Ab Initio Study of Substitutional Chlorine and Related Complexes in GaN

G. Alfieri[1,*], Y. Fujii[2], R. Micheletto[2]

[1]*ABB Corporate Research Center, Segelhofstr. 1K, Baden-Dättwil 5405, Japan*

[2]*Yokohama City University, Dept. of Nanosystem Sciences Yokohama 236-0027, Japan*

*E-mail: giovanni.alfieri@ch.abb.com

Chlorine based reactive ion etching (RIE) is known to decrease ohmic contact resistivity in n-type GaN [1,2] and to reduce carrier concentration in p-type GaN [3]. The improvement of contact resistivity was attributed to nitrogen vacancies (V_N) [1, 3]. However, the formation energy (E_{form}) is such [4] that, V_N may not be responsible for the increased surface donor density in n-type GaN. On the other hand, the decreased carrier concentration, in p-type GaN, was attributed to defects other than V_N [3]. In order to shed light on these two effects, we carried out a theoretical study of Cl, substitutional and related defects, in wurtzite GaN.

An ab-initio study was carried out by using SIESTA (LDA). 3d-electrons of Ga were treated as valence electrons. Formation energies were calculated by using the Makov-Payne correction or the potential alignment [5] correction.

First, we found that Cl is more stable in an N-site (Cl_N), than in a Ga-site, by ~2 eV. After geometry relaxation, Cl_N has T_d symmetry and our Watkins model predicts the presence of ten electrons (three from V_N and seven from Cl). These are accommodated in two singlets and one triply degenerate level. Analysis of its E_{form} reveals that Cl_N is a double donor for every value of E_F in the Kohn-Sham E_{gap} (~2.0 eV). The defect-molecule model of Cl_NMg_{Ga} (C_1) consists of nine electrons with a spare electron in a singlet level (a). We found that Cl_NMg_{Ga} is a single donor for each value of the E_F.

For Cl_NV_{Ga} (C_{3v}), we predict the presence of seven electrons, five from V_{Ga} and two from the Cl_N donor. This suggests that a spare electron is present in a singlet level (a_1) and our results show the presence of a (0/+) and (-/0) level, located at E_V+0.20 eV and E_V+1.43 eV, respectively. By applying the potential alignment corrections [5], these transition levels are found at E_V+0.41 eV and E_V+1.22 eV.

Cl_N possesses a lower E_{form} than V_N in the upper part of the Kohn-Sham E_{gap}. This can explain why Cl-based RIE is beneficial in terms of ohmic contacts in n-type GaN [1]. Furthermore, the observed reduction of carrier concentration in Cl-plasma etched p-type GaN [3] can be also explained in terms of lower E_{form}, of both Cl_N and Cl_NMg_{Ga}, compared to V_N.

[1] T. Fujishima et al., Appl. Phys. Lett. 103, 083508 (2013)

[2] S. Joglekar et al., Appl. Phys. Lett. 109, 041602 (2016)

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

[4] J.L. Lyons et al., Computational Materials 3, 12 (2017)

[5] C.G. Van de Walle et al., J. Appl. Phys. 95, 3851 (2004)

Supplementary information

Table.1. Test for evaluating the methodology employed in our study. With the Potential alignment correction the transition level of the Mg_{Ga} acceptor is found at 0.20 eV above the valence band edge (E_V) and V_N shows a negative-U behavior (the +2 charge state is not stable). By using the Makov-Payne correction, Mg_{Ga} is at E_V+0.22 eV and no negative-U behavior is found for V_N.

Correction used	Mg_{Ga}	V_N
Potential Alignment	E_V+0.20 eV	negative-U behavior
Makov-Payne	E_V+0.22 eV	no negative-U behavior

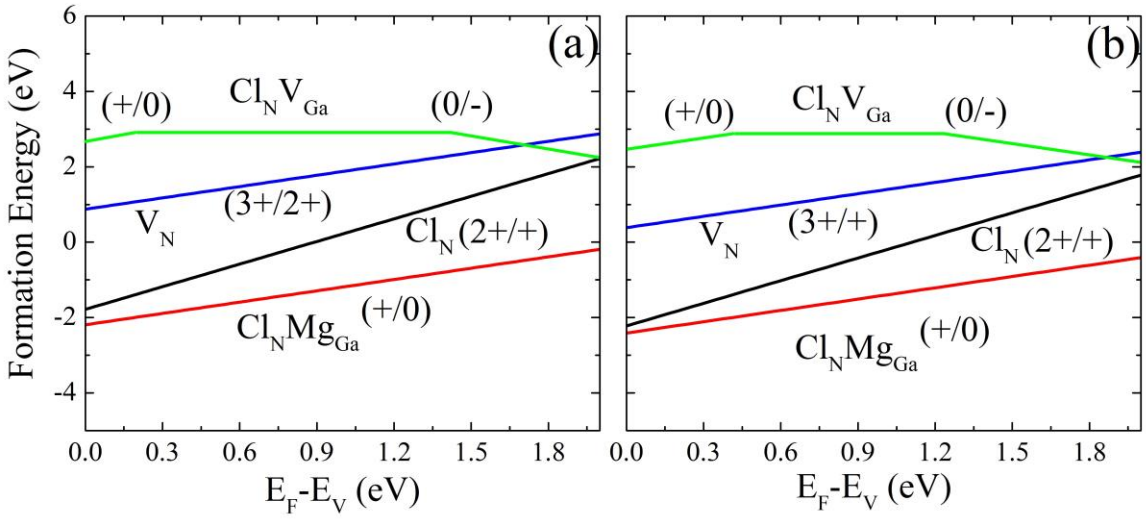

Fig.1. Formation energies of V_N, Cl_N, Cl_NMg_{Ga} and Cl_NV_{Ga}, for Ga-rich conditions, adjusted by using (a) Madelung correction and (b) the potential alignment. Unlike for the Madelung correction, the negative-U behavior of V_N is observed by employing the potential alignment.

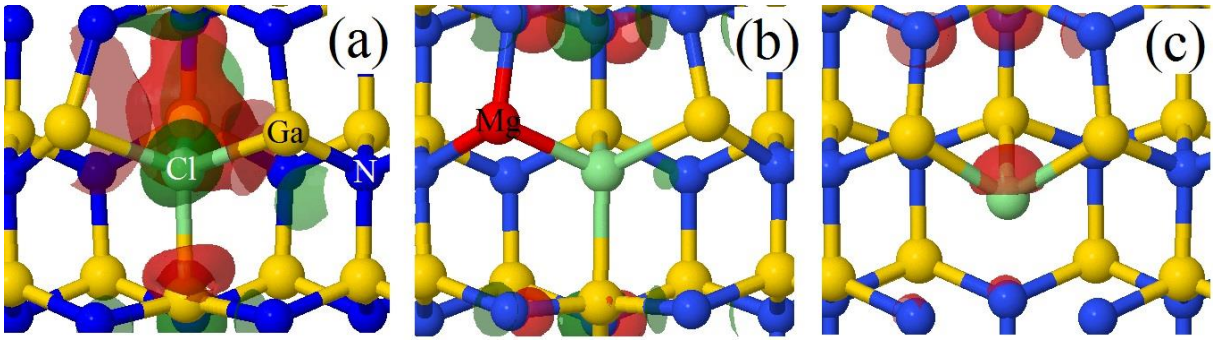

Fig.2. Isosurfaces of the highest occupied orbitals of (a) Cl_N, (T_d) (b) Cl_NMg_{Ga} (C_1) and (c) Cl_NV_{Ga} (C_{3v}). Red is for the positive values of the wave function, green for negative ones. Isovalues were set to 0.05 $e^-/Å^3$ for Cl_N, 0.09 $e^-/Å^3$ for Cl_NMg_{Ga} and 0.07 $e^-/Å^3$ for Cl_NV_{Ga}.