AIP | Applied Physics Letters

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Citation: Applied Physics Letters **96**, 142114 (2010); doi: 10.1063/1.3383236
View online: http://dx.doi.org/10.1063/1.3383236
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/96/14?ver=pdfcov
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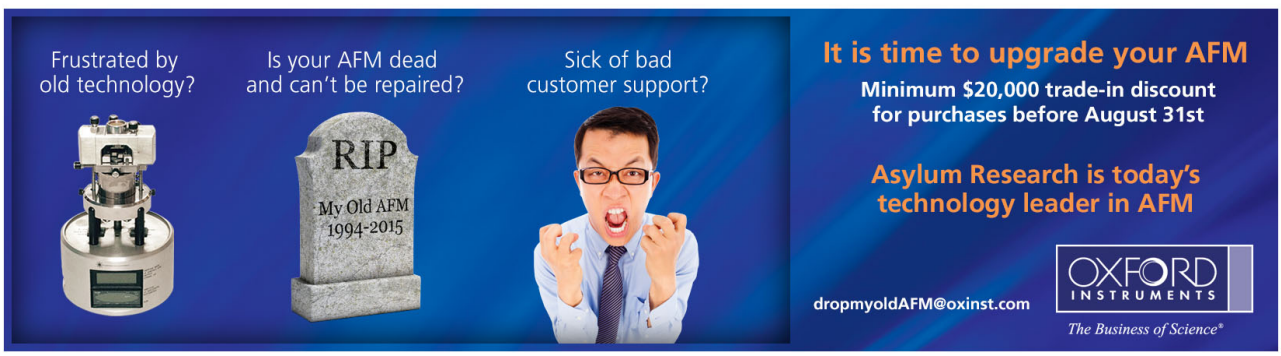

Dual nature of acceptors in GaN and ZnO: The curious case of the shallow Mg_{Ga} deep state

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(Received 3 March 2010; accepted 17 March 2010; published online 9 April 2010)

Employing a Koopmans corrected density functional method, we find that the metal-site acceptors Mg, Be, and Zn in GaN and Li in ZnO bind holes in deep levels that are largely localized at single anion ligand atoms. In addition to this deep ground state (DGS), we observe an effective-masslike delocalized state that can exist as a short lived shallow transient state (STS). The Mg dopant in GaN represents the unique case where the ionization energy of the localized deep level exceeds only slightly that of the shallow effective-mass acceptor, which explains why Mg works so exceptionally well as an acceptor dopant. © *2010 American Institute of Physics*. [doi:10.1063/1.3383236]

The achievement of *p*-doping in the wide-gap semiconductor GaN using Mg as an acceptor dopant[1,2] was a prerequisite for the development of a semiconductor-industry sector based on blue light emitting and laser diodes.[3] Remarkably, GaN:Mg is to date the one and only example where a host+dopant combination for a *p*-type wide-gap semiconductor has matured into commercial technologies. The technological success of GaN:Mg should, however, not conceal the fact that quite generally, the basics of acceptor doping in wide-gap semiconductors remain fairly poorly understood. Indeed the very nature of the Mg acceptor state is still under discussion: Two acceptor states with distinct properties have recently been observed in optical measurements in GaN:Mg.[4] Likewise, magnetic resonance experiments find different Mg related signals pointing either toward a lattice-relaxed, noneffective-mass state[5] that is typically the signature of a deep level, or toward a shallow effective-masslike state.[6] Ironically, the *p*-type conductivity in GaN:Mg seems to stem from the deeper Mg acceptor that prevails[4] after the annealing treatment that is usually used to activate the Mg acceptors.[1] In analogy to GaN:Mg, two different acceptor states are also observed in ZnO:Li,[7,8] suggesting the shallow versus deep (effective-mass versus localized) behavior is a possibly a rather general phenomenon, key to the understanding of acceptors in wide-gap semiconductors.

To address *p*-type doping theoretically requires a quantitative method to predict acceptor states. However, research in ZnO and other oxides over the past years has shown that standard density functional theory (DFT) is not accurate enough to predict even qualitatively the *localization* of the acceptor wave function, let alone to make *quantitative* predictions for the acceptor binding energy.[9–11] Computationally much more expensive hybrid-DFT calculations have recently been used to restore the correct hole-localization in oxides[12–14] but the results depend to some extent on the choice of the hybrid functional and its associated parameters and the predicted acceptor levels are not necessarily very accurate.[9,12] Thus, we use here instead a recently developed DFT-based method[10] that employs a generalized Koopmans condition to systematically restore the correct localization of the acceptor wave function and to quantitatively predict acceptor binding energies. We find that the metal-site acceptors Mg, Be, Zn in GaN, and Li in ZnO have a dual nature in that they exhibit in their deep ground state (DGS) a highly noneffective masslike acceptor wave function being mostly localized on a single N atom, yet they also feature a shallow transient state (STS) with an effective-masslike delocalized wave function. Depending on sample conditions, this transient state can be observed in, e.g., in photoluminescence (PL) experiments, and can account for the observation of two states (i.e., a deeper one and a shallower one) in GaN:Mg (Ref. 4) and in ZnO:Li.[7,8] This duality was not revealed by previous calculations using standard DFT functionals,[15] because there the self-interaction error causes a strong bias toward delocalized acceptor states.[9,10] We explain the unique success of Mg acceptor doping in GaN by the fact it represents the exceptional case where the localized deep level has a binding energy that only slightly, by 30 meV, exceeds that of the ideal effective-mass state, and is still shallow enough to provide for good *p*-type conductivity. Other metal-site acceptors in GaN or ZnO exceed the effective-mass binding energy by 200–400 meV and are thus far less suitable as *p*-type dopants.

It is well known that local density functionals and GGA functionals generally underestimate the energy splitting between occupied and unoccupied states due to residual self-interaction.[16] In order to cure this deficiency for localized acceptor states (i.e., unoccupied hole states) in oxides, we recently introduced an on-site hole-state potential,[10] $V_{\mathrm{hs}} = \lambda_{\mathrm{hs}}(1 - n_{m,\sigma}/n_{\mathrm{host}})$. Here, $n_{m,\sigma}$ is the fractional occupancy $0 \le n_{m,\sigma} \le 1$ of the m-sublevel of spin σ (diagonal representation), and n_{host} is the respective occupancy in the respective defect-free GaN or ZnO host. Since, in compound semiconductors, the states at the valence band maximum (VBM) that dominate the acceptor wave-functions are formed by anion-*p* states, we define V_{hs} here for N-*p* orbitals in GaN and for O-*p* in ZnO. The parameter λ_{hs} is determined through a generalized Koopmans condition,[10] which restores the physically correct piecewise linearity of the energy as a function of the fractional electron number.[17] Thus, there are no free parameters. We apply these hole-state potentials to an otherwise standard DFT calculation using the projector augmented wave method as implemented in the VASP code,[18] and the exchange-correlation functional of Ref. 19. For the shallow Zn *d* shell, which exhibits considerable interaction with the valence band states, we additionally employ the

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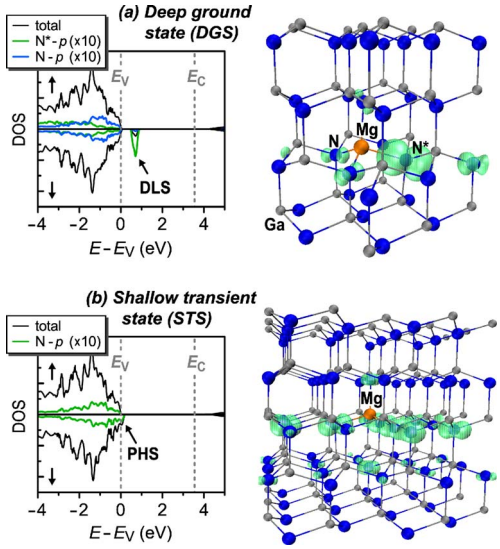

FIG. 1. (Color online) The density of states (DOS, left) and the respective isosurface spin-density (green, right) for the two configurations of the Mg_{Ga} acceptor in GaN; (a) the deep ground state; (b) the transient shallow state. The local DOS is shown for the N neighbors of Mg. In (a), N^* denotes the N-neighbor at which the hole is localized.

DFT+U correction[20] with $U-J=6$ eV. We used supercells of 72 atoms and corrected finite-size effects as described in Ref. 21.

For the following discussion, we now define "deep" versus "shallow" behavior in terms of the wave function character of the acceptor state. (This qualitative distinction is here more useful than drawing the line at an arbitrary value of the ionization energy.) We described the primary impurity orbital as resulting from the interaction of the impurity atom orbital with the dangling bond states of the ligands.[22] If the resulting "defect localized state" (DLS) occurs inside the band gap, the wave function of the defect state is strongly localized at the site of the impurity and its ligands. This is the signature of a deep defect. If, however, the DLS occurs as a resonance inside the continuum of the host bands, e.g., *below* the VBM, then the holes introduced by acceptor doping cannot occupy the DLS, and instead occupy a "perturbed host state" (PHS) that is formed by the valence bands of the host in the presence of the (screened) Coulomb potential due to the charged acceptor. This is the signature of a shallow acceptor that exhibits effective-masslike characteristics.

Figure 1 shows that Mg_{Ga} in GaN can assume both types of behavior for two different geometries. In its lowest energy ground state, Mg_{Ga} creates a DLS in the gap at $E_V+0.7$ eV which is localized mostly in one *p*-orbital of a N neighbor in the basal plane [see Fig. 1(a)]. Due to a Jahn–Teller type symmetry breaking, the N atom hosting the hole has a much larger distance (2.23 Å) to the Mg site than the other three N (about 2.02 Å). We refer to this configuration as the "deep ground state" (DGS). Note that a similar Jahn-Teller distorted localized state has been found also for Zn_{Ga} in self-interaction corrected DFT calculations.[11] The second configuration is more symmetric, i.e., all N–Mg distances are practically identical (about 2.05 Å). In this configuration, the acceptor-wave function has the character of a fairly delocalized effective-masslike state [see Fig. 1(b)], and the hole occupies a PHS just above the VBM (due to finite-size effects this state merges with the valence band at typical supercell sizes). Note that the N-*p* ligand states forming the DLS create a broad resonance around 1 eV below the VBM [Fig. 1(b)]. We refer to this configuration as the "shallow transient state" (STS), since it lies 30 meV higher in energy than the DGS, and will decay into the DGS (see below). The DGS and STS, respectively, can account for the observation of both noneffective-mass[5] and effective-mass behavior[6] of the Mg acceptor state in magnetic resonance experiments.

TABLE I. Acceptor binding energies ε_A of the DGS and STS of metal-site acceptors (A) in GaN and ZnO. Also given is the vertical transition energy ε_O for $A^0 \rightarrow A^-$ (*cf.* "PL2" in Fig. 2). All energies are in electron volt and given relative to the VBM.

	GaN:Mg	GaN:Be	GaN:Zn	ZnO:Li
ε_A (DGS)	0.18	0.45	0.32	0.64[a]
ε_A (STS)	0.15	0.15	0.25	0.21
ε_O ($A^0 \rightarrow A^-$)	0.62	1.48	0.90	1.62

[a]Reference 24.

Table I gives the calculated acceptor levels for the two configurations of the metal site acceptors Mg_{Ga}, Be_{Ga}, and Zn_{Ga} in GaN, and Li_{Zn} in ZnO. We see that for all acceptors except Mg_{Ga} the DGS is stabilized by a significantly larger (by 0.2–0.4 eV) hole binding energy compared to the STS. In case of GaN:Mg, however, the difference between the two acceptor configurations is very small, only 0.03 eV, which explains why Mg acceptors are good *p*-type dopants despite the highly noneffective masslike character of the acceptor state that has been determined in magnetic resonance experiments.[5] Thus, the Mg_{Ga} acceptor is a peculiar case of a lattice relaxed defect with a strongly localized wave function whose ionization energy is nevertheless (accidentally) very close to that of the shallow effective-masslike state. We further see in Table I that the binding energy of the STS of Mg and Be are identical, indicating that they correspond the to the ideal effective mass value. In contrast, the STS of Zn_{Ga} exhibits a central-cell contribution which can be attributed to the *p-d* repulsion between the Zn *d* and N *p* shells and which increases the binding energy by 0.1 eV compared to Mg and Be (Table I). The free-hole density is, however, always determined by the deep ground state configuration, and our calculated binding energy of 0.18 eV for Mg_{Ga} agrees well the experimentally observed activation energies around 0.2 eV.[23] The largest ionization energy in GaN is found for Be acceptors, which falls in line with our previous observation[10] that the strongly lattice mismatched first-row elements B and Be form exceptionally deep levels in oxides, e.g., in case of SnO_2:B and In_2O_3:Be.

A crossover between the shallow ("DLS below VBM") and deep ("DLS above VBM") behaviors discussed above leads usually to an energy barrier in the configuration coordinate diagram.[22] Such a barrier opens the possibility to experimentally observe metastable configurations before they decay into the lowest energy ground state, if there exists a pathway to prepare the metastable state. In order to study the conditions under which the DGS or the STS is observed in a PL experiment, we calculated the configuration coordinate diagram, shown in Fig. 2. For example, in a compensated sample, most acceptors exist in their ionized state Mg^-_{Ga} in equilibrium. The neutral Mg^0_{Ga} state is then created by vertical excitation ("PE" in Fig. 2), and initially relaxes into a local minimum close to the symmetric configuration of the Mg^-_{Ga} state. If the PL recombination occurs before the accep-

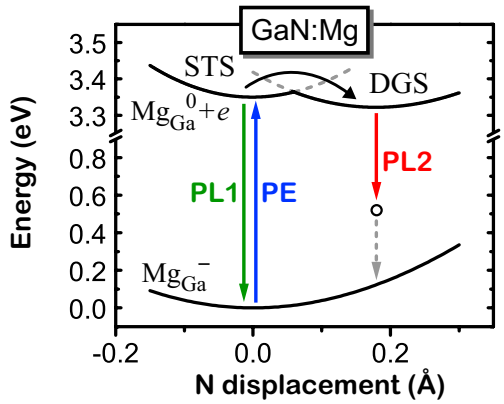

FIG. 2. (Color online) Configuration coordinate diagram of the Mg_{Ga} acceptor in GaN. The reaction coordinate is the displacement of the N atom from its equilibrium position in the ionized Mg_{Ga}^{-} state. PE: Photoexcitation creating the neutral acceptor state Mg_{Ga}^{0}. PL1: Vertical PL transition from the STS. PL2: Vertical PL transition from the DGS.

tor overcomes the energy barrier to the deep ground state, a PL energy is observed that corresponds to the shallow effective-masslike state ("PL1" in Fig. 2). In this case, excitation (PE) and recombination (PL1) energies are similar. If, however, the recombination occurs after the decay of the STS into the DGS across the energy barrier, the deep level PL is observed ("PL2" in Fig. 2). In this case, the recombination energy (PL2) shows a large Stokes-shift. (Note that due to the multidimensionality of the configuration space, the transition ends at an energy above the one-dimensional projection of the Mg_{Ga}^{-} energy surface). As shown in Table I, the $Mg_{Ga}^{0} \rightarrow Mg_{Ga}^{-}$ transition lies 0.62 eV above the VBM. Thus, using the experimental value of 3.55 eV for the GaN band gap, we predict an energy of 2.93 for the vertical free-to-bound transition ("PL2" in Fig. 2).

We can now compare the expectations of our two-state model with experimental observations. Specifically, we expect that the PL strength of the shallow acceptor correlates with the electron concentration: The time scale on which the transition from the STS into the DGS (*cf.* Fig. 2) occurs depends on the height of the energy barrier which we find is very small, approximately 0.02 eV. Such a small barrier implies that the transition can occur on a time scale comparable to the PL lifetime. Whether the shallow or the deep state is observed will depend on the electron concentration: The higher the electron concentration, the shorter the lifetime of the photoexcited neutral acceptor A^0 and the higher the probability that the PL recombination takes place before the relaxation from the STS into the DGS. Thus, we expect that the shallow state will dominate in *n*-type samples, whereas in less compensated *p*-type samples the deep state will dominate. This expectation aligns well with the experimental evidence that has been established so far: The PL intensity of the shallower of two states observed in GaN:Mg (Ref. 4) is reduced after the activation of Mg acceptors during annealing (out-diffusion of compensating H donors). In fact, at a high level of activation of Mg acceptors (i.e., a low compensation ratio), most acceptors exist already in the deep ground state of the neutral A^0 acceptor in equilibrium. In this situation, the metastable shallow acceptor state is not produced by photoexcitation, and, hence, no PL signal due to the transient shallow acceptor is expected, in accordance with experimental observation.[4]

Our calculations in ZnO further suggest that there, Li_{Zn} acceptors should show a behavior analogous to Mg_{Ga} in GaN. Indeed, both deep and shallow PL related to Li are observed in ZnO.[7,8] The deep Li PL around 2.0 eV is long known experimentally.[25] For comparison, using again the experimental gap of 3.44 eV for ZnO and the vertical transition energy 1.62 eV relative to the VBM (Table I), we obtain 1.82 eV for the vertical recombination of the deep Li state (analogous to "PL2" in Fig. 2). In accordance with the expected correlation with the electron concentration, the shallow Li-related PL has more recently been observed in ZnO under conditions that are conducive to *n*-type conditions, i.e., after heteroepitaxial growth on GaN substrates (likely to cause in-diffusion of Ga_{Zn} donors),[7] or after treatment with hydrogen.[8]

In conclusion, metal-site acceptors in the wide-gap semiconductors GaN and ZnO exhibit an interesting dual nature of their acceptor states. The lowest energy state is always a lattice distorted structure with a strongly localized, noneffective masslike wave function. In most cases this deep state has too large hole binding energies for efficient *p*-type doping but Mg_{Ga} in GaN is the manifestation of the exceptional case where a lattice relaxed acceptor with a strongly localized hole wave function has an ionization energy small enough to allow for sufficient thermal activation of free-holes.

This work was funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, under Contract No. DE-AC36-08GO28308 to NREL. The use of MPP capabilities at the National Energy Research Scientific Computing Center is gratefully acknowledged.

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