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Group-II acceptors in wurtzite AlN: A screened hybrid density functional study

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We systematically studied the group-II acceptors in wurtzite AlN by screened hybrid density functional calculations. We show that the shallowest isolated group-II substitutional defect is Mg, while codoping of Mg and O may yield even shallower acceptor level. © 2010 American Institute of Physics. [doi:10.1063/1.3429086]

Wide gap semiconductors such as diamond and group-III nitrides are promising candidates for fabricating ultraviolet light-emitting diodes (LEDs), which could replace gas lasers and mercury lamps in many applications—like biomedicine, air and water purification, and disinfection—where the use of existing light sources are limited due to their low efficiency, large size, and toxicities.^{1–5} AlN is a leading candidate in high density optical data storage, high-resolution photolithography, and other LED applications operating in the (deep) UV region.^{6,7} It has the widest direct gap ($E_g = 6.2$ eV) among the group-III nitrides.

While the shortest wavelength (210 nm) light emitter diode has been already demonstrated made from Si and Mg doped AlN further effort is still needed to improve the properties of AlN LEDs due to their low quantum efficiency.⁸ For practical applications, a hole concentration of at least 10^{18} cm⁻³ is required, while the highest achieved value was about 10^{12} cm⁻³ at room temperature in Mg-doped AlN.⁸ Since the ratio of carrier concentration to impurity concentration follows $\exp(-E_A/k_B T)$ —where E_A is the thermal ionization energy of the acceptor, k_B is the Boltzmann constant, and T is the temperature—the main challenge is to find a more appropriate dopant with significant lower thermal ionization energy than for Mg which is about 0.5 eV.^{9,10}

Recently, density functional theory (DFT)-based studies have been published in this topic.^{11–14} Wu *et al.*¹² claimed based on a DFT study with local functionals that beryllium (Be) substituting Al site is a more efficient acceptor than Mg. The calculated ionization energy ($E_A = 0.34$ eV) is in good agreement with a previous calculation based on effective mass theory.¹⁵ A recent photoluminescence (PL) study on Be-doped AlN has supported this conclusion.¹⁶ Wu *et al.*¹³ also carried out calculations on Mg_x-O(x=2,3,4) complexes, and they found their ionization energies to be even lower (≈ 0.17 – 0.12 eV) than for Be.

These calculations were performed in relatively small (72-atom) supercell and they applied traditional (semi)local functionals, like local density approximation (LDA) or a type of generalized gradient approximation (GGA). The accurate calculations of shallow acceptor states require (i) larger supercell, (ii) nonlocal functionals that may compensate the self-interaction error in semilocal functionals at large extent. We note that a recent non-local screened hybrid functional

study has shown that LDA/GGA may fail to describe well the acceptor states in wide band-gap semiconductors.¹⁷ Based on these considerations the reinvestigation of group-II acceptors in AlN is highly desirable.

We systematically studied the group-II acceptors in wurtzite AlN by means of screened hybrid density functional calculations in a large supercell. In this Letter we show that among the group-II substitutional defects, Mg is the shallowest acceptor ($E_A = 0.5$ eV). We found that only the Mg–O–Mg complex has shallower acceptor level, at about $E_{VBM} + 0.34$ eV, where E_{VBM} is the valence band maximum. Particularly, we show that Be has high ionization energy (≈ 0.97 eV). We propose that the interpretation of the Be-related PL measurements claimed in Ref. 16 should be revised.

We utilized the VASP code for the calculations on a $6 \times 6 \times 3$ supercell containing 432 atoms, constructed from the optimized wurtzite AlN primitive cell. The lattice vectors of the supercell were kept fixed in the defect calculations. We sampled the Brillouin zone in the Γ point which resulted in convergent charge density in the large supercell and allowed us to monitor the degeneracy of the valence band states. The ion-electron interaction was described by the projector augmentation wave method.^{18,19} We applied the PBE (Ref. 20) exchange-correlation functional in geometry optimization. The HSE06 functional^{21,22} reproduces well the band gap²³ and defect levels^{24,25} in semiconductors, thus HSE06 screened hybrid functional was applied for band-structure calculations at fixed geometry as obtained from the PBE calculation. The electronic wave function was expanded in plane waves with a cutoff of 420 eV. In the geometry optimization, the maximum force was less than 0.01 eV/Å on every atom. The adiabatic (thermal) ionization energies were then calculated as the difference of the total energies of the negatively charged ($E_D^{(-1)}$) and neutral ($E_D^{(0)}$) defective supercells, then subtracting the VBM calculated in the perfect supercell (E_{VBM}), plus two correction terms as follows:

$$E_A = E_D^{(-1)} - E_D^{(0)} - E_{VBM} + \frac{1}{3} \frac{\alpha}{\epsilon L} + \Delta V_{av},$$

where α is the Madelung constant of the lattice, ϵ is the average dielectric constant of AlN,²⁶ L is the (average) lattice constant of the supercell, and ΔV_{av} is the shift in the average potential between the charged and neutral defective supercells. The first correction term is for considering the self-

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TABLE I. The calculated adiabatic ionization energies (E_A) and bond lengths [as shown on Fig. 1(a)] of the substitutional defects with the HSE06 functional. The experimental value for Mg is known to be 0.51 eV (Refs. 9 and 10).

Defect type	E_A (eV)	d_1 (Å)	d_2 (Å)
Be _{Al}	0.97	1.74	2.40
Mg _{Al}	0.50	2.03	2.10
Ca _{Al}	1.21	2.21	2.26
Sr _{Al}	1.46	2.31	2.37
Ba _{Al}	1.66	2.42	2.49
Mg _{Al} -O _N -Mg _{Al}	0.34

interaction of a point charge in a periodic system. It was shown that about the 2/3 of the leading term in Makov-Payne correction²⁷ yields a good approximation.²⁸ In our supercell, this value is 0.09 eV for single negatively charged defects. The second correction term is for aligning the average electrostatic potentials of the charged and neutral defective supercells. In our calculations this value varied between 0.01 and 0.05 eV. Finally, we note that our calculations are strictly valid at $T=0$ K limit as we basically apply the Born-Oppenheimer approximation.

First, we investigated the Al substitutional defects with the following group-II elements: Be, Mg, Ca, Sr, and Ba. The calculated ionization energies are 0.97 eV (Be), 0.5 eV (Mg), 1.21 eV (Ca), 1.46 eV (Sr), and 1.66 eV (Ba). We also carried out calculations on the Mg-O-Mg complex, and its calculated ionization energy is 0.34 eV. The results are collected in Table I. The relaxed geometries of the defects are shown in Fig. 1.

We analyze the Mg_{Al} defect first. The calculated ionization energy (0.5 eV) fits very well the experimental value (0.51 eV), that suggests the HSE06 functional describes the investigated system well. Figure 2 shows the acceptor state of Mg. Apparently it is an effective mass state consisting of

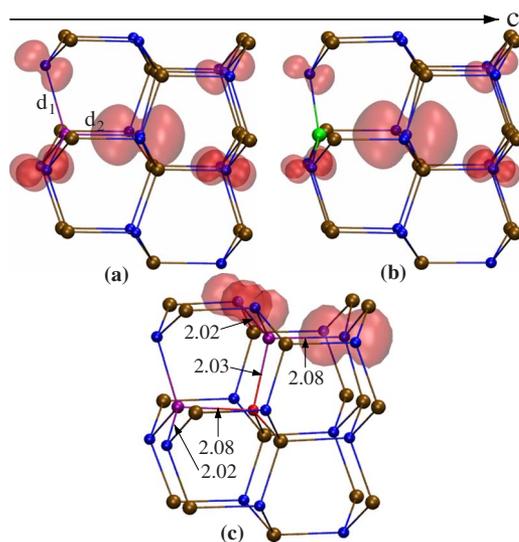


FIG. 1. (Color online) The relaxed geometry of the (a) Mg, (b) Be, and (c) Mg-O-Mg defects. The atom types are represented by colored balls. Yellow: Al; blue: N; purple: Mg; green: Be; and red: O. The other investigated single substitutional defects have the same characteristics as Mg, by differing only in their bond lengths labeled as d_1 and d_2 . Their values are listed in Table I. The distance between Be and its nearest neighbor N along c-axis (d_2) is large, and a dangling bond forms on this N atom.

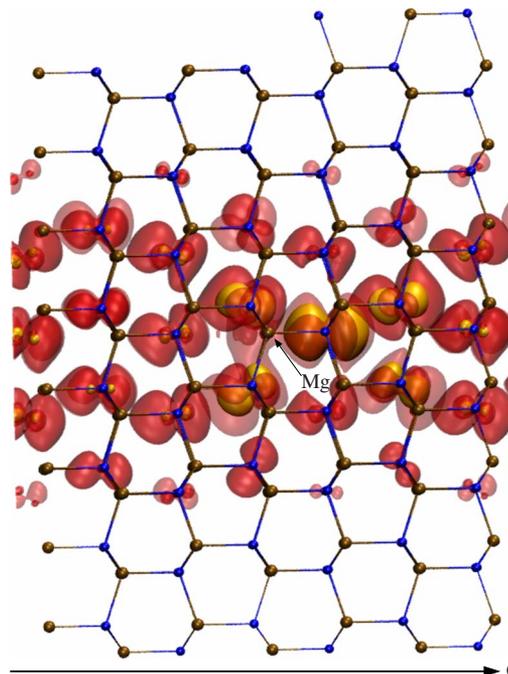


FIG. 2. (Color online) The isosurface of the acceptor state of the neutral Mg_{Al} defect in the 432-atom supercell. The yellow color shows the isosurface value at $1/\Omega$, while red color shows a higher value, where Ω is the volume of the supercell. The yellow isosurface corresponds to the value of homogeneously delocalized state.

the valence states localized exclusively on N atoms. The anisotropic distribution of the acceptor state is due to the anisotropic dielectric constants of wurtzite AlN (Ref. 29) that screen the interactions of the effective mass state less along the c-direction than in the basal plane. The delocalization of the state explains the need of such a large supercell for the calculations. Although our cell is convergent in the basal plane, the delocalization would justify even larger lattice constant along the c-direction but considering the fast growing computational time with increasing size of the supercell, our chosen supercell seemed to be a reasonable compromise. We found that the valence band state in the Γ -point splits to e and a_1 level where the hole occurs at a_1 level, thus the defective supercell preserves the C_{3v} symmetry. Figure 1(a) shows the relaxed geometry around the defect where two characteristic bond lengths occur due to the high symmetry of the defect. The bond along c-axis is labeled as d_2 while out of c-axis bonds are labeled as d_1 . In our perfect supercell the Al-N bond length is about 1.9 Å, which is slightly elongated if Al is substituted by Mg resulting in Mg-N bond lengths of about 2.1 Å. This is relatively small relaxation which is typical for a shallow effective mass acceptor.

The nice agreement between theory and experiment on Mg substitutional defect allowed us to study the less known defects in AlN. Next, we considered Be substitutional defect. The calculated ionization energy of Be is 0.97 eV that is significantly higher than that of Mg, while previous studies claimed it is a shallower acceptor.^{12,15,16} In our large supercell, PBE functional calculations indeed predicts shallow ionization energy for Be just like for Mg ($E_A \approx 0.25$ eV). However, the self-interaction error of (semi)local functionals (like PBE) is severe for Be substitutional which contains a well-localized dangling bond in contrast to other defects considered in this study. Our HSE06 calculations show that Be is

a deep acceptor in AlN. We checked this result including full relaxation with HSE06 functional, and the result differs only by 0.01 eV compared to the result at a geometry obtained from PBE calculations; it is a minor change. Figure 1(b) shows the relaxed geometry of the defect. The distance between Be and its first neighbor N along the *c*-direction (2.4 Å) is larger than in the case of Mg (2.1 Å), and considering that Be is even a smaller atom than Mg that leads to a frustrated bonding situation. That N-atom will have a dangling bond [see Fig. 1(b)] and Be is not a typical effective mass acceptor for this reason. A recent PL study on Be-doped AlN concluded that Be is a shallow acceptor in AlN.¹⁶ In this PL study the binding energy of the exciton bound to a Be-related defect is measured directly in AlN where the defect was associated with the substitutional Be. By assuming an effective mass state for Be defect they applied the Haynes' rule to derive the ionization energy of the Be acceptor from the measured exciton binding energy and they arrived at a shallow acceptor level at about 0.3 eV.¹⁶ While our calculations cannot entirely exclude that Be-related shallow acceptor level might exist in AlN but we definitely showed that Be substitutional is not an effective masslike shallow acceptor. Further experimental investigation is needed to resolve this puzzling contradiction; we speculate that the interpretation of the PL signal may be revisited.

Next, we studied the other group-II elements in AlN. For the Ca, Sr, and Ba substitutional defects we found an increasing bond length along the *c*-axis (2.26 Å, 2.37 Å, and 2.49 Å, respectively) together with increasing ionization energies (1.21, 1.46, and 1.66 eV). All these group-II defects show very similar effective masslike defect states. According to our calculations, Mg element fits the best at Al-site in AlN from structural point of view with making Mg the shallowest effective mass acceptor among the group-II elements.

We also investigated the Mg–O–Mg complex that was predicted to be a shallow acceptor in AlN based on semilocal DFT calculation.¹³ The common neighbor oxygen atom of the two Mg atoms shortens the bonds between Mg and N atoms in the host AlN crystal [see Figs. 1(a) and 1(c) with Table I]. We found that Mg–O–Mg complex is indeed a relatively shallow defect. The calculated ionization energy is 0.34 eV with HSE06 functional which is higher than 0.17 eV obtained in Ref. 13 by DFT-LDA, but we still can confirm their conclusion, that codoping of Mg and O may lead to shallower acceptor level than that from Mg-doping in AlN.

Finally, we note that while the HSE06 functional greatly improves the band gap of AlN (5.4 eV) compared to PBE calculations (4.0 eV), still HSE06 underestimates the fundamental band gap. Recent theoretical studies have shown^{30,31} that HSE06 should rather reproduce the optical gap where screening is responsible to mimic the excitonic effect. The binding energy of the free exciton in wurtzite AlN is less than 0.1 eV, so the optical and fundamental band gaps are within 0.1 eV.³² We found that by varying the screening parameter in the HSE functional to 0.05 from 0.2 1/Å we reproduce the experimental band gap at 0 K but the ionization energies of acceptors also shift up by about 0.25 eV *independently* of the defect. This would indicate a slight deviation between the calculated and measured thermal ionization energies for Mg defect. However, we note that the temperature dependence of the band gap of AlN is considerable and it is reduced by about 0.2 eV between 0 K and room

temperature³³ that would also reduce the calculated thermal ionization energies of the acceptors at the measurement temperatures compared to those at 0 K where our simulation is valid. All in all, we believe that our main conclusion still holds the following: (i) Be is a deep acceptor, (ii) Mg is the shallowest acceptor among the isolated substitutional group-II defects, and (iii) Mg–O–Mg is shallower acceptor than Mg.

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