First principles study of calcium in wurtzite GaN

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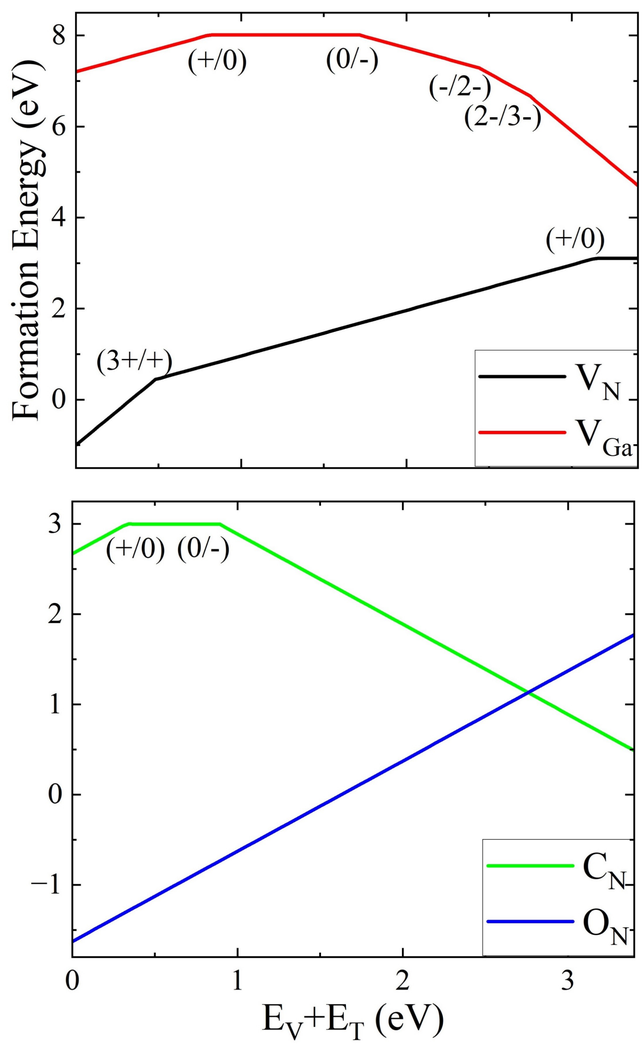
Introduction

Calcium is a rather common impurity in III-V that can be found in concentrations ranging from 10^{15} to 10^{17} cm^{-3}. Ca can be unintentionally incorporated during growth. As a matter of fact, Ca is found in InGaN, originating from the In source during molecular beam epitaxy and even from substrate polishing steps. Overall MBE grown InGaN layers can show [Ca]~10^{18} cm^{-3}.

In this study we want to use density functional theory (DFT) to quantify the Ca complexes forming in the GaN crystalt, determine their formation energy and their electronic properties



Methodology

Density functional theory (DFT) calculations were carried out on a 96-atom wurtzite GaN supercell. We used Troullier-Martins normconserving pseudopotential and the PBE form of the GGA for the exchange correlation potential. The equilibrium configurations of the pristine and defected supercells were obtained by relaxing the atomic coordinates with a conjugate gradient algorithm, until the maximum atomic forces were less than 0.025 eV/Å and the stress tensor less than 0.5 GPa. The charge density was projected onto a real space grid with an equivalent cutoff of 425 Ry and 10 Monkhorst-Pack special k-points were employed. The a=b and c lattice constants were 1% and 0.8% larger than the experimental values, respectively, with a direct band gap of 1.67 eV. The formation energy (E_{form}) was calculated according to:

$$E^q_{form} = E^q_{tot} - E^{bulk}_{tot} - \sum_i n_i\mu_i + q(E_F + E_V + \Delta v_{0/b}) + E_{corr}(q)$$

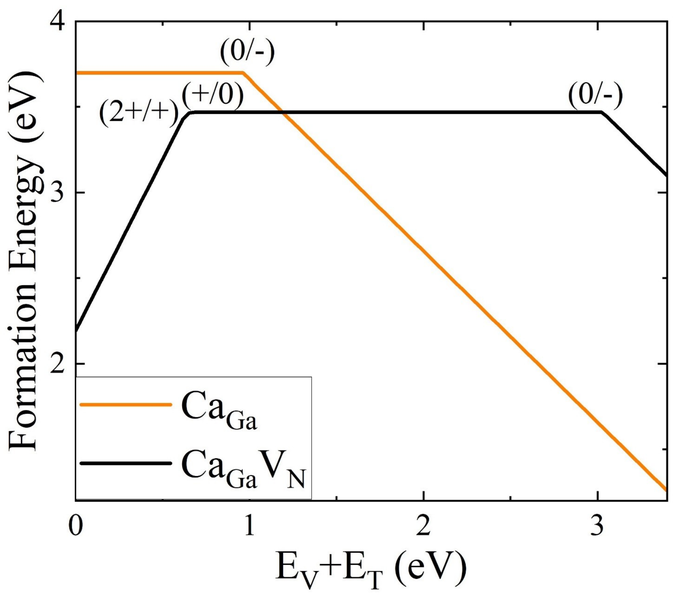
E_{corr} was calculated according to the scheme proposed by Freysoldt et al [1]. Since it is known that variations of E_{form} (and thus of the charge transition levels) depend on the choice of the functional, we applied a further correction scheme based on the alignment of the electrons and chemical potential of the atomic species, as described in Ref. [2].

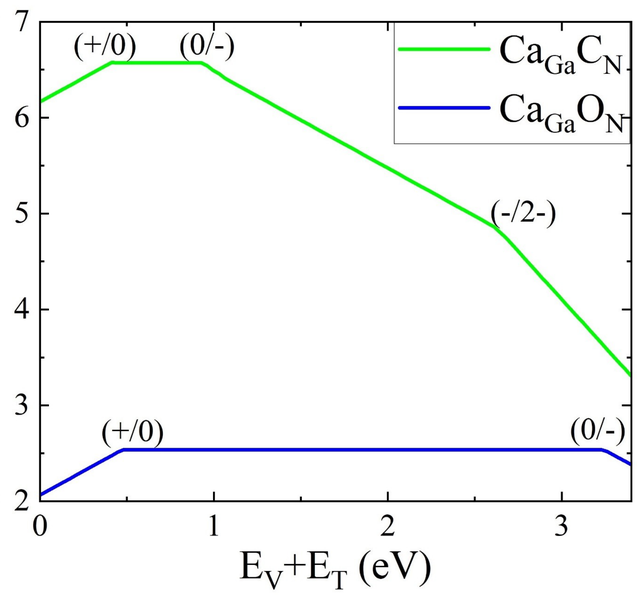
V_{Ga}	(+/0)	(0/-)	(-/2-)	(2-/3-)
Present study	0.8	1.7(!)	2.42	2.73
Matsubara et al.[3]	0.8	1.7	2.2	2.4
Lyons et al.[5]	1.0	1.7(!)	2.3	2.8

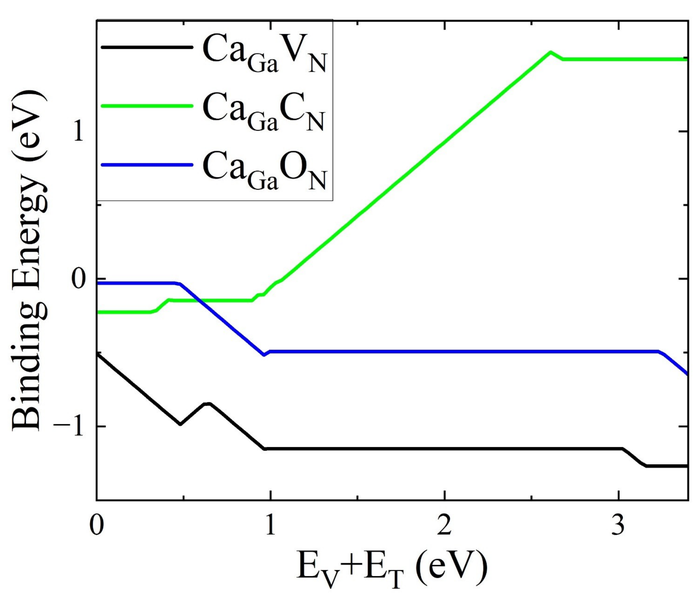
V_N	(3+/+)	(+/0)
Present study	0.48(!)	3.18
Matsubara et al.[3]	0.5	3.25
Lyons et al.[4]	0.48(!)	3.16

C_N	(+/0)	(0/-)
Present study	0.33	0.90 (!)
Matsubara et al.[3]	0.25	0.89
Lyons et al.[4]	0.35	0.90 (!)

Defect	(2+/+)	(+/0)	(0/-)	(-/2-)
$Ca_{Ga}V_N$	0.61	0.64	3.05	-
$Ca_{Ga}C_N$	-	0.4	0.91	2.63
$Ca_{Ga}O_N$	-	0.46	3.24	-







Results

We confirmed that Ca is stable at an N-site (CaN) as in heavily doped p-type GaN. Ca resides at a Ga-site (CaGa) for most of the Fermi energy values in the bandgap and CaGa gives rise to an acceptor level at 1 eV above the valence band edge (EV). This can severely limit the quantum efficiency of III-V LED.

Moreover, we calculated the electronic properties of V_N, V_{Ga}, C_N and O_N. After geometry relaxation, Ca_{Ga} shows T_d symmetry, the only negative charge state is aligned at E_V+1.0 eV. The $Ca_{Ga}V_N$ complex shows a C_{3v} symmetry and two positive and one negative charge state are found. When Ca_{Ga} binds to either C_N or O_N, also both positive and negative charge states arise. However, while $Ca_{Ga}C_N$ might be difficult to form in p-type GaN. $Ca_{Ga}O_N$ shows a relatively low E_{form} for any value of the E_F in the bandgap.

Possibly, when also O impurities are present, e.g. ammonothermal grown substrates, such complex can form and compensate charge carriers. This can be particularly true in the case of n-type GaN whose binding energy is negative (in our study, the more the negative, the more stable the complex). On the other hand, due to the low binding energy, both n- and p-type doping compensation might occur when Ca_{Ga} binds to native (or implantation induced) V_N defects.

References

[1] C. Freysoldt et al., PRL 102, 016402 (2009) [2] C. Freysoldt et al., PRB 93, 165206 (2016) [3] M. Matsubara et al., 121, 195702 (2017) [4] J.L. Lyons et al., JAP 129, 111101 (2021) [5] J.L. Lyons et al., pss(b) 252, 900 (2015)