average Cl-Ga bond length=2.4 Å
Average Ga-Cl-Ga bond angle=110.1°
Number of electrons (Watkins model)=10
These can be accommodated in two singlet ($a_1$) levels and one triplet level ($t_2$). It can be predicted that $Cl_N$ is a double donor (oxygen is a single donor).

**$Cl_NMg_{Ga}$**: geometry relaxation shows that this defect has $C_1$ symmetry.
Cl-Mg bond length=2.27
Average Ga-Cl-Mg bond angle=108.3°
Average Ga-Cl bond length=2.34
Average Ga-Cl-Ga bond angle=110.5°
Number of electrons (Watkins model)=9
These can be placed in singlet ($a$) levels, so there is one spare electron. This defect can be a donor (or an acceptor).

**$Cl_NV_{Ga}$**: the relaxed structure has $C_{3v}$ symmetry.
Average Ga-Cl bond length=2.34 Å
Average Ga-Cl-Ga bond angle=95.6°
Number of electrons (Watkins model)=7
These electrons can be found in two singlet ($a_1$) levels and one doubly degenerate ($e$) level. Similarly to $Cl_NMg_{Ga}$, the level can be predicted to be a donor (or an acceptor).




## Computational Details

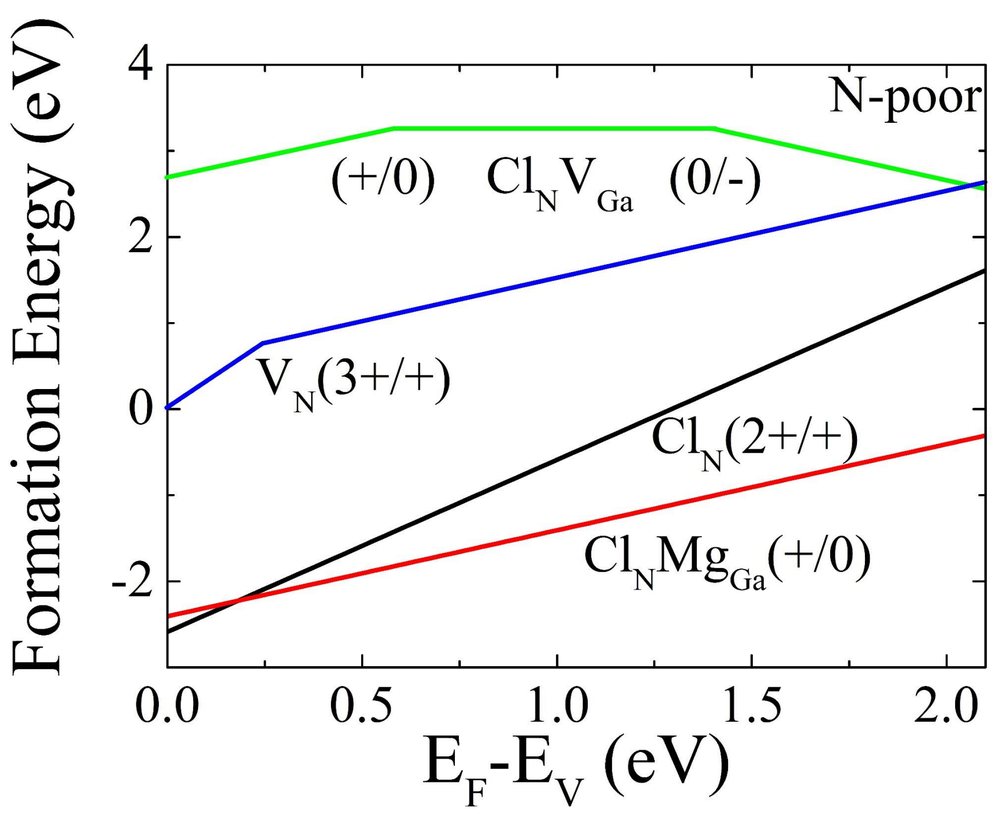
SIESTA spin-polarized DFT calculations. We used:

- a 96-atom supercell
- LDA (CA)
- Troullier-Martins norm-conserving pseudopotentials
- double-ζ plus plus polarization as atomic orbital basis set
- Charge density projection with an equivalent cutoff of 375 Ry
- 8 Monkhorst-Pack special k-points

The d-orbital electrons were treated as valence electrons.
Equilibrium configurations of the pristine and defected supercell were obtained by relaxing the atomic coordinates by a CG algorithm

- max atomic forces <0.025 eV/Å
- stress tensor <0.5 GPa.

The formation energy ($E_{FORM}$) was calculated by using Zhang-Northrup formalism.




$Cl_N$ is a double donor for any Fermi energy ($E_F$) value in the Kohn-Sham band gap.
$Cl_NMg_{Ga}$ is a single donor for any $E_F$ in the band gap.
For both defects, the $E_{FORM}$ is negative, especially in the case of p-type GaN.

$Cl_NV_{Ga}$ displays two transition levels: a donor level at $E_V$+0.58 eV and an acceptor level at $E_V$+1.4 eV.

## Conclusions

Cl in GaN (and complexes) behave as donors.

The relatively low $E_{FORM}$ of $Cl_N$ can explain why Ohmic contacts improve by RIE, in n-type GaN. Furthermore, the low $E_{FORM}$ of $Cl_NMg_{Ga}$ can explain why RIE reduces the hole concentration in p-type GaN.

Investigation of $Cl_NSi_{Ga}$, $Cl_i$ (and complexes) is in progress.

## Bibliography

[1] Z. Fan et al., APL 68, 1672 (1996)

[2] S. Joglekar et al., APL 109, 041602 (2016)

[3] J.M. Lee et al., J. Vac. Sci. Technol. B 22, 479 (2004)

[4] G. makov et al., PRB 51, 4014 (1995)

[5] C.G. van de Walle et al., JAP 95, 3851 (2004)