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Effects of hole localization on limiting *p*-type conductivity in oxide and nitride semiconductors

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We examine how hole localization limits the effectiveness of substitutional acceptors in oxide and nitride semiconductors and explain why *p*-type doping of these materials has proven so difficult. Using hybrid density functional calculations, we find that anion-site substitutional impurities in AlN, GaN, InN, and ZnO lead to atomic-like states that localize on the impurity atom itself. Substitution with cation-site impurities, on the other hand, triggers the formation of polarons that become trapped on nearest-neighbor anions, generally leading to large ionization energies for these acceptors. Unlike shallow effective-mass acceptors, these two types of deep acceptors couple strongly with the lattice, significantly affecting the optical properties and severely limiting prospects for achieving *p*-type conductivity in these wide-band-gap materials. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4838075]

I. INTRODUCTION

In traditional semiconductors such as Si and GaAs, the recipe for finding effective dopants is relatively straightforward. In most cases, elements from adjacent rows in the periodic table act as efficient hole and electron dopants, with acceptors on the left and donors on the right. For instance, in Si, B (a *p*-type dopant) and P (an *n*-type dopant) have ionization energies on the order of ∼50 meV.[1] In GaAs, Zn substituting on the Ga site is a shallow acceptor with an ionization energy of 31 meV,[2] and Si substituting on the Ga site is an effective donor with an ionization energy of about 10 meV.[1] Because of their small ionization energies, electrons and holes are only weakly bound to these dopants (an interaction described by effective mass theory[3]), meaning that they are easily ionized to give rise to free carriers. Adding small concentrations of these aliovalent impurities can thus give rise to well-controlled conductivity.

With band gaps larger than those of Si and GaAs, ZnO and the nitride semiconductors are suitable for optoelectronic devices that operate in the visible and ultraviolet. Nitrides have allowed for the development of efficient UV/blue/green light-emitting diodes and laser diodes. However, ambipolar doping is a major problem for the wide-band-gap semiconductors. *n*-type conductivity can be obtained in the same way as in traditional semiconductors, for instance, Si substituting on the Ga site in GaN is an effective *n*-type dopant, and Al is an effective dopant that can give rise to highly *n*-type-conductive ZnO.[1] However, *p*-type doping has proven much more difficult. Despite years of research, no reliable, reproducible technique for producing *p*-type ZnO has been developed.[4,5] And despite the success of GaN, only *one* workable *p*-type dopant (Mg) has been identified, and therefore all optoelectronic devices currently depend on this crucial impurity. However, even the Mg acceptor has a very low doping efficiency due to its high ionization energy (∼200 meV).[6] AlN, another member of the nitride semiconductor family which can be alloyed with GaN to create shorter-wavelength devices, suffers from even lower Mg doping efficiency.[7]

Using first-principles calculations, we find that the major barrier to achieving *p*-type conductivity in these materials is that acceptor dopant candidates create "deep" levels, in the sense that the corresponding wave functions are highly localized. The root cause of this problem is that the valence bands (VBs) of the nitrides and oxides are derived mainly from N $2p$ or O $2p$ orbitals, and thus the position of their VBs on an absolute energy scale is very low.[8] This low energetic positions leads to two separate problems for obtaining shallow acceptors in these materials. First, acceptors substituting on the anion site give rise to defect states that lie above the VB, leading to deep levels. We therefore call the anion-site acceptors "atomic-like". Second, the low-lying O $2p$ and N $2p$-derived VBs have very small dispersion and heavy hole effective masses. These features make these semiconductors susceptible to the formation of small polarons.[9] Although self-trapped polarons are not stable in these pure bulk materials, we will see that polarons can be stabilized in the vicinity of impurities. For shallow acceptors, the neutral charge state of the acceptor corresponds to a delocalized hole; when the hole becomes localized due to impurity-stabilized polaron formation, the acceptor becomes deep. This polaronic behavior leads to a significant increase in ionization energy for the cation-site acceptors in the materials studied here, and we therefore refer to this class of acceptors as "polaronic".

We begin by first introducing the methods used to investigate these acceptors (Sec. II). In Sec. III, we first discuss the properties of effective-mass acceptors that act as effective dopants in traditional semiconductors, and elaborate on the two classes of deep acceptors in wide-band-gap semiconductors (atomic-like and polaronic). Secs. IV and V contain explicit results for acceptors in III-nitrides and ZnO and discuss how they limit *p*-type conductivity.

II. METHODS

In this work, we employ first-principles techniques to uncover the origins of *p*-type doping difficulties in wide-band-gap semiconductors. Theoretical methods long lacked the ability to accurately and quantitatively describe the properties of deep defects in wide-band-gap materials. Density functional theory (DFT) based on the local density approximation (LDA) or the generalized gradient approximation (GGA) severely underestimates semiconductor band gaps, giving rise to large uncertainties in defect levels. Furthermore, these methods fail to accurately describe charge localization.[10] For instance, previous theoretical work on $\mathrm{Li_{Zn}}$ in ZnO, performed using the LDA, failed to reproduce the hole localization that is experimentally observed,[11] instead predicting shallow acceptor behavior and an ionization energy of only 200 meV.[12,13]

Here, we employ a hybrid functional in DFT, an approach which has proven capable of providing accurate semiconductor band structures[14] and more reliable for predicting localization in deep defect centers.[15] As we have shown in previous work,[16,17] employing these techniques to study defects in wide-band-gap semiconductors yields results that can be significantly different from calculations based on LDA or GGA, albeit at a significantly higher computational cost. Our calculations are based on the generalized Kohn-Sham (KS) scheme[18] using the projector-augmented wave method[19,20] with the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE)[21] as implemented in the VASP code.[22] The impurity calculations are performed using a 96-atom supercell, a plane-wave basis set with a 400 eV cutoff, and a $2 \times 2 \times 2$ Monkhorst-Pack k-point set. Spin polarization is explicitly included and symmetry-breaking distortions are always considered. Relaxations are performed consistently with the HSE functional. More details on these calculations are given in Refs. 16 and 17. Defect formation energies and transition levels were calculated with the standard formalism.[23]

III. ELECTRONIC STRUCTURE OF ACCEPTORS

A. Shallow, effective-mass acceptors

The electronic structure of an effective-mass (EM) acceptor in the neutral charge state can be understood within a tight-binding picture, as illustrated in Fig. 1(a). In tight-binding theory, the bulk band structure arises from interactions between sp^3 orbitals [with energy $(\varepsilon_s + 3\varepsilon_p)/4$] on the cations and anions.[24] Filled bonding states give rise to the VB (which ends up having predominantly anion *p* character), and empty antibonding states give rise to the conduction band (CB) (with predominantly cation *s* character). When Zn is substituted on a Ga site, the interactions lead to a bonding state within the GaAs VB that is missing one electron (due to Zn having valence 2, rather than valence 3 for the host cation). This leads to a hole at the valence-band maximum (VBM), which is loosely bound to the acceptor (whose "core" is now in a -1 charge state).

The situation described here is that of a hydrogenic EM acceptor, whose electronic structure is largely determined by the properties of the host material: dielectric constant and valence-band EM.[3] The wave function of such an acceptor is spread out over a large volume, characterized by the Bohr radius (a_B)

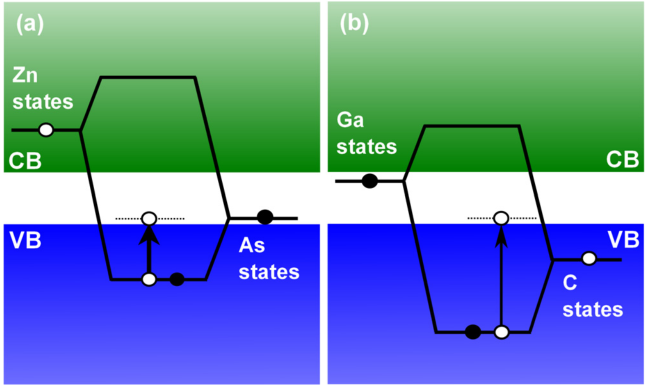

FIG. 1. (a) Electronic structure of a cation-site shallow acceptor in GaAs, for the example of $\mathrm{Zn_{Ga}}$. The atomic states of Zn lie higher than those of Ga. Interaction between Zn and As orbitals leads to a state within the GaAs VB. Since Zn has one less valence electron than Ga, this state is missing an electron, and the resulting hole "bubbles up" to the VBM, where it is bound to the ionized $\mathrm{Zn_{Ga}^-}$ acceptor in an effective-mass state. (b) Electronic structure of an anion-site shallow acceptor in GaAs, for the example of $\mathrm{C_{As}}$. The atomic states of C lie below the VBM of GaAs, and the hole in this state "bubbles up" to the VBM, where it is bound to the ionized $\mathrm{C_{As}^-}$ acceptor in an effective-mass state.

$$a_B = \frac{m}{m^*}\varepsilon_r a_0, \tag{1}$$

where m^* is the hole effective mass of the semiconductor, m is the free electron mass, ε_r is the relative dielectric constant of the semiconductor, and a_0 is the Bohr radius of the hydrogen atom (0.53 Å). The ionization energy (E_A) of a hydrogenic EM acceptor is given by[25]

$$E_\mathrm{A} = 13.6\ \mathrm{eV}\,\frac{m^*}{m\varepsilon_r^2}. \tag{2}$$

The large dielectric constant and small EM of traditional semiconductors lead to a large Bohr radius and small ionization energy: in GaAs, $\varepsilon_r = 12.80$ and $\frac{m^*}{m} = 0.75$,[1] leading to $a_B = 9.05$ Å and $E_a = 62$ meV for acceptors in GaAs. Indeed, experimental ionization energies for EM acceptors in Si, GaAs, and other traditional semiconductors are on the order of ~50 meV.[1] This implies that these acceptors will be efficient dopants, since nearly all of the impurities will be ionized at room temperature.

Because of the delocalized nature of the hole wave function in the neutral charge state, the atomic structure of EM acceptors (i.e., lattice relaxations in the vicinity of the impurity) is almost identical in the neutral and negative charge state. These acceptors will therefore lead to optical signals very near the band-gap energy of the host material, representative of the small ionization energy.[26]

B. "Atomic-like" deep acceptors

Unlike EM acceptors, the anion-site acceptors studied in this work lead to defect states that reside within the fundamental band gap of the semiconductor. The distinguishing feature of these acceptors can be discerned in the negative charge state, when the impurity is surrounded by an octet of electrons and no holes are present in the vicinity: the electronic structure shows that the impurity-related states are clearly separated from the bulk VB states and occur well above the VBM. In the neutral charge state, one of these states becomes unoccupied. The hole wave function will be derived from these states in the gap, and will therefore be highly localized on the acceptor impurity, as is shown for the case of C_N in GaN in Fig. 2(a). This localized behavior renders the acceptors deep, as opposed to effective-mass-like. These atomic-like acceptors will thus have a large ionization energy, making them ineffective dopants.

Atomic-like deep acceptors feature large electron-phonon coupling, unlike EM acceptors. This is related to the fact that the neutral and negative charge states have very different atomic configurations. For instance, in the case of C_N, the negative charge state features only small relaxations of nearest neighbors, while in the neutral charge state, the length of one of the C-Ga bonds increases by 8% compared to the bulk bond length.

The localized behavior of the C_N acceptor is directly related to the fact that the *p* states of the C atom lie higher in energy than the *p* states of the N host atom, from which the VB is mainly derived.[24] It is this feature that leads to the impurity-related states of C_N in GaN lying well above the VBM. We note, however, that the mere fact that the *p* states in the acceptor atom lie higher in energy than the *p* states of the host anion atom does not imply that an acceptor will necessarily be deep. Si and Ge acceptors in GaAs are a counterexample: in spite of the fact that their atomic states are higher in energy than those of As,[24] when incorporated on the As site these impurities form shallow acceptors. This is because, in addition to the energy of atomic states, factors such as broadening of host bonding states into VB states also play a role in determining the energies of impurity levels relative to the band structure of the host. The more ionic nature of the wide-band-gap materials, which limits such broadening, contributes to the fact that impurity states end up above the VBM. What can be stated with more certainty is that anion-site acceptors whose atomic *p* states lie *below* those of the host anion are more likely to lead to shallow acceptors (at least in the absence of the polaron-related issues discussed in Sec. III C). Unfortunately, the position of N and O in the periodic table is such that no acceptor elements with this property can be identified.

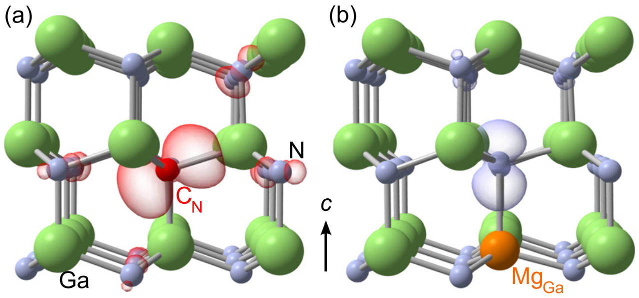

FIG. 2. (a) Wave function of the acceptor hole for C_N, an example of an atomic-like deep acceptor. C_N gives rise to states above the VBM of GaN that are derived from C 2*p* orbitals, as can be seen by the hole in the neutral state being highly localized on the C_N acceptor. (b) Polaron binding to a cation-site acceptor, for the example of the Mg acceptor in GaN. The hole is trapped by the acceptor and localized on a nearest-neighbor anion (here, N). In both cases, the isosurface is set to 5% of the maximum.

The properties of these atomic-like acceptors clearly depend on how the electronic levels of the impurity align with the valence and conduction bands of the semiconductor host. As we will see in Sec. IV, C_N has the highest ionization energy in the material with the lowest valence band (AlN), and the smallest ionization energy in the material with the highest valence band (InN).

C. "Polaronic" deep acceptors

We now turn to the electronic structure of "polaronic" deep acceptors, which also differ from EM acceptors. To put this discussion in context, we first devote a short discussion to the concept of polarons.

Hole localization in semiconductors has been studied for many years. Self-trapping holes have been long known in insulator materials with wide band gaps and low effective hole masses, such as the alkali halides, even in the absence of impurities.[27] In these materials, hole carriers spontaneously localize on anion atoms, concurrent with a local lattice distortion, and the unpaired electron can be observed in electron paramagnetic resonance (EPR).[28] It is, again, the low position of the VBM on an absolute energy scale[8] that is responsible for this behavior: rather than placing a (delocalized) hole in a VB state that is very low in energy, the overall energy of the system can be lowered by placing the hole in an electronic state at an energy higher than that of the VBM. Such a state, which does not exist in the ideal bulk crystal, can be created by locally deforming the lattice; if the gain in electronic energy exceeds the elastic energy cost of this deformation, polaron formation will be favorable. Recent first-principles calculations, employing the HSE hybrid functional, have found that self-trapped holes are stable in a number of technologically relevant oxides.[29]

As predicted in Ref. 29, isolated self-trapped holes are not stable in bulk ZnO. We also do not find them to be stable in the nitride semiconductors. The nearest case we find is AlN, in which polarons can be metastable (i.e., a configuration corresponding to a local minimum), but they are higher in energy than free holes by 0.3 eV. The differences in hole-trapping behavior between the nitrides (and ZnO) and the materials studied in Ref. 29 can likely be attributed to higher VB masses and more ionic bonding of the oxides investigated in that study.

Even though self-trapped holes are not stable in bulk ZnO, InN, GaN, and AlN, we find in this work that the presence of impurities can trigger charge localization in the form of a small polaron. Whereas effective-mass theory predicts that shallow acceptors should have ionization energies of a few hundred meV (~200 meV for GaN (Ref. 30)), hole-trapping at these acceptors can cause their ionization energies to be several hundred meV higher. Hole-trapping by acceptor impurities thus has a drastic effect on their electronic and optical properties.

Unlike the anion-site acceptors discussed in Sec. III B, the cation-site acceptors do not exhibit any atomic-like states in the band gap of the semiconductor host in the *negative* charge state. Rather, it is only when the *neutral* charge state is considered that the deep nature of the acceptor becomes evident. The hole that is present in the neutral charge state is not delocalized, as would be the case for an EM acceptor. It is also not localized on the impurity itself, as is the case for the "atomic-like" deep acceptors. Rather, the hole spontaneously localizes onto a nearest-neighbor anion atom. While hole polarons are not stable in the bulk of the semiconductors discussed here, the additional binding to the cation-site acceptors leads to their stabilization.

The hole localization that occurs in the neutral charge state of cation-site acceptors gives rise to a Kohn-Sham state well above the VBM. The hole is localized on a 2*p* orbital of the host anion, i.e., on a N (or O, in ZnO) nearest-neighbor of the acceptor impurity [Fig. 2(b)]. The atomic distortions associated with these cation-site acceptors reflect the polaronic character, in which a single impurity-anion bond length expands by up to 30% of the bulk bond length; the anion on which the hole is localized is always the one that moves outwards.

In the *negative* charge state of these acceptors, only relatively small breathing relaxations of nearest-neighbor atoms occur. Combined with the fact that no KS states appear in the gap, inspection of these cation-site acceptor in the negative charge state therefore does not allow distinguishing them from EM shallow acceptors; only accurate calculations of the *neutral* charge state reveal their nature.

Ultimately, the stability of the acceptor-stabilized polaron (and thus, the ionization energy of the acceptor) will depend on the atomic size of the dopant, its electronic structure, and the properties of the host semiconductor. We will discuss specific scenarios in Secs. IV and V, but in general, a better size match of the dopant impurity leads to lower ionization energies. Also, materials with lower hole effective masses lead to smaller ionization energies. This interplay between properties is best illustrated for InN (Sec. IV C), which exhibits shallow-acceptor behavior for $\mathrm{Mg_{In}}$, but polaronic acceptor behavior for other cation-site acceptors.

The optical transition energies of these acceptors are strongly affected by their polaronic behavior, indicative of large electron-phonon coupling. Unlike shallow acceptors, which usually lead to donor-acceptor pair transitions very near the band-gap energy of the host,[26] polaronic acceptors give rise to deep, broad luminescence, due to the large difference in atomic configurations between the neutral and negative charge states.

IV. ACCEPTORS IN NITRIDE SEMICONDUCTORS

We now quantitatively discuss substitutional acceptor impurities in III-nitrides. We also discuss the implications for achieving *p*-type conductivity, and compare our calculated electronic and optical properties with experimental studies of acceptor-doped material.

A. GaN

The ability for GaN to be doped *p*-type makes it one of the most important wide-band-gap semiconductors for technology. Although Mg is currently the only known effective dopant, other possibilities have been considered. For instance, the carbon acceptor ($\mathrm{C_N}$) in GaN was often discussed as a potential *p*-type dopant.[30,31] However, more recent experimental studies showed that carbon leads to semi-insulating GaN.[32,33] Our calculations[16] indicated that $\mathrm{C_N}$ is indeed a deep acceptor with a large ionization energy. Using hybrid functional calculations, we found that $\mathrm{C_N^-}$ gives rise to Kohn-Sham states above the VBM of GaN, and these states are derived from C 2*p*-like orbitals. For $\mathrm{C_N^0}$, the hole is localized on the C impurity, leading to an acceptor ionization energy (900 meV) that is far too large to lead to hole conductivity.

Other Group-IV elements substituting on the N site are expected to lead to even deeper levels, since their atomic *p* states are higher in energy than those of C. We indeed find that Si, when placed on the N site, also exhibits hole localization in the neutral charge state, with the hole localized in a Si orbital. This acceptor has an ionization energy of 2.10 eV, significantly larger than $\mathrm{C_N}$ in GaN. In addition, Si and Ge are not very stable on the anion site, and much more stable when substituting on the Ga site, largely because of a better atomic size match. Therefore, $\mathrm{Si_{Ga}}$ and $\mathrm{Ge_{Ga}}$ act as effective shallow donors, and doping strategies involving substitution of these impurities on the N site are ineffective.

The only known viable *p*-type dopant in GaN is Mg, which substitutes on the Ga site. Despite its effectiveness, our calculations indicate that $\mathrm{Mg_{Ga}}$ is a polaronic deep acceptor as described in Sec. III C. In its neutral charge state, $\mathrm{Mg_{Ga}}$ stabilizes a polaron, which is localized on a nearest neighbor N atom and causes a local distortion whereby a Mg-N bond length increases by 15%.[34] Other groups have also predicted that hole localization can occur at $\mathrm{Mg_{Ga}}$.[35] However, despite this localization, we calculate the thermodynamic transition level of the acceptor to be only 260 meV above the VBM of GaN. This ionization energy is small enough to give rise to sufficiently high concentrations of free holes at room temperature and allow for *p*-type conductivity.[6]

The other Group-II dopants are also polaronic acceptors with larger ionization energies than $\mathrm{Mg_{Ga}}$.[36] For instance, $\mathrm{Be_{Ga}}$ exhibits a hole state higher above the VBM than $\mathrm{Mg_{Ga}}$ and a larger distortion (34%) of a Be-N bond, leading to an ionization energy of 550 meV. The differences between $\mathrm{Be_{Ga}}$ and $\mathrm{Mg_{Ga}}$ can likely be attributed to atomic size,[37,38] with the smaller $\mathrm{Be_{Ga}}$ giving rise to a more stable polaron and a larger ionization energy. The other Group-II acceptors (Ca, Sr, Ba) are also found to trap localized holes, with ionization energies even larger than $\mathrm{Be_{Ga}}$.

Although $\mathrm{Zn_{Ga}}$ is more similar in size to Ga than Mg, it also exhibits polaronic acceptor behavior, with a calculated ionization energy (460 meV) larger than that of $\mathrm{Mg_{Ga}}$, and a larger polaronic distortion (17% of the bond length).[36] This difference has previously been explained based on *p-d* repulsion.[39,40] Zinc is therefore a much less effective *p*-type dopant than Mg. So, while all cation-site acceptors are found to stabilize polarons, $\mathrm{Mg_{Ga}}$ is the only acceptor with a small enough ionization energy to allow for *p*-type GaN. This can be attributed to the good size match of Mg to Ga, as well as its lack of *d* states.

B. AlN

The general properties of substitutional acceptors in AlN are analogous to what we find for GaN. $\mathrm{C_N}$ is an atomic-like deep acceptor in AlN, giving rise to states in the band gap that are derived from C 2*p* orbitals. We calculate the acceptor ionization energy of C_N to be 1.88 eV, much too deep to give rise to *p*-type conductivity. Similar results have also been reported by Collazo *et al.*[41] The deeper nature of C_N in AlN is due to the lower-lying VBM, roughly 0.7 eV deeper than that of GaN.[8] This result indicates that Group-IV impurities behave in AlN as they do in GaN, acting as atomic-like deep acceptors, incapable of being effective dopants.

The Group-II acceptors substituting on the cation site are similarly found to act as polaronic deep acceptors, with properties as described in Sec. III C. As we recently showed,[34] Mg_{Al} in AlN shows polaronic acceptor behavior, trapping a hole on a nearest-neighbor N site. The ionization energy of Mg_{Al} in AlN is 780 meV, much higher than in GaN and impeding *p*-type doping (as has been observed experimentally[7]). The higher ionization energy of Mg in AlN is due to the lower-lying VB and heavier holes, which make this material more susceptible to hole trapping. This is also indicated by the fact that bulk polarons (self-trapped holes) are metastable in AlN, something that is not true for any of the other materials studied in this work.

Other Group-II impurities also trap holes in AlN. Our own hybrid functional calculations produce results very similar to those reported earlier by Szabó *et al.*[42] They showed that Be_{Al} also acts as a deep acceptor in AlN, trapping a hole at a nearest-neighbor N site with a concurrent distortion of the Be-N bond, and with a large ionization energy of 970 meV. Other Group-II acceptors were found to have ionization energies even larger than Be.[42] Be_{Ga} and the other Group-II impurities thus exhibit polaronic behavior, with Mg exhibiting the smallest ionization energy, just like in GaN.

C. InN

Although InN is not technically a wide-band-gap semiconductor, it is often alloyed into GaN and AlN, and shares many of their properties. Only in InN do we find that cation-site substitutional acceptors can lead to effective-mass behavior. We previously reported[34] that Mg_{In} leads to EM acceptor behavior as described in Sec. III A, with an ionization energy of 190 meV. A metastable state in which a hole is bound to the acceptor in a polaronic, localized state was also identified for Mg_{In}, but it was higher in energy than the delocalized EM state by 0.2 eV. The different behavior of Mg in InN compared to GaN and AlN is due to the higher VBM and smaller hole mass of InN, which makes this semiconductor less susceptible to hole-trapping.

Interestingly, other Group-II cation-site acceptors do lead to polaronic acceptor behavior in InN. For instance, we calculate that Be_{Ga} can stabilize a polaronic acceptor state with an ionization energy of 350 meV that is more stable than the EM acceptor state. This indicates that even in materials where *some* cation-site impurities do not lead to localization of holes, other impurities (with larger atomic size differences with respect to the cation) may lead to polaronic behavior.

As for GaN and AlN, we find deep acceptor behavior for all anion-site impurities in InN. C_N acts as an atomic-like deep acceptor as described in Sec. III B. We calculate the C_N acceptor to have a (0/−) charge state transition level at 0.59 eV above the VBM (placing it close to the conduction-band minimum), with states derived from C 2*p* orbitals that reside within the band gap of InN. As described at the end of Sec. III B, the smaller ionization energy of C_N in InN compared to GaN is due to the fact that the VBM of InN is about 0.4 eV higher than GaN.[8]

Comparing the behavior of C_N across the III-nitrides confirms the atomic-like deep acceptor character derived from C 2*p* orbitals. Using the band alignments of Ref. 8, we plot the charge-state transition levels of C_N on an absolute energy scale in Fig. 3. Comparing the positions of the C_N (0/−) levels in InN, GaN, and AlN, we find that they align to within 0.2 eV on an absolute scale.

V. ACCEPTORS IN ZnO

We finally turn to ZnO, in which the properties of acceptors and the possibility of *p*-type material have been the subject of heated debate.[43] Many reports claim *p*-type conductivity in ZnO, but despite decades of effort, no known method yet exists for achieving reproducible *p*-type ZnO. ZnO has a VB that is very low-lying, nearly 8 eV below vacuum,[8] and also a heavy hole effective mass,[1] causing substitutional acceptors to exhibit deep behavior. We find that Group-V elements substituting on the O site act as atomic-like deep acceptors as described in Sec. III B. Group-I elements, which replace Zn, are found to act as polaronic deep acceptors as described in Sec. III C.

The Group-V impurities have frequently been employed in efforts to obtain *p*-type ZnO. In particular, N has often been regarded as the most suitable *p*-type dopant, and the other group-V elements (P, As, and Sb) have been explored as well. Our hybrid functional calculations[17] showed that N_O

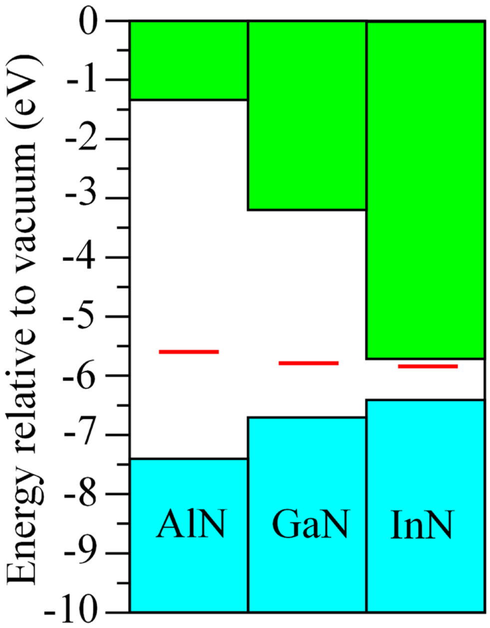

FIG. 3. Charge-state transition levels of the C_N acceptor in AlN, GaN, and InN, with the band structures aligned on an absolute energy scale.[8] The (0/−) charge-state transition levels are indicated by the lines within each band gap.

is a very deep acceptor in ZnO, with an ionization energy of 1.3 eV, and exhibits the atomic-like deep acceptor characteristics described in Sec. III B. Similar to what was found for C_N in GaN, N_O in ZnO exhibits very different charge-state configurations. For N_O^0, the axial N-Zn bond length increases by 8% of the bulk bond length, while for N_O^-, the nearest-neighbor Zn atoms move inwards by 3% of the ZnO bond length. The atomic-like acceptor behavior of N_O is related to the N 2*p* orbitals lying higher in energy than the O 2*p* orbitals which comprise the low-lying VB of ZnO. Calculations employing other techniques have also subsequently confirmed the deep nature of N_O.[44]

The behavior of N_O in ZnO can be further understood by comparing its behavior to the N_{Se} acceptor in ZnSe, as shown in Fig. 4. Unlike ZnO, ZnSe can be *p*-type doped with N (or Li and Na, albeit with some difficulty[45]). This is because in ZnSe, N_{Se} does not lead to states in the band gap as N_O does in ZnO. Instead, N_{Se} induces states *below* the VBM of ZnSe that are deficient an electron. This leads to an effective-mass state with a delocalized hole wave function and a small ionization energy, calculated to be 150 meV.[17]

Based on the fact that the *p* orbitals of P, As, and Sb are higher in energy than those of N,[24] other Group-V elements are expected to be even less attractive acceptor dopants than N in ZnO. In fact, even in ZnSe, such Group-V elements have been shown to have deep acceptor levels.[46] This deep nature of these acceptors in ZnO has been confirmed by HSE hybrid functional calculations for Sb_O, P_O, and As_O, which found that the acceptor ionization energies are much larger than that of N_O, making them very poor acceptor dopants.[47]

It has also been suggested, based on LDA or GGA calculations, that Group-V elements may not incorporate on the O substitutional site, but instead form three-member complexes (such as V_{Zn}-Sb_{Zn}-V_{Zn}).[48,49] More recent HSE calculations have found that these complexes are actually exceedingly deep acceptors,[47] incapable of giving rise to *p*-type material. Such deep behavior can be ascribed to the fact that the complexes contain Zn vacancies, which are themselves very deep acceptors in ZnO.[50]

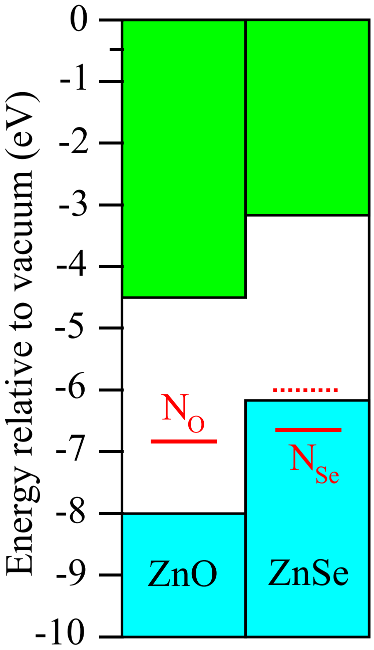

FIG. 4. Charge-state transition levels of N_O in ZnO and N_{Se} in ZnSe, both indicated by the solid red lines. In ZnSe, the level occurs below the VBM, giving rise to a shallow, effective-mass behavior (indicated by the dotted red line).

In light of the fact that Group-V substitution on the O site is not an effective doping technique, one might instead consider Group-I substitution on the Zn site. The properties of such acceptors in ZnO have actually been studied extensively since the 1960 s.[11,51–54] Experimentally, Li_{Zn} has long been known to bind an acceptor hole. EPR studies have shown that the unpaired electron is localized on a nearest-neighbor O atom, causing a large distortion of a Li-O bond and making Li a deep acceptor in ZnO.[11] These properties are consistent with Li_{Zn} acting as a polaronic deep acceptor as described in Sec. III C. Recent theoretical studies on Li_{Zn} have also reported this hole localization for Li_{Zn}, employing a hybrid functional[15] and an LDA + *U*-based method.[35] Na_{Zn} has also been found to trap localized holes,[55] supporting the fact that Group-I impurities substituting on the cation site are polaronic acceptors in ZnO.

Overall, due to the atomic-like behavior of anion-site acceptors and the polaronic behavior of cation-site acceptors, there may not be any viable candidates for substitutional *p*-type dopants in ZnO.

VI. CONCLUSIONS

We have investigated the difficulties of *p*-type doping of wide-band-gap semiconductors, and found the cause to be the tendency for hole localization. The energetically deep nature of the valence bands and heavy hole masses lead to hole localization, which occurs in two distinct ways. Anion-site impurities are atomic-like deep acceptors that give rise to defect states within the semiconductor band gap, even in the negative charge state of the acceptor. Cation-site impurities are polaronic acceptors that bind a highly localized hole on a nearest-neighbor anion. In both cases, the net result is a significant increase in the position of the (0/−) charge-state transition level, i.e., a large ionization energy. For AlN and ZnO, all substitutional acceptors exhibit this behavior and have large ionization energies. In GaN, all acceptors exhibit this behavior as well, but polaronic Mg_{Ga} has a small enough ionization energy to give rise to concentrations of free holes that are large enough for device applications. InN is the one material in which we find true effective-mass behavior for a cation-site acceptor (Mg_{In}); other acceptors are still deep.

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