Extrinsic levels, diffusion, and unusual incorporation mechanism of lithium in GaN

Fabio Bernardini(1) and Vincenzo Fiorentini(1,2)

(1) Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Cagliari, Italy
(2) Walter Schottky Institut, Technische Universität München, Germany

Results of a first-principles study of the Li impurity in GaN are presented. We find Li is a channel interstitial, with an onset for diffusion at T ∼ 600 K. Above this temperature, Li can transform to a Ga-substitutional acceptor by exothermic recombination with Ga vacancies. This process implies capture of at least one electron; therefore Li acts as an electron sink. LiGa is stable again interstitially, and has a shallow first ionization levels of 0.16 eV, and second ionization at 0.63 eV. Lattice locations and their temperature dependence are in close agreement with recent experiments.

PACS numbers: 71.25.Eq, 61.72.Vv, 61.72.Ss

Doping III-V nitrides p-type is a conceptually intriguing and practically relevant problem. The current practical recipe for GaN p-doping is based on the Mg acceptor, but the search for alternative dopants is still ongoing. Useful informations on the mechanism involved in Mg incorporation and on possible alternative acceptors has come from theoretical investigations. While Group-II dopants have been treated in detail, little attention has been devoted so far to potential Group-I double acceptors.

In this Communication we discuss the physics of Li as an impurity in GaN, building on direct calculations of energetics, equilibrium geometries, and diffusion paths. Li is found to be preferentially incorporated in GaN as an interstitial. Since its chemical incorporation is costly, incorporation should be effected by ionic implantation. Diffusion of Li in GaN is activated, with a threshold temperature of about 600 K, and occurs in three dimensions with a slight preference for motion within the basal plane. Li recombination with Ga vacancies is a highly exothermic, barrier-less reaction. Hence, if diffusion is activated, Li is efficiently incorporated substitutionally into any available Ga vacancy. In the recombination process, capture of one or two electrons occurs for almost all values of the Fermi level EF. The substitutional double acceptor LiGa thus realized is highly stable again interstitially (as the Ga vacancy-Li interstitial pair is highly disfavored with respect to LiGa) and, most importantly, it exhibits a thermal first ionization energy of 0.16 eV, smaller than the ionization energy of MgGa, and a second ionization level at 0.63 eV. Because of the strong dependence on precursor defects (the Ga vacancy), the role of Li as an acceptor or compensator will be significant only if its precursors are the dominant native defects of the system. Of course, this limits its practical relevance for GaN doping.

We used local density-functional theory ultrasoft-pseudopotential plane-wave calculations of total energies and forces in GaN wurtzite supercells (typically encompassing 32 atoms), and with plane wave cutoff of 25 Ry, to predict from first principles the total energies and equilibrium geometries relevant to our problem. All atomic coordinates are fully relaxed until residual forces are below 0.01 eV/Å. Further technicalities and the formalism to calculate defect formation energies have been reported previously in detail (see e.g. Refs. 1 and 2). One point worth mentioning here is the solubility limit being metallic bulk Li, rather than Li3N as could be expected.

The formation energies of relevant defects and impurity configurations are summarized for reference in Figure 1. We begin by examining the substitutional LiGa. In this configuration Li behaves as a double acceptor: we determined directly its first and second thermal ionization energies, that are 0.16 eV and 0.63 eV, respectively, above the valence band. This gives us additional motivation for this study, since the first ionization energy is comparable than that of MgGa; the second ionization is fourfold the first as expected from hydrogenic models.

Since the chemical formation energy of LiGa is rather high (3.83 eV in the neutral state in N-rich conditions), plain chemical solubility does not seem an easily viable incorporation pathway for substitutional Li in GaN in moderately p-type conditions. Ion implantation could possibly surrogate chemical reaction. It is then natural to investigate precursors to substitutional incorporation, selected among native defects and Li complexes therewith. Specifically, we studied the Ga vacancy and a selection of Li interstitials and VGa– Li pairs. We also mapped out the diffusion path and estimated the activation barriers for Li interstitial motion along high symmetry directions in undefected wurtzite GaN, and towards a neighboring Ga vacancy in cation-vacancy defected GaN.

The results for VGa and VN are quite compatible with previous calculations. The cation vacancy, in particular, is a deep triple acceptor, with formation energy going from fairly high in p-type conditions to very low in n-type. Local relaxations are in agreement with previously reported data.

As for Li pairs in undefected GaN, we looked for stable sites in the open channels of the wurtzite structure and in the adjacent trigonal cages. In all configurations the stable charge state is +1. We found that the marked
preference for antibonding or bond-center configurations exhibited by hydrogen in GaN is not shared at all by Li. None of the various sites suggested by a naive analogy with H is found to be stable. The lowest-energy configuration of Li$_{\text{Ga}}$ is at the center of the open wurtzite channel, and has C$_{3v}$ symmetry. The site can be viewed as delimited at the top and bottom by three-fold asymmetric boat-shaped Ga-N rings, and laterally by symmetric boat-shaped three-fold rings. The coarse-grained picture is that Li simply tries to maximize its distance from all other atoms, but on closer inspection a slight preference is revealed towards N atoms. In particular, Li$_{\text{int}}$ sits at 3.61 bohr from the N atoms protruding from the upper ring, and at 4.33 bohr from the Ga atoms in the lower ring. The equilibrium sites along the $c$ axis are 0.23 $c$ and 0.73 $c$, which compare well with the measured $c$-axis values of 0.25 $c$ and 0.75 $c$ [the implicit convention here is that Ga atoms have $c$-coordinates zero and 0.5 $c$, and N atoms have 0.376 $c$ and 0.876 $c$]. Inside the trigonal cage, we only find a marginally stable site near the cage center, at about 1.3 eV higher than the channel site, and with a confinement barrier of only 0.1 eV. Again, Li prefers to sit closer to N atoms (Li-N distance $\sim$ 3.18 bohr) than to Ga atoms (Li-Ga distance $\sim$ 3.59 bohr).

These results can be largely understood with a simple Madelung-like electrostatic model, whereby we calculate the electrostatic energy of channel-interstitial Li as a function of its coordinate along the $c$ axis, assuming it interacts with point-charge ions placed on a wurtzite lattice. N and Ga are assigned their dynamical Born charges of $\pm$ 2.7, while Li is assumed to have a dynamical charge of 0.9. The equilibrium site is found at 0.31 $c$, close to 0.23 $c$ and 0.25 $c$ given by direct calculation and experiment, respectively; the barrier for displacement along $c$ is 3 eV, which compares well with 2.7 eV from direct calculation for the unrelaxed lattice. This shows that basically Li sits at the site dictated by the minimization of the electrostatic interactions with the ionic lattice. The sizable deviation in the equilibrium coordinate is due to the large size of the N ions, assumed to be pointlike in the model.

Starting from these sites, we investigated the diffusion paths for Li in GaN. The barrier for diffusion between equilibrium sites along the (0001) direction is 1.55 eV, and the vibrational frequency at the equilibrium site along (0001) is 13 THz. When the diffusion path from channel to channel across a cage is considered, the maximum barrier is found to occur near the cage center, at 1.4 eV above the channel site. At temperatures at which this diffusion path is activated, the previously mentioned marginally stable pocket near the cage center is of course irrelevant, given its confinement barrier of only $\sim$ 0.1 eV. The vibrational frequency at the channel equilibrium site along the cross-cage diffusion direction is 9 THz. The effective activation temperature for Li diffusion can be estimated from the above data to be about 600 K. At the activation temperature, cross-cage motion, i.e., motion approximately within the basal plane, is more probable than motion along the $c$ axis by a factor of 10 on account of its lower barrier.

We now consider the propensity of Li to recombine into Ga vacancies, which we assume henceforth to be already present in the system. In Figure 2 we compare a distant Li$^{+}$-V$_{\text{Ga}}$ pair with substitutional Li$_{\text{Ga}}$; the latter is always vastly favored energetically (by over 5 eV for a semi-insulating crystal, i.e., midgap Fermi level), so Li-vacancy recombination is highly favorable. This recombination process involves several steps. First, Li diffuses across the crystal towards the neighborhood of a vacant Ga site; as discussed previously, this requires a temperature above about 600 K. Second, Li recombines with the vacancy: upon direct calculation, we find that Li drops into V$_{\text{Ga}}$ from the wurtzite channel without any activation barrier, irrespective of the vacancy charge state. Third, the substitutional Li thus produced assumes a charge state consistent with the Fermi energy.

As to the latter step we note that, on account of the charge state of the precursor Ga vacancy and depending on the Fermi level, the metastable V$_{\text{Ga}}$-Li$_{\text{int}}$ distant pair exists in charge states from +1 to –2. Upon recombination with the vacancy, Li$_{\text{Ga}}$ may therefore need to capture electrons to reach its equilibrium charge state (0 to –2, but in fact equal to the latter for most of the accessible E$_{\text{F}}$ range). The level diagram in Fig. 2 shows indeed that either one or two electrons will be captured over practically all the Fermi level range. For example, in process A the pair is singly negative (Li recombines with V$_{\text{Ga}}^{1-}$), hence Li captures one electron to reach its equilibrium charge state of –2. In process B, Li recombines with V$_{\text{Ga}}^{-1}$ (neutral pair) and capture of two electrons ensues. Processes in $p$-type conditions, such as C in Fig. 2, are complicated by the acceptor levels of Li$_{\text{Ga}}$, but all imply the capture of either one or two electrons.

In short, the reason is that all charge states of the Li-vacancy pair overlap in energy only with more negative charge states of Li$_{\text{Ga}}$. The only exception is the doubly negative Li-vacancy pair (Li recombination with triply negative Ga vacancies): the latter, however, only occurs in extreme $n$-type conditions, where in fact the direct chemical incorporation of Li becomes favorable. For all other Fermi levels, Li acts as an electron sink, i.e., as an effective acceptor, or more properly, compensator. Fig. 2 also shows that electron capture is more likely at lower Fermi levels, i.e., towards $p$-type conditions: in particular, if Li$_{\text{Ga}}$ were always –2, the number of captured electrons would change from 0 through 3 as E$_{\text{F}}$ moves downwards across the gap. This is quite clearly the opposite of what happens to normal “chemical” acceptors. Unfortunately, the mechanism is limited by the availability of Ga vacancies as precursors; any Li not paired to a Ga vacancy will remain interstitial.

Let us summarize the picture we arrived at. Isolated Li in GaN sits in the wurtzite channels. It will be very strongly attracted towards any neighboring Ga vacancy, and it will recombine with it to give rise to substitutional Li$_{\text{Ga}}$. To reach a vacancy, Li must diffuse into GaN; dif-
fusion sets in at approximately 600 K (with a preference for the basal plane near the onset). Once in the neighborhood of the vacancy, Li recombines with the vacancy without further energetic barrier hindering the process. Given the gain upon recombination of Li into the vacancy, the reverse process \( \text{Li}_\text{Ga} \rightarrow \text{Li}_{\text{int}} + \text{V}_{\text{Ga}} \) is completely ruled out, i.e., \( \text{Li}_\text{Ga} \) is stable against interstitialcy. At the end of the recombination transient, the \( \text{Li}_\text{Ga} \) concentration will equal that of the pre-existing Ga vacancies (which will have vanished), and the electron density will have been reduced by one to two times the smaller of the two concentrations of \( \text{Li}_{\text{int}} \) and \( \text{V}_{\text{Ga}} \), depending on the initial Fermi level. Clearly, compensation of \( n \)-type carriers will effectively occur if Li is incorporated in GaN in its +1 ionized state, as in ion implantation. Any Li population in excess of the Ga vacancy concentration will remain interstitial.

We close our investigation making contact with the only piece of experimental evidence on Li in GaN, a study of decay emission from implanted radioactive Li isotopes.\(^4\) At room temperature, channeling \( \gamma \)-ray emission is observed, showing that Li is indeed interstitial; as mentioned earlier on in this paper, our calculated locations agree closely with those deduced from angle-dependent channeling. After annealing at 700 K, the \( \gamma \) emission from Li decay is shadowed, indicating that Li has either moved into a trigonal cage, or to a substitutional site. On the basis of our results, the natural explanation is Li-Ga vacancy recombination. While shadowing may occur also if Li would remain confined in a trigonal cage, our calculated diffusion barriers show that this is not possible, as the cage center is not a stable site at the relevant temperature. Our estimate of 600 K for the onset of diffusion (and consequent recombination with Ga vacancies) is in rather good agreement with experiment, given our neglect of entropic contributions to the free energy diffusion barrier.

In summary, we have shown by first-principles calculations that Li can be easily incorporated as an interstitial in GaN, and that it will efficiently recombine with cation vacancies to yield \( \text{Li}_\text{Ga} \). The resulting substitutional double acceptor is predicted to have first and second thermal ionization energies at 0.16 eV and 0.63 eV above the valence band, energies which are comparable or smaller to those of acceptors commonly used in GaN. Due to limitations due to the availability of its precursor \( \text{V}_{\text{Ga}} \), Li is expected to function only as compensator of \( n \)-type carriers.

We acknowledge dedicated funding from INFM through Iniziativa Calcolo Parallelo and the Computational Semiconductor Physics Network of Section E. VF was supported by the Alexander von Humboldt-Stiftung during his stay at WSI.

---

1. J. Neugebauer and C. G. van de Walle, Appl. Phys. Lett. 68, 1829 (1996).
2. F. Bernardini, V. Fiorentini, and A. Bosin, Appl. Phys. Lett. 70, 2990 (1997).
3. V. Fiorentini, F. Bernardini, A. Bosin, and D. Vanderbilt, in *The Physics of Semiconductors* M. Scheffler and R. Zimmermann eds. (World Scientific, 1996), p. 2877. F. Bernardini, V. Fiorentini, and R. M. Nieminen, *ibid*, p. 2881.
4. J. Neugebauer and C. G. van de Walle, Festkörperprobleme/Advances in Solid State Physics, vol. 35, R. Helbig ed. (Vieweg, Braunschweig 1996), p.25.
5. J. Neugebauer and C. G. van de Walle, J. Appl. Phys. 85, 3003 (1998).
6. R. Dreizler and E. Gross, *Density functional theory*, (Springer, Berlin, 1990).
7. D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
8. The thermal first ionization energy \( \epsilon[0/−] \), corresponding to hole release from the acceptor state, is the formation-energy difference of charge states \( Q=−1 \) and \( Q=0 \) at \( \mu_e=0 \). The second ionization energy is the same as above for charge states \( Q=−2 \) and \( Q=−1 \).
9. J. Neugebauer and C. G. van de Walle, Phys. Rev. Lett. 75, 4452 (1995).
10. M. Dalmer et al., J. Appl. Phys. 84, 3085 (1998).
11. A. Bosin, V. Fiorentini, and D. Vanderbilt, in *Gallium Nitride and related compounds*, R. D. Dupuis, J. A. Edmond, F. Ponce, and S. Nakamura eds., MRS Proceedings 395, 503 (1996).
12. F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. B 56, R10024 (1997).
13. The formation energy of this pair is the sum of the formation energies of \( \text{Li}_{\text{int}} \) and \( \text{V}_{\text{Ga}} \), calculated individually in separate simulation cells, i.e. for non-interacting defects. Conversely, the substitutional is the strongly interacting limit for this pair.
FIG. 1. Formation energies of Li and native defects discussed in the text, in N-rich conditions.

FIG. 2. Formation energies of Li$_{Ga}$ and the Li$_{int}$–V$_{Ga}$ pair. Vertical lines schematize possible recombination processes. Dashed lines indicate metastable charge states of Li$_{Ga}$.