Understanding band alignments in semiconductor heterostructures: Composition dependence and type-I–type-II transition of natural band offsets in nonpolar zinc-blende $Al_xGa_{1-x}N/Al_yGa_{1-y}N$ composites

M. Landmann, E. Rauls, and W. G. Schmidt

Theoretische Physik, Universität Paderborn, Warburger Strasse 100, D-33098, Germany (Received 24 January 2017; revised manuscript received 15 March 2017; published 12 April 2017)

The composition dependence of the natural band alignment at nonpolar $Al_x Ga_{1-x}N/Al_y Ga_{1-y}N$ heterojunctions is investigated via hybrid functional based density functional theory. Accurate band-gap data are provided using Heyd-Scuseria-Ernzerhof (HSE) type hybrid functionals with a composition dependent exact-exchange contribution. The unstrained band alignment between zincblende (*zb*) $Al_x Ga_{1-x}N$ semiconductor alloys is studied within the entire ternary composition range utilizing the Branch-point technique to align the energy levels related to the bulklike direct $\Gamma_v \rightarrow \Gamma_c$ and indirect, *pseudodirect*, respectively, $\Gamma_v \rightarrow X_c$ type transitions in *zb*- $Al_x Ga_{1-x}N$. While the *zb*- $GaN/Al_x Ga_{1-x}N$ band edges consistently show a type-I alignment, the relative position of fundamental band edges changes to a type-II alignment in the Al-rich composition ranges of *zb*- $Al_x Ga_{1-x}N/AlN$ and *zb*- $Al_x Ga_{1-x}N$ semiconductor alloys gives rise to a notably different composition dependence of band discontinuities in the direct and indirect energy-gap ranges. Below the critical direct-indirect Al/Ga-crossover concentration, the band offsets show a close to linear dependence on the alloy composition. In contrast, notable bowing characteristics of all band discontinuities are observed above the critical crossover composition.

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I. INTRODUCTION

In the recent past substantial breakthroughs in group-III nitride (AlN, GaN, and InN) based materials science have advanced design and fabrication of optoelectronic devices as diodes [1,2], transistors [3–6], catalysts [7,8], or sensors [9,10] from fundamental research to commercial distribution. Group-III nitrides naturally crystallize as stable hexagonal (hex) crystals in a polar wurtzite (wz) structure belonging to space group $P6_3mc$ (C_{6v}^4). Artificially grown, nonpolar group-III nitrides have been synthesized in a metastable cubic (c) phase with $F\overline{4}3m(T_d^2)$ symmetry zincblende (zb) structure as well as a $Fm\overline{3}m$ (O_h^5) symmetry rocksalt (rs) polytype at high pressure [11-13]. In addition to these conventional three-dimensional bulk phases, the recent interest in twodimensional materials also promoted substantial research on quasi-two-dimensional ultrathin film quantum structures of GaN [14] and led to quite recent preparation breakthroughs in the preparation of two-dimensional GaN via graphene encapsulation [15] promising the extension of group-III nitride-based optoelectronics, beyond two-dimensional BN [16], towards the regime of artificial two-dimensional van der Waals-type semiconductors. The hexagonal group-III nitrides AlN and GaN exhibit direct Brillouin-zone centered $\Gamma_v \rightarrow \Gamma_c$ band gaps of ~3.3 eV in wz-GaN [17,18] and ~6.0 eV in wz-AlN [19–21] at room temperature (300 K). The corresponding zero-temperature band gaps amount to \sim 3.5 eV for *wz*-GaN [17,18] and \sim 6.2 eV for *wz*-AlN [19]. The band gaps of the cubic analogs have been determined by room-temperature spectroscopic ellipsometry to 3.23 eV in zb-GaN [22] and 5.3 eV (indirect $\Gamma_v \rightarrow X_c$) [23,24] and 5.93 eV (direct $\Gamma_v \rightarrow \Gamma_c$) in *zb*-AlN [24]. A low temperature zb-GaN band gap of 3.293 eV was reported [22], while the low temperature zb-AlN band gap has been estimated to 5.997 eV assuming similar low-to-room-temperature (direct) band-gap differences in the polar and nonpolar phases [25].

The group-III nitride-based design of novel functional materials for optoelectronic devices as diodes, transistors, photodetectors, and sensors, and in particular solar cells, commonly involves the formation of small-scale multicomponent semiconductor complexes to exploit the material system's full technological potential beyond simple bulk-band gap engineering. Group-III nitride materials, especially, show beneficial material properties for utilization in intersubband devices working at both the near-infrared telecommunication wavelength regime as well as the far-infrared THz wavelength edge by exploiting electronic transitions between nanostructureconfined electronic states in single or multiple quantum well as well as quantum-dot heterostructures [26-29]. In any semiconductor heterostructure the alignment of electronic bands at built-in heterojunctions, by means of valence-band edge and conduction-band edge offsets, is crucial for the electron-transport dynamics and charge carrier confinement. Thereby, the large range of accessible band-gap energies in zb-Al_xGa_{1-x}N semiconductors translates into a broad range of valence band offsets (VBOs) and conduction band offsets (CBOs) that determine how the band-gap difference between the interfacing materials is distributed among valence and conduction band states and, thus, the fundamental heterojunction type with electron and hole wave-function confinement in either a common spatial region (type I-straddling gap) or different spatial regions (type II-staggered gap). Consequentially, a transition from a type-I to a type-II alignment of electronic states substantially impacts the optoelectronic properties of heterostructure devices. Especially, the chargecarrier separation in type-II aligned heteromaterials represents an appealing characteristic for *light harvesting* in high-efficient photovoltaic devices.

The determination of band discontinuities from *ab initio* calculations inevitably necessitates the alignment of energy levels of the respective interfacing semiconductor alloys to

a common energy reference. Common choices of universal alignment levels are the vacuum level following Anderson's electron-affinity rule [30], characteristic marker levels in the electronic structure (e.g., core-level energies) [31–35], microscopic and macroscopic averages of the (electrostatic) onsite potentials [36–38], or charge neutrality levels [39–41], branchpoint energies, respectively [42-44]. Band offsets derived from alignment to a *universal* reference point as the vacuum level or branch-point energies, without making reference to particular strain conditions of the involved materials, are termed natural or unstrained. The alignment of electronic states under particular strain conditions at the interfaces of *real* semiconductor heterostructures can be incorporated a posteriori via volume deformation potentials [45-48], which is the common modus operandi in numerically efficient simulation approaches relying on parametrized model theories. A more direct approach to strained band offsets is provided via the heterostructure-alignment approach. Thereby, the influence of lattice deformation through interfacial strain is directly incorporated via atomistic modeling of the involved interfaces within the supercell approach [36–38]. An extended overview on different alignment techniques and case study on natural and strained band offsets between nonpolar group-III nitrides will be published elsewhere [49]. In general, the *ab initio* calculation of band offsets via heterostructure alignment is computationally rather expensive due to the involved interface modeling. On the contrary, branch-point alignment allows an efficient treatment of the composition dependence of band offsets, even by computationally demanding hybrid functional DFT, due to the restriction to bulk calculations. Hence we rely on the branch-point approach to align the energy states of different zb-Al_xGa_{1-x}N semiconductor alloys. The natural valence and conduction band offsets ΔE_v^{bp} and ΔE_c^{bp} , derived via branch-point alignment, are intrinsically commutative and transitive, hence they satisfy $\Delta E_{v,c}^{bp}(A,B) = -\Delta E_{v,c}^{bp}(B,A)$ and $\Delta E_{v,c}^{bp}(A,C) = \Delta E_{v,c}^{bp}(A,B) + \Delta E_{v,c}^{bp}(B,C).$

Within the present study, we will focus on the less common nonpolar zincblende phases of Al_xGa_{1-x}N alloys, whose centrosymmetric crystal structure effectively prevents the technologically limiting emergence of polarization fields [6,27,50]. A key characteristic of the electronic structure and, thus, related physical properties of the nonpolar zb-Al_xGa_{1-x}N semiconductors, is the presence of a *direct-indirect* band-gap crossing around $x \approx 0.65$ in the fundamental alloy-energy gap [51]. This transition is related to the fact that, in contrast to the direct semiconductor zb-GaN, zb-AlN exhibits an indirect $\Gamma_c \rightarrow X_c$ fundamental band gap between the Γ -point valence-band maximum and global Brillouin-zone edge Xpoint minimum of the conduction band, which lies roughly 1 eV below the Γ -point conduction-band valley [51]. Similar composition dependent direct-indirect band-gap crossings are known for ternary Al containing (cubic) group-III arsenides and antimonides, as well as certain Ga containing (cubic) group-III phosphides [52–55]. Considering the alignment of electronic states to a common energy scale in order to extract the band discontinuities between two materials, material compositions, respectively, one might expect a similar transition becoming manifested in the natural conduction band offsets between different $zb-Al_xGa_{1-x}N$ materials at sufficiently high Al concentration. This direct-indirect transition inevitably leads to an alloy-characteristic composition dependence of conduction band offsets that discriminates between the *direct*, predominantly Ga-rich, and an *indirect* Al-rich composition regimes of zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N heterostructures. Examining the extraordinary role of group-III nitride heterostructure components, integrated into current state-of-the-art optoelectronic devices, a detailed understanding of the material-intrinsic band-alignment characteristics is indispensable for the optimization and enhancement of current generation devices, as well as future design of efficient and high-capacity heterostructure devices.

While manifold experimental and theoretical data on band offsets between the binary group-III nitrides has been reported in literature (e.g., see data review and discussion in Ref. [49]), literature data on band offsets in ternary nitride compounds and a detailed characterization of composition dependence is sparse. Using modulation spectroscopy and photoluminescence combined with deep-acceptor level alignment, Hang et al. [56] investigated the composition dependence of band offsets between wz-GaN and ternary wz-Al_xGa_{1-x}N using material samples in the composition range 0 < x < 0.22. Band-offset dependencies of $\Delta E_{\rm v}(wz$ -GaN/Al_xGa_{1-x}N) = $-0.45x - 2.57x^2 \pm 0.05x$ (eV) and $\Delta E_c(wz-\text{GaN}/\text{Al}_x\text{Ga}_{1-x}\text{N}) = 0.6x + 5.05x^2 \pm$ 0.03x (eV) were determined indicating an average conduction-to-valence band-offset ratio of 65:35. Most notable, both the valence and the conduction band offsets are characterized by a massive downward bowing. Therefore, straightforward extrapolation clearly leads to substantially biased band offsets in an Al-rich alloy regime. The origin of this overestimation of band-offset bowing features is traceable to the reported composition dependencies of the changes in the yellow shallow-donor-deep-acceptor level luminescence and the measured band-gap differences between wz-GaN and wz-Al_xGa_{1-x}N. Reddy *et al.* [57] comprehensively studied the band alignment at c-plane surfaces and interfaces of wz-AlGaN thin-film samples grown on c-plane sapphire and native single-crystalline wz-AlN substrates. The composition dependence of (natural) valence and conduction band offsets at polar wz-Al_xGa_{1-x}N/Al_yGa_{1-y}N interfaces has been estimated within the entire composition range from the measured charge-neutrality levels and the interface-induced gap-states model as well as Anderson's electron affinity rule to $\Delta E_v(wz\text{-Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}) \approx -|0.9(x-y)| \text{ (eV) and} \\ \Delta E_c(wz\text{-Al}_x\text{Ga}_{1-x}\text{N}/\text{Al}_y\text{Ga}_{1-y}\text{N}) \approx |x^2 - y^2 + 0.8(x-y)|$ (eV) indicating a linear composition dependence of the valence band offset but a nonlinear dependence of the conduction band offset characterized by an assumed bowing parameter of 1.0 eV. Thereby, the band gap difference at the group-III nitride interfaces with comparable Al and Ga concentrations is split approximately two-third to one-third between the conduction and valence band offsets. In the limiting material system wz-GaN/Al_xGa_{1-x}N the band-offset ratio is found to decrease with decreasing Al concentration reaching approximately a 50:50 ratio. Likewise, the band-offset ratio of wz-Al_xGa_{1-x}N/AlN increases with increasing Al concentration to an approximate ratio of 75:25. Wan et al. [58] determined a wz-GaN/Al_{0.17}Ga_{0.83}N valence band offset of -0.13 ± 0.07 (eV) from x-ray photoelectron spectroscopy forming a type-I band lineup together with the calculated conduction band offset of 0.22 ± 0.07 (eV). Both values roughly fall into line with the band-offset dependencies discussed above. Assuming a linear interpolation between the binary end components $\Delta E_{\rm v}(wz$ -GaN/Al_xGa_{1-x}N) = -0.8x (eV), Litvinov of et al. [59] calculated a (strained) conduction band offset of $\Delta E_{\rm c}(wz$ -GaN/Al_xGa_{1-x}N) $\approx 0.603x + 0.99x^2$ (eV)for wz-Al_xGa_{1-x}N layers pseudomorphically strained to wz-GaN. These composition trends are virtually identical to the Reddy et al. data. Bhouri and Lazzari [60] investigated the composition dependence of band offsets at strained and unstrained binary AN/BN as well as ternary $A_x B_{1-x} N/A_y$ $B_{1-v}N(A, B = Al, Ga, In)$ wz-group-III nitride heterojunctions from theoretical model calculations relying on parametric input. The wz-GaN/Al_xGa_{1-x}N heterojunctions were characterized as type-I heterostructures. The composition dependence of strained band offsets in wz-Al_xGa_{1-x}N/Al_y $Ga_{1-\nu}N$ was found to follow the analytical expressions ΔE_{ν} $(wz-Al_xGa_{1-x}N/Al_yGa_{1-y}N)=(x-y)[(0.5073x-0.8162)-$ (0.0228 + 0.0614x)(x + y)] (eV) and $\Delta E_c(wz-Al_xGa_{1-x})$ $N/Al_yGa_{1-y}N = (x - y)[(0.0034x + 1.116) + (0.6729 - 1.0034x)]$ (0.0371x)(x + y)] (eV). The unstrained band offsets in the binary system wz-GaN/AlN have been estimated as $\Delta E_{\rm v}(wz$ -GaN/AlN) ≈ 0.8 eV and $\Delta E_{\rm c}(wz$ -GaN/AlN) ≈ 2.0 eV which agrees well with the previous results. The comparison between the strained and unstrained cases indicated that the conduction band offset is less affected by interfacial strain, while the valence band offset behaves differently under tensile or compressive strain.

In summary, the reported experimental and theoretical band-offset data on the polar wz-Al_xGa_{1-x}N/Al_yGa_{1-y}N material system strongly indicate an almost linear dependence of the untrained (natural) valence band offset on the alloy composition. Thereby, the composition dependence of the valence band offset closely follows the linear change of measured charge-neutrality levels, the branch-point energy, respectively, in wz-Al_xGa_{1-x}N samples [57]. Besides, the conduction band offset, originating from direct electronic transitions located at the Brillouin-zone centers, shows a nonlinear composition.

In addition to investigations on the band-offset dependence on chemical composition, an order driven heterostructure-type transition was reported by Dudiy and Zunger [61]. This type-I-to-type-II transition occurs between random and ordered domains of wz-Al_xGa_{1-x}N at a composition parameter of $x \simeq 0.4$. The origin of the transition was found to be the hole confinement on Ga-rich monolayers which pushes the valence-band maximum of the ordered material below the valence-band maximum of the surrounding random alloy. A type-II alignment has also been reported by Belabbes *et al.* [62] for cubic *zb*-AlN inclusions in hexagonal *wz*-AlN on the basis of hybrid-functional DFT and $G_0 W_0$ quasiparticle theory based electronic structure simulations.

In contrast to the polar wurtzite phases, substantially less data have been reported on the composition dependence of band offsets between the nonpolar cubic polytypes. Wei *et al.* [63] used a combination of electron holography and

cathodoluminescence measurements to determine the strained band offsets in a zb-GaN/Al_{0.3}Ga_{0.7}N heterostructure grown on 3C-SiC substrate yielding valence and conduction band offsets of -0.13 and 0.65 eV, respectively, and a high conduction-to-valence band-offset ratio of 5:1. A smaller *zb*-GaN/Al_{0.3}Ga_{0.7}N band-offset ratio of $0.5/0.15 \approx 3.3$ was determined by Mourad [44] using branch-point alignment of empirical tight-binding band energies to determine unstrained natural band offsets. These values are slightly different from the previously discussed band offsets between the wurtzite-type group-III nitride analogs [57,60]. Especially, a different conduction-to-valence band-offset ratio is indicated for the cubic polytypes. Differences existing in the natural band offsets of the hexagonal and cubic group-III nitride material systems, despite common tetrahedral coordination, point towards the fundamental influence of symmetry related polarization fields on the band alignment, in general. Besides the predominantly reported type-I alignment between alloys on the Ga-rich composition side, a type-II band alignment with valence and conduction band offsets of -0.39 and -0.17 eV, was reported by Buongiorno Nardelli et al. [64] for a strained zb-Al_{0.5}Ga_{0.5}N/AlN (001) heterojunction from electronic structure theory. The possible formation of type-II aligned group-III nitride heterojunctions discriminates the hexagonal and cubic material systems, fundamentally.

The origin of infrequent experimental band-offset data is most likely related to the limited availability of high quality samples of cubic group-III nitrides in the entire composition range. However, present growth techniques allow for high quality growth of zb-Al_xGa_{1-x}N bulk semiconductors, thin films, and multiple quantum well heterostructures meeting the demands on phase purity and chemical composition which are necessary to extract fundamental alloy parameters not only for the binary but also the multicomponent nonpolar group-III nitride semiconductors [23,27,65-69]. Another complication in dealing with nonpolar group-III nitrides is the fundamentally indirect nature of the *zb*-AlN band gap. The *zb*-Al_xGa_{1-x}N alloy intrinsic indirect electronic-structure features at high Al content are difficult to detect in optical spectroscopy which is an essential component in the experimental process of band-offset determination.

Within the present study we utilize density functional theory based first-principles theory to investigate the composition dependence of natural band offsets in nonpolar zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N composites. To this purpose the present paper is organized as follows: Section II summarizes numerical and methodological details involved in the *ab initio* band-offset calculation via the branch-point alignment approach. Section III is used for presentation of numerical results and discussion of the character and the composition dependence of natural band discontinuities in nonpolar zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N materials. Finally, Sec. IV summarizes the present study and highlights essential results.

We expect that the detailed quantitative and qualitative understanding of natural band offsets in nonpolar group-III nitride systems as zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N provides a useful orientation guide to future utilization and optimization of optoelectronics devices based on this promising class of materials.

II. METHODOLOGY

The present calculations are performed using density functional theory (DFT) within the generalized gradient approximation (GGA) to the electron exchange and correlation (XC) interaction as well as using hybrid XC functionals. Specifically, the Perdew-Becke-Ernzerhof (PBE) [70] GGA functional and Heyd-Scuseria-Ernzerhof (HSE) type [71-74] hybrid functionals were used for structural relaxations and electronic structure calculations, respectively. In the latter, the fraction of exact exchange (EXX) from Hartree-Fock theory, 25% in the conventional HSE03/HSE06 functionals, was increased to match the experimentally observed band gaps as well as to reproduce features of the GW quasiparticle band structure [51]. EXX adjusted HSE-type hybrid functionals, henceforward referred to as HSEmod, provide an efficient way to approximate more rigorous band-structure calculation schemes within the framework of Greens function based quasiparticle theory, thus, effectively overcome limitations due to the so called *band-gap problem* [75-79] existing in conventional (semi)local XC-functional-based DFT. In detail, EXX fractions of 30% and 36% have been used for the limiting binary components zb-GaN and zb-AlN, respectively [80]. The EXX fractions for hybrid-functional calculations on ternary zb-Al_xGa_{1-x}N have been interpolated linearly. The accurate description of band discontinuities via EXX adjusted HSE-type functionals has been demonstrated for several group III-V semiconductor heterostructures [81].

All calculations were performed using the Vienna *ab initio* simulation package (VASP) [82,83]. The electron-ion interaction is described by the projector-augmented wave (PAW) scheme [83,84], where the Ga_{3d} semicore electrons are treated as valence states. The electronic wave functions are expanded into plane waves up to a kinetic energy cutoff of 400 eV. The Brillouin zone integration is performed using regular Γ -centered meshes with a **k**-point density of 2 × 2 × 2.

The ternary zb-Al_xGa_{1-x}N alloys are modeled by cubic 64 atom unit cells and random distributions of Ga and Al ions in the cation sublattice. As demonstrated previously, see Ref. [51], this unit-cell setup sufficiently reduces finite-size periodicity errors originating from the enforced artificial alloy periodicity. The calculations are performed at the experimental lattice parameters of 4.503 Å for zb-GaN [85] and 4.373 Å for *zb*-AlN [68]. The lattice constants of ternary *zb*-Al_{*x*}Ga_{1-*x*}N alloys have been interpolated linearly between the binary compounds in terms of Vegard's law. The validity of Vegard's law for group-III nitride alloys has been confirmed experimentally for polar wz-Al_xGa_{1-x}N [86] as well as theoretically for nonpolar zb-Al_xGa_{1-x}N [66] in several studies on group-III nitride-semiconductor alloys [87-89]. All atomic positions were relaxed on the DFT-PBE level of theory until the forces on each atom were less then 0.01 meV/Å.

The band-edge positions are extracted by averaging the bulk-degenerate Γ_v valence-band and X_c conduction-band manifolds which are splitted in the ternary materials due to local fluctuations in the alloy compositions. In order to estimate the band discontinuities, the valence and conduction band edges are aligned according to the branch-point energies of the semiconducting systems which are commonly believed to represent a universal energy reference point. In detail, we rely on the Brillouin zone averaging technique over

valence and conduction band states proposed by Schleife *et al.* [42] to approximate the natural band discontinuities in zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N over the entire composition range [42,90]. Following this approach, the branch-point energy E_{bp} of a semiconducting system is approximated as

$$E_{\rm bp} \approx \frac{1}{2N_{\rm k}} \sum_{\mathbf{k}} \left[\frac{1}{N_{\rm vb}} \sum_{i}^{N_{\rm vb}} \varepsilon_{\rm v_i}(\mathbf{k}) + \frac{1}{N_{\rm cb}} \sum_{j}^{N_{\rm cb}} \varepsilon_{\rm c_j}(\mathbf{k}) \right], \quad (1)$$

where N_k is the number of **k** points used to sample the Brillouin zone and $\varepsilon_{v_i}(\mathbf{k})$ and $\varepsilon_{c_i}(\mathbf{k})$ are the *i*th highest and *j*th lowest valence and conduction band states at wave vector **k**, respectively. Commonly, inclusion of the two highest valence bands and the lowest conduction band allows a reasonable estimation of branch point energies in case of the primitive two-atom unit cells of binary zincblende semiconductors [42,90]. Variations in the number of electronic bands, included in the branch-point evaluation, tend to shift the branch point energies uniformly while roughly preserving the alignment characteristics [91]. Here the 64 highest valence and 32 lowest conduction states are included in the evaluation of branch-point energies for the 64 atom unit cells of zb-Al_xGa_{1-x}N [92]. The mean absolute error of branch-point aligned band offsets has been estimated by Hinuma *et al.* as ~ 0.1 eV for a broad selection of zincblende semiconductors [91].

Throughout the present paper the following sign convention is used for all band offsets. All band offsets are given relative to the valence band edge of the particular small-gap material. Hence, all valence band offsets are negative while the conduction band offsets are either positive or negative, with the sign discriminating between a type-I (positive CBO) or a type-II energy-level alignment (negative CBO). The sign convention is also consistently applied to cited literature data in order to maintain consistent data throughout the entire paper. Analog to the determination of band-gap bowing characteristics, the composition dependencies of band offsets between zb-Al_xGa_{1-x}N and the binary end compositions zb-GaN and zb-AlN are fitted to a second order polynomial via

$$\Delta E_{v,c}^{bp}(A_x B_{1-x}/A, B) = A + B x + C x^2$$

$$\equiv \Delta E_{v,c}^{bp}(A, B) x - b_{v,c}^{bp} x(1-x) + \Delta E_{v,c}^{bp}(A_x B_{1-x})(1-x), \quad (2)$$

where $A_x B_{1-x}$ is the composition dependent ternary alloy and A and B are the respective binary end semiconductors. The fitting parameters are related according to $A \equiv \Delta E_{v,c}^{bp}(A_x B_{1-x}), B \equiv [\Delta E_{v,c}^{bp}(A,B) - b_{v,c}^{bp} - \Delta E_{v,c}^{bp}(A_x B_{1-x})],$ and $C \equiv b_{v,c}^{bp}$. The parameter $b_{v,c}^{bp}$ represent chemical (dis)order induced deviations from a linear Vegard's-law-type composition dependence of physical material parameters in multicomponent solid solutions. b_v^{bp} and b_c^{bp} indicate a *so called* downward bowing in case of $b_{v,c}^{bp} > 0$ and an upward bowing in case of $b_{v,c}^{bp} < 0$.



FIG. 1. DFT-HSEmod valence and conduction-edge diagram of zb-Al_xGa_{1-x}N. Both the conduction states related to the lowest bulklike Γ_c -type energy levels (solid lines) as well as the conduction states related to the lowest bulklike X_c -type energy levels (dashed lines) are indicated. The given numbers indicate the positions of energy levels aligned relative to their branch-point energies (zero point of energy scale) and gray numbers are the fundamental energy gaps of the alloys. Regions of direct and indirect fundamental alloy-energy gaps are indicated.

III. RESULTS AND DISCUSSION

A. A short recap on energy gaps

Before we turn to the band-offset characteristics of zb- $Al_xGa_{1-x}N/Al_yGa_{1-y}N$, we briefly recapitulate the fundamental nature of the electronic band gap in zb-Al_xGa_{1-x}N. Fundamental electronic band gaps of 3.28 eV (direct, $\Gamma_v \rightarrow$ $\Gamma_{\rm c}$) and 5.12 eV (indirect, $\Gamma_{\rm v} \rightarrow X_{\rm c}$) have been found in the binary end semiconductors zb-GaN and zb-AlN using exact exchange adjusted hybrid functionals of the HSE type. The corresponding indirect, direct, respectively, transition energies are 4.70 eV for the indirect $\Gamma_v \rightarrow X_c$ band gap of *zb*-GaN and 6.16 eV for the direct $\Gamma_v \rightarrow \Gamma_c$ band gap of *zb*-AlN. In the ternary zb-Al_xGa_{1-x}N alloys the composition dependence of the direct $(\Gamma_v \rightarrow \Gamma_c)$ -type energy gap is fitted according to $E_{\text{gap}}^{\text{dir}}(zb\text{-Al}_x\text{Ga}_{1-x}\text{N}) = 6.16x - 0.50x(1-x) + 3.28(1-x)$ (eV). The composition dependence of the indirect ($\Gamma_v \rightarrow X_c$)-type band gap reads $E_{gap}^{ind}(zb-Al_xGa_{1-x}N) =$ 5.12x + 0.04x(1 - x) + 4.70(1 - x) (eV). The fundamental alloy-energy gap of nonpolar zb-Al_xGa_{1-x}N exhibits a distinct transition between these direct ($\Gamma_v \rightarrow \Gamma_c$)-type and indirect $(\Gamma_v \rightarrow X_c)$ -type energy gaps occurring at a critical aluminum content of $x_c = 0.63$. Hence, the fundamental energy gap of zb-Al_xGa_{1-x}N increases with a moderate downward bowing of $b_{\Gamma} = 0.50 \text{ eV}$ for $0 \leq x < 0.63$, changes nonmonotonically at the crossover composition $x_c = 0.63$, and progresses virtually linear with $b_X = -0.04$ eV at high Al concentrations (0.63 > $x \leq 0.63$). The calculated band gaps, branch-point aligned band-edge energies, as well as direct and indirect energy-gap regions are illustrated in Fig. 1.

While most *ab initio* studies on multicomponent semiconductor alloys focus on details of the fundamental energy gaps, only a few studies dedicated the same level of accuracy to investigate the composition dependence of the fundamental alloy band offsets. Similar experiments profiling the entire composition dependence of an alloy's band-offset profile are rare either to limited availability of high quality samples in the entire composition ranges or technical limitations of the experimental setup. By way of example, a thorough experimental study on band offsets has, recently, been conducted by Yi *et al.* [53] on the composition dependence of ternary (AlGaAs) and quaternary (AlGaInP) semiconductor alloys.

B. Band offsets between nonpolar *zb*-Al_{*x*}Ga_{1-*x*}N semiconductor alloys

The intermixed unoccupied Γ_c -type and X_c -type electronic states, responsible for the fundamental band gaps of the binary composition ends, not only give rise to a direct-indirect crossover but also four possible alignment types of unoccupied bands and conduction band offsets, respectively, at zb-Al_xGa_{1-x}N heterojunctions. In detail, direct-direct ($\Gamma_c \rightarrow \Gamma_c$)-type, direct-indirect ($\Gamma_c \rightarrow X_c$)-type, indirect-direct $(X_c \rightarrow \Gamma_c)$ -type, and indirect-indirect $(X_c \rightarrow$ $X_{\rm c}$)-type conduction band offsets can be determined. Depending on the alloy composition (and strain conditions) a proper subset of these offsets will form the fundamental conduction band offset. In order to elucidate the fundamental character of the band offsets between nonpolar zb-Al_xGa_{1-x}N semiconductor alloys, the composition dependence of all offset types is analyzed in detail. The natural band offsets at the binary/ternary group-III nitride heterojunctions *zb*-GaN/Al_xGa_{1-x}N and *zb*-Al_xGa_{1-x}N/AlN are presented in Fig. 2 while the full ternary/ternary composition dependence is considered in Figs. 3 and 4.

The composition dependence of all ternary/binary offsets has been fitted to a second order polynomial [cf. Eq. (2)] across the entire composition range of the ternary zb-Al_xGa_{1-x}N component yielding the bowing parameters b. However, the obtained band offsets point to a characteristic composition dependence of all involved band offsets, which clearly discriminates the composition regimes below and above the critical direct-indirect crossing at $x_c = 0.63$. Separate fitting in the predominantly Ga-rich composition regime $0 \le x \le 0.63$ and the Al-rich composition regime $0.63 \le x \le 1$ indicate a transition from a more linear dependence on composition to a considerably nonlinear dependence in the natural valence as well as conduction band offsets of both *zb*-GaN/Al_xGa_{1-x}N and $zb-Al_xGa_{1-x}N/AlN$. The band-offset bowing parameter $b_{\rm dir}$ in the direct, predominantly Ga-rich, regime does not go above an absolute value of 0.29 eV while the bowing parameter in the Al-rich regime does not fall below 1.22 eV. The degree of nonlinearity, indicated by the global bowing parameter b, falls in between b_{dir} and b_{ind} in most cases (see Table I). The natural band-offset bowing parameters b, b_{dir} , and b_{ind} are summarized in Table I for the zb-GaN/Al_xGa_{1-x}N



FIG. 2. Composition dependence of branch-point aligned DFT-HSEmod natural valence band offsets ΔE_v^{bp} and conduction band offsets ΔE_c^{bp} between (a) *zb*-GaN and *zb*-Al_xGa_{1-x}N and (b) *zb*-Al_xGa_{1-x}N and *zb*-AlN. In detail, the direct-direct ($\Gamma_c \rightarrow \Gamma_c$)-type, direct-indirect ($\Gamma_c \rightarrow X_c$)-type, indirect-direct ($X_c \rightarrow \Gamma_c$)-type, and indirect-indirect ($X_c \rightarrow X_c$)-type conduction band offsets are illustrated. The solid colored offsets represent the fundamental natural conduction band offsets in the *zb*-GaN/Al_xGa_{1-x}N and *zb*-Al_xGa_{1-x}N/AlN systems. All band offsets are given in eV. For *zb*-GaN/Al_xGa_{1-x}N the direct-indirect crossover of the conduction band offset is indicated. Sign change in the *zb*-Al_xGa_{1-x}N/AlN conduction band offsets indicates the transition from a type-I to a type-II energy-level alignment. The composition dependence of band offsets is fitted separately to Eq. (2) below and above the direct-indirect crossover. The particular bowing parameters are given. The lower panels show the conduction-to-valence band-offset quotient $\Delta E_c^{bp}/\Delta E_v^{bp}$ calculated from the fitted band-offset curves.

and zb-Al_xGa_{1-x}N/AlN systems. An overview of fitting parameters, used to illustrate the composition dependencies in Fig. 2, is provided in Table II. Moreover, the different bowing features in the direct and indirect alloy regimes are well reproduced by data fitting to a conventional fifth order polynomial of the form $y = A_0 + A_1 x + A_2 x^2 + A_3 x^3 + A_4 x^4 + A_5 x^5$. The corresponding fitting parameters are provided in Table III for the binary/ternary systems. According to this, the two-dimensional composition dependencies of ternary/ternary zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N band offsets are fitted to a two-dimensional fifth order polynomial of the form $z = z_0 + A_1 x + A_2 x^2 + A_3 x^3 + A_4 x^4 + A_5 x^5 + B_1 y + B_2 y^2 + B_3 y^3 + B_4 y^4 + B_5 y^5$ (see Figs. 3 and 4 and parameter list Table IV).

Subsequently, we discuss the respective composition dependencies in detail.

1. zb-GaN/Al_xGa_{1-x}N

The natural valence band alignment of *zb*-GaN/Al_xGa_{1-x}N [cf. Fig. 2(a)] increases, according to an amount, with a minor downward bowing of $b_{dir} = 0.16$ eV in the direct gap regime. The valence band offset decreases further in the Al-rich regime with an enhanced downward bowing of $b_{ind} = 1.22$ eV and reaches maximum of -1.04 eV for valence-band alignment

between the binary end semiconductors *zb*-GaN and *zb*-AlN. The overall monotonic valence band-offset dependence on allov composition can be attributed to the fact that the valence-band extrema are located at the Brillouin-zone centers in both zb-GaN as well as zb-AlN and, hence, within all ternary alloys. The fundamental conduction band offset in *zb*-GaN/Al_xGa_{1-x}N is determined by the alignment of the $\Gamma_{\rm c}$ -type conduction band minima below $x_{\rm c} = 0.63$. The Al $X_{\rm c}$ -type conduction state minima, lowering in energy with increasing alloy composition, determines the fundamental conduction band offsets in the Al-rich composition range. Hence, the fundamental conduction band offset exhibits a distinct maximum marking the direct-indirect transition. Analog to the valence band offset, the bowing characteristics of all considered conduction band offsets are substantially enhanced beyond the direct-indirect crossover composition.

In detail, the direct-direct ($\Gamma_c \rightarrow \Gamma_c$)-type conduction band offset, representing the fundamental *zb*-GaN/Al_xGa_{1-x}N conduction band offset in the composition range from $0 \le x \le 0.63$, increases from zero to 1.05 eV with a moderate downward bowing of $b_{dir} = 0.29$ eV. Above x_c , the downward bowing is much more pronounced ($b_{ind} = 2.16$ eV) and the direct-direct conduction band offset grow to 1.84 eV across the Al-rich composition range. The direct-indirect



FIG. 3. (a) and (b) Three-dimensional illustrations of the two-dimensional x, y-composition dependence of branch-point aligned DFT-HSEmod natural valence band offsets ΔE_v^{bp} and conduction band offsets ΔE_c^{bp} in zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N. (c)–(e) Two-dimensional contour plots of the zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N valence band offset, the conduction-to-valence band-offset quotient $\Delta E_c^{bp}/\Delta E_v^{bp}$, the $|\Delta E_c^{bp}|$: $|\Delta E_v^{bp}|$ ratio, respectively, and the conduction band offset. Isovalue lines of the band-offset quotient as well as boundary lines between direct and indirect composition regimes (dashed white lines) and type-I–type-II alloy composition regimes (solid white line) are highlighted.

 $(\Gamma_c \rightarrow X_c)$ -type conduction band offset decreases continuously from 1.41 eV in *zb*-GaN to 1.06 eV at the crossover concentration. The fundamental direct-indirect conduction offset branch decreases to 0.81 eV in *zb*-AlN with an intermediate downward bowing of $b_{ind} = 1.25$ eV.

Since the fundamental band offsets do not change their sign upon alloy composition, the band-edge alignments

between *zb*-GaN and *zb*-Al_{*x*}Ga_{1-*x*}N exclusively form type-I aligned heterojunctions, whose composition dependence is characterized by two distinct bowing parameters indicating downward bowing throughout the entire composition range. The conduction-to-valence band ratio of the fundamental *zb*-GaN/Al_{*x*}Ga_{1-*x*}N band offsets, illustrated in the lowest panel of Fig. 2, illustrates the changes in basic material



FIG. 4. Three-dimensional representations of the two-dimensional x, y-composition dependence of direct-direct ($\Gamma_c \rightarrow \Gamma_c$)-type, direct-indirect ($\Gamma_c \rightarrow X_c$)-type, indirect-direct ($X_c \rightarrow \Gamma_c$)-type, and indirect-indirect ($X_c \rightarrow X_c$)-type branch-point aligned DFT-HSEmod conduction band offsets.

TABLE I. Bowing parameters of the natural valence and conduction band offsets fitted via Eq. (2) in the predominantly Ga-rich direct (b_{dir}) and Al-rich indirect (b_{ind}) composition ranges below and above the critical direct-indirect crossover composition ($x_c = 0.63$) as well as across the bowing parameter (b) fitted to the entire composition range (cf. Fig. 2). Also given are the bowing parameters of the conduction-to-valence band-offset quotient $\Delta E_c^{bp}/\Delta E_v^{bp}$ of the fundamental alloy band offsets.

				Bowing parameter (eV)		
System	Offset	Туре	b	$b_{ m dir}$	$b_{ m ind}$	
zb-GaN/Al _x Ga _{1-x} N	$\Delta E_{ m v}^{ m bp}$	$(\Gamma_v - \Gamma_v)$	-0.09	0.16	1.22	
	$\Delta E_{ m c}^{ m bp}$	$(\Gamma_{\rm c} - \Gamma_{\rm c})$	0.42	0.29	2.16	
		$(\Gamma_{\rm c}-X_{\rm c})$	-0.11	-0.06	1.25	
		$(X_{\rm c}-\Gamma_{\rm c})$	-0.42	-0.28	-2.12	
		$(X_{\rm c}-X_{\rm c})$	-0.11	-0.03	1.25	
	$\Delta E_{ m c}^{ m t}$	$e^{p}/\Delta E_{v}^{bp}$		-0.08	- 6.51	
zb-Al _x Ga _{1-x} N/AlN	$\Delta E_{ m v}^{ m bp}$	$(\Gamma_v - \Gamma_v)$	0.09	-0.16	- 1.34	
	$\Delta E_{ m c}^{ m bp}$	$(\Gamma_{\rm c}-\Gamma_{\rm c})$	-0.42	-0.28	-2.14	
		$(\Gamma_{\rm c} - X_{\rm c})$	-0.42	-0.28	- 2.16	
		$(X_{\rm c}-\Gamma_{\rm c})$	-0.11	0.06	-1.22	
		$(X_{\rm c}-X_{\rm c})$	0.11	-0.06	1.25	
	$\Delta E_{ m c}^{ m t}$	$e^{\mathrm{pp}}/\Delta E_{\mathrm{v}}^{\mathrm{bp}}$		-0.08	- 6.51	

parameters originating from mixing the direct and indirect electronic-structure features, insistently. Below the directindirect crossover, the ratio decreases virtually linearly ($b_{dir} = -0.08 \text{ eV}$) from a 58:42 ration in the *dilute limit* of vanishing Al concentration to 63:37 at the crossover composition. A characteristic 60:40 ratio is estimated for the *zb*-GaN/Al_{0.26}Ga_{0.74}N system. Beyond x_c , the *zb*-GaN/Al_xGa_{1-x}N band-offset ratio increase to a 50:50 equipartition at a composition parameter of x = 0.83 and a 44:56 ratio for the binary end system *zb*-GaN/AlN. This substantial change in band-offset ratios is reflected in the extreme bowing characteristics ($b_{ind} = -6.51 \text{ eV}$) in the Al-rich composition range.

In summary, zb-GaN/Al_xGa_{1-x}N represents a prototypical example of a type-I heterojunction forming material system, whose alloy characteristics are determined by a

direct-indirect band-gap crossing. In that the nonpolar Al/Ga based nitrides exhibit electronic structure features quite similar to the archetypical group-III arsenide representative of this class, *zb*-GaAs/Al_xGa_{1-x}As. In Al_xGa_{1-x}As the direct-indirect band-gap crossover transition occurs at a composition parameter of $x_c \approx 0.38$ [46,55,93,94] between the direct ($\Gamma_v \rightarrow \Gamma_c$)-type energy gap and the indirect ($\Gamma_v \rightarrow X_c$)-type energy gap. Similar to the cubic nitride alloys, the direct energy gaps show a moderate bowing characteristic ($b_{\Gamma} = 0.03$ eV), whereas the indirect alloy gap depends virtually linearly ($b_x = 0.055$ eV) on the alloy composition [55,94]. The resulting type-I band alignment in *zb*-GaAs/Al_xGa_{1-x}As heterostructures exhibits a valence band offset depending linearly on Al concentration and a conduction band offset increasing continuously as a function

TABLE II. Valence and conduction band-offset parameters fitted according to Eq. (2). The composition dependencies are fitted separately in the direct (b_{dir}) and indirect (b_{ind}) composition ranges below and above the critical direct-indirect crossover composition ($x_c = 0.63$) (cf. Fig. 2). Also included are the fitting parameters for the conduction-to-valence band-offset quotient $\Delta E_c^{bp} / \Delta E_v^{bp}$ of the fundamental alloy band offsets.

			Band-offset fitting parameters (eV)									
System			0 <	$\leq x \leq 0.63$		$0.63 \leqslant x \leqslant 1$						
composition	Offset	Туре	$\Delta E_{\rm v,c}^{\rm bp}({\rm A}_x{\rm B}_{1-x})$	$b_{ m dir}$	$\Delta E_{\rm v,c}^{\rm bp}({\rm A,B})$	$\Delta E_{\rm v,c}^{\rm bp}({\rm A}_x{\rm B}_{1-x})$	$b_{ m ind}$	$\Delta E_{\rm v,c}^{\rm bp}({\rm A,B})$				
\overline{zb} -GaN/Al _x Ga _{1-x} N	$\Delta E_{\rm v}^{\rm bp}$	$(\Gamma_v - \Gamma_v)$	-0.92	0.16	0.00	- 1.04	1.22	0.88				
	$\Delta E_{ m c}^{ m bp}$	$(\Gamma_{\rm c} - \Gamma_{\rm c})$	1.78	0.29	0.00	1.84	2.16	1.07				
		$(\Gamma_{\rm c} - X_{\rm c})$	0.84	-0.06	1.41	0.81	1.25	2.27				
		$(X_{\rm c}-\Gamma_{\rm c})$	-0.37	-0.28	1.42	-0.43	-2.12	0.38				
		$(X_{\rm c}-X_{\rm c})$	-0.57	-0.03	0.00	-0.61	1.25	0.87				
	ΔE_{c}	$E^{ m bp}_{ m c}/\Delta E_{ m v}^{ m bp}$	- 1.93	-0.08	- 1.37	-0.80	-6.51	- 7.30				
zb-Al _x Ga _{1-x} N/AlN	$\Delta E_{ m v}^{ m bp}$	$(\Gamma_v - \Gamma_v)$	-0.11	- 0.16	- 1.03	0.00	- 1.34	- 1.98				
	$\Delta E_{ m c}^{ m bp}$	$(\Gamma_{\rm c} - \Gamma_{\rm c})$	0.06	-0.28	1.84	0.00	-2.14	0.79				
		$(\Gamma_{\rm c} - X_{\rm c})$	-0.97	-0.28	0.81	-1.04	-2.16	-0.26				
		$(X_{\rm c} - \Gamma_{\rm c})$	-0.03	0.06	-0.61	0.00	-1.22	- 1.45				
		$(X_{\rm c}-X_{\rm c})$	-1.01	-0.06	-0.43	-1.04	1.25	0.43				
	ΔE_{c}	$E^{\rm bp}_{ m c}/\Delta E_{ m v}^{ m bp}$	2.51	3.35	-0.74	0.40	-0.51	0.58				

TABLE III.	Valence and	conduction	band-offset	parameters	obtained	from fitti	ng a fifth	ı order p	olynomial	of the form	$y = A_0$	$+A_{1}x +$
$A_2 x^2 + A_3 x^3 +$	$+A_4x^4+A_5$	x^{5} .										

			Band-offset fitting parameters (eV)										
System	Offset	Туре	A_0	A_1	A_2	A_3	A_4	A_5					
zb-GaN/Al _x Ga _{1-x} N	$\Delta E_{ m v}^{ m bp}$	$(\Gamma_v - \Gamma_v)$	0.00	-0.71	- 3.88	13.95	- 18.68	8.29					
	$\Delta E_{ m c}^{ m bp}$	$(\Gamma_{\rm c} - \Gamma_{\rm c})$	0.00	1.45	0.28	1.36	- 3.39	2.15					
		$(\Gamma_{\rm c}-X_{\rm c})$	1.42	-0.68	0.65	-0.20	-1.87	1.49					
		$(X_{\rm c}-\Gamma_{\rm c})$	1.41	-1.45	-0.28	- 1.36	3.39	- 2.15					
		$(X_{\rm c}-X_{\rm c})$	0.00	-0.68	0.65	-0.20	-1.87	1.49					
zb-Al _x Ga _{1-x} N/AlN	$\Delta E_{ m v}^{ m bp}$	$(\Gamma_v - \Gamma_v)$	- 1.03	0.71	3.88	- 13.95	18.68	- 8.29					
	$\Delta E_{ m c}^{ m bp}$	$(\Gamma_{\rm c} - \Gamma_{\rm c})$	1.84	-1.45	-0.28	- 1.36	3.39	- 2.15					
		$(\Gamma_{\rm c}-X_{\rm c})$	0.81	-1.45	-0.28	- 1.36	3.39	- 2.15					
		$(X_{\rm c}-\Gamma_{\rm c})$	-0.43	-0.68	0.65	-0.20	-1.87	1.49					
		$(X_{\rm c}-X_{\rm c})$	- 0.61	0.68	- 0.65	0.20	1.87	- 1.49					

of x with a distinct change in slope when going from the direct to the indirect energy-gap regime at the crossover composition [53,95,96]. Nonmonotonic composition dependencies have also been observed in experimental band-offset data on quaternary group-III phosphides as lattice-matched GaAs/(Al_xGa_{1-x})_{0.51}In_{0.49}P heterostructures [53]. In general, similar composition-dependence trends of physical properties can be expected as a common fundamental characteristic of cubic semiconductor alloys, which admix nondirect electronic features of at least one of the alloying binary semiconductors.

2. $zb-Al_xGa_{1-x}N/AlN$

The natural band alignment of the zb-Al_xGa_{1-x}N/AlN material system is visualized in Fig. 2(b). Due to the commutativity and transitivity of the branch-point aligned band offset, the natural offsets in zb-Al_xGa_{1-x}N/AlN qualitatively show the same basic trends just shifted on the energy scale due to alignment with zb-AlN and partially changed by the used sign convention (cf. Table III). In contrast to zb-GaN/Al_xGa_{1-x}N, the fundamental conduction band offset between zb-Al_xGa_{1-x}N and zb-AlN is completely determined

by indirect offset features, namely direct-indirect ($\Gamma_c \rightarrow X_c$)-type and indirect-indirect ($X_c \rightarrow X_c$)-type alignment.

In detail, the valence band offset between direct gap zb-Al_xGa_{1-x}N and indirect gap zb-AlN is found to decrease, according to an amount almost linear ($b_{dir} = -0.16 \text{ eV}$) from -1.03 to -0.42 eV. Passing the direct-indirect crossover point, the valence band offset continues to decrease further to zero with an enhanced upward bowing of $b_{\text{ind}} = -1.34 \text{ eV}$. The fundamental branch of the direct-indirect energy offset between Γ_c and X_c conduction-edge states decreases from 0.81 to -0.24 eV with a characteristic upward bowing of $b_{\rm dir} = -0.28$ eV. At higher x the upward bowing increases substantially to $b_{ind} = -2.16 \text{ eV}$ and the offset reaches a value of -1.04 eV for x = 1.0 representing the difference between the direct and indirect DFT-HSEmod band gaps of zb-AlN. The indirect-indirect $(X_c \rightarrow X_c)$ -type conduction band offset decreases, according to an amount, from -0.61 to -0.26 eV with almost negligible downward bowing of $b_{dir} = 0.06$ eV. The fundamental branch above x_c decreases to zero with an intermediate upward bowing of $b_{dir} = -1.22$ eV. In addition to the direct-indirect crossover, the natural conduction band offset exhibits a change from type-I-to-type-II alignment at an almost

TABLE IV. zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N valence and conduction band-offset parameters obtained from fitting a two-dimensional fifth order polynomial of the form $z = z_0 + A_1 x + A_2 x^2 + A_3 x^3 + A_4 x^4 + A_5 x^5 + B_1 y + B_2 y^2 + B_3 y^3 + B_4 y^4 + B_5 y^5$. The fitted graphs are visualized in Figs. 3 and 4.

			Band-offset fitting parameters (eV)										
Offset	Туре	Composition	z_0	A_1	A_2	A_3	A_4	A_5	B_1	B_2	<i>B</i> ₃	B_4	B_5
$\Delta E_{\rm v}^{\rm bp}$	$(\Gamma_v - \Gamma_v)$	$ \begin{array}{l} x < y \\ x > y \end{array} $	$0.00 \\ 0.00$	0.71 - 0.71	3.88 - 3.88	- 13.95 13.95	18.68 - 18.68	- 8.29 8.29	$-0.71 \\ 0.71$	- 3.88 3.88	13.95 - 13.95	- 18.68 18.68	8.29 - 8.29
$\Delta E_{ m c}^{ m bp}$	$(\Gamma_c-\Gamma_c)$	$ \begin{array}{l} x < y \\ x > y \end{array} $	$\begin{array}{c} 0.00\\ 0.00\end{array}$	- 1.45 1.45	$-0.28 \\ 0.28$	- 1.36 1.36	3.39 - 3.39	- 2.15 2.15	1.45 - 1.45	0.28 - 0.28	1.36 - 1.36	- 3.39 3.39	2.15 - 2.15
	$(\Gamma_{\rm c} - X_{\rm c})$	$ \begin{array}{l} x < y \\ x > y \end{array} $	1.41 1.41	-1.45 - 0.68	$-0.28 \\ 0.65$	-1.36 - 0.20	3.39 - 1.87	- 2.15 1.49	- 0.68 - 1.45	0.65 - 0.28	-0.20 - 1.36	- 1.87 3.39	1.49 - 2.15
	$(X_{\rm c}-\Gamma_{\rm c})$	$ \begin{array}{l} x < y \\ x > y \end{array} $	1.41 1.41	-0.68 -1.45	0.65 - 0.28	-0.20 - 1.36	- 1.87 3.39	1.49 - 2.15	-1.45 - 0.68	$-0.28 \\ 0.65$	-1.36 - 0.20	3.39 - 1.87	- 2.15 1.49
	$(X_{\rm c}-X_{\rm c})$	$ \begin{array}{l} x < y \\ x > y \end{array} $	$\begin{array}{c} 0.00\\ 0.00 \end{array}$	0.68 - 0.68	$-0.65 \\ 0.65$	$0.20 \\ -0.20$	1.87 - 1.87	- 1.49 1.49	$-0.68 \\ 0.68$	0.65 - 0.65	$-0.20 \\ 0.20$	-1.87 1.87	1.49 - 1.49

equipartitionally occupied cation sublattice as indicated by the conduction band-offset sign change in Fig. 2(b). Starting from a composition parameter of x = 0.49, well below the direct-indirect crossover transition, the zb-Al_xGa_{1-x}N/AlN system retains its type-II character throughout the entire Al-rich composition range. The most pronounced type-II alignment occurs at the direct-indirect transition, where the fundamental conduction band offset exhibits its extremal reversal point. In contrast to the direct-indirect crossover, the type-I-to-type-II transition represents a pure alignment feature rather than an electronic structure feature. Therefore, the alignment-type transition, occurring in both the direct and indirect alloy-gap regimes, shows no influence on the slope of the natural band offset.

Our data are in reasonable agreement with numerical data on the *zb*-Al_{0.5}Ga_{0.5}N/AlN (001) heterojunction reported by Buongiorno Nardelli *et al.* [64]. Utilizing plane-wave DFT at the local density approximation level, the virtual crystal approximation to model the ternary alloy, and electrostaticpotential alignment, Buongiorno Nardelli *et al.* reported a staggered type-II band alignment with strained (average inplane lattice constant) valence and conduction band offsets of -0.39 and -0.17 eV, respectively. In addition, valence and conduction band offsets of -0.37 and -0.09 eV were reported for a fully relaxed *zb*-AlN₁GaN₁/AlN (001) superlattice. These values compare well with the corresponding natural valence and conduction band offsets of -0.53 and -0.01 eV, obtained within the present study.

The conduction-to-valence band ratio of the fundamental *zb*-GaN/Al_xGa_{1-x}N band offsets increases with a large downward bowing ($b_{dir} = 3.35$ eV) from the 44:56 ratio in *zb*-GaN/AlN towards a 37:63 ratio at the direct-indirect transition point. A 40:60 ratio is passed at a composition parameter of x = 0.14. The offset ratio approximately reaches a plateau in the indirect Al-rich composition range, where the offset ratio decreases only slightly to 31:69 in the limit of dilute Ga concentration. Hence, aligning conduction-edge states of different fundamental symmetry type, Γ_c and X_c type, respectively, causes a substantial nonlinearity in the conduction-to-valence band-offset ratio, while the ratio shows only small and almost linear variation in case of conduction band offsets calculated from Γ_c -type or X_c -type states only.

In summary, the cubic symmetry, and the associated indirect nature of the fundamental zb-AlN band gap, introduce the possibility of forming staggered gap type-II heterojunctions in Al-rich zb-Al_xGa_{1-x}N/AlN or, in other words, control the heterostructure type by alloying. Such type-II alignment as well as composition dependent type-I-to-type-II transitions in multicomponent semiconductor alloys have been observed in other group-III-V semiconductor materials. Especially indium containing nitride/arsenide and antimonide/arsenide quantum well or quantum dot heterostructures show promising material characteristics, in this respect [97–104]. Very recently, Reddy et al. [105] conducted a x-ray photoelectron-spectroscopy study on the band alignment between silicon nitride (Si₃N₄) and wz-Al_xGa_{1-x}N. Despite the large (indirect) Si₃N₄ band gap of 5.3 eV [106], which is comparable to the indirect band gap of cubic zb-AlN, the relative positions of the valence and conduction-edge bands of Si₃N₄ cause all $Si_3N_4/Al_xGa_{1-x}N(0001)$ interfaces to form a staggered typeII alignment, independent of the nitride-alloy composition. Type-II band alignment for technological application has also been studied in various other semiconducting material classes. Due to the recently rising interest in two-dimensional materials, various experimental and theoretical studies on the electronic structure features of single- and few-layer transition metal dichalcogenides have demonstrated the basic potential for type-II aligned lateral heterostructures [107]. In addition, transition metal dichalcogenides also show bulk-to-thin-film indirect-direct transitions [108-110]. Type-II alignment between binary materials and composition dependent type-Ito-type-II transitions have been reported for selenide and sulfide based core/shell quantum-dot heterojunctions [111– 115]. Type-I-to-type-II transitions have also been observed in magnetic semiconductor-quantum wells and superlattices based on different selenide and telluride alloys as a response to external magnetic fields [116–118]. In all these materials type-II alignment is provided by a delicate combination of binary, ternary, and also quaternary semiconductor alloys. Hence, precise tailoring of heterostructures nanomaterials for technological application substantially benefits from profound reference data on the composition dependence of band discontinuities. In that spirit, we proceed in our study with the analysis of band alignments within the complete two-dimensional composition range of nonpolar $zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N$ bulk nitrides.

3. $zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N$

In contrast to strained band offsets, where one material is strained to the other at a time, the absolute values of natural band offsets do not show a symmetry breaking *forwardbackward asymmetry* upon interchange of the composition parameters x and y, in general. Following the sign convention, according to agreement above, the natural band-offset data on zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N inevitably exhibit the characteristic mirror symmetry (cf. Figs. 3 and 4) with respect to the equal-composition diagonal ($x \equiv y$).

The roughly linear composition dependence of the natural valence band offsets, which originate from the alignment of Brillouin-zone center localized Γ_v -type alloy states at the top of the valence band, extends straightforward throughout the entire two-dimensional composition range of nonpolar zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N composites.

Due to the mixing of direct and indirect-type alloy states, the fundamental conduction band offset changes discontinuously at the direct-indirect transition lines [see dashed lines in Fig. 3(e)]. The composition dependencies of the four possible alignment types of Γ_c -type and X_c -type conduction-edge states are illustrated in Fig. 4. The fundamental conduction band offset of nonpolar *zb*-Al_xGa_{1-x}N/Al_yGa_{1-y}N alloys represents a combination of these different alignment types. Four distinct composition ranges, each showing a characteristic alignment type, are predefined by the critical direct-indirect crossover concentrations of the two *zb*-Al_xGa_{1-x}N alloys [cf. Fig. 3(e)]. In detail, distinct conduction-band alignment features can be observed in the pure direct regime (dir-dir) for ($0 \le x \le 0.63$) \land ($0 \le y \le 0.63$), two mixed direct-indirect composition regimes (dir-ind) for ($0 \le x \le 0.63$) \land ($0.63 \le y \le 1$)

and $(0.63 \le x \le 1) \land (0 \le y \le 0.63)$, and the pure indirect regime (ind-ind) for $(0.63 \le x \le 1) \land (0.63 \le y \le 1)$.

Due to the restriction to Brillouin-zone center-type electronic states, the fundamental conduction band offset changes roughly linearly with (x, y) composition in the predominantly Ga-rich direct alloy regime. The related conduction-to-valence band-offset quotient $\Delta E_c^{bp} / \Delta E_v^{bp}$, the $|\Delta E_c^{bp}| : |\Delta E_v^{bp}|$ ratio, respectively, show only moderate changes in this regime [cf. Fig. 3(e)]. Nonpolar zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N alloys exhibit a similar band-offset ratio close to 65:35 in a wide composition range around the equimolar/equimolar composite zb-Al_{0.5}Ga_{0.5}N/Al_{0.5}Ga_{0.5}N. The ratio is slightly modified to roughly 60:40 at low Al content $[(x \le 0.25) \land (y \le 0.25)]$ heterojunctions. These band-offset ratios show strong resemblance to the experimentally determined band-offset ratios between polar wz-Al_xGa_{1-x}N nitride alloys reported by Reddy et al. [57]. The overall comparable composition dependencies of conduction band offsets in the cubic and hexagonal $Al_xGa_{1-x}N/Al_yGa_{1-y}N$ material systems highlight the common nature of direct-gap states in polar as well as nonpolar tetrahedrally coordinated III-V semiconductors, in general.

The natural band-offset ratio shows substantial variations in the transition regions around the direct-indirect crossover lines. This strong variation in the ratio of natural band offsets suggests that a precise control of the band-offset profile will be more delicate close to the direct-indirect crossover composition. Clearly, composition fluctuations and small band-offset variations due to interfacial strain might be most crucial for device design in this composition range. The conduction-to-valence band ratio flattens out in the vicinity of the binary/binary heterojunctions and reaches a ratio of roughly 45:55 in *zb*-GaN/AIN.

The conduction-to-valence band ratio reaches a plateau of roughly 35:65 in the pure indirect regime, that is to say the ratio will virtually be inverted with respect to the direct-direct composition range. Due to the the weak nonlinear nature of the valence band offsets, the band-offset ratio clearly reflects the existing types of conduction band offsets in the zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N system, overall.

The type-II alignment range includes the entire indirectindirect composition regime, but also extends towards the mixed direct-indirect regime with the equimolarternary/binary system zb-Al_{0.5}Ga_{0.5}N/AlN roughly marking the lowest Al content, hence smallest energy gap, type-II alignment limit. The most pronounced type-II alignment character is formed between zb-Al and the ternary alloys close to the crossover composition. I detail the valence and conduction band offsets between zb-Al_{xc}Ga_{1-xc}N with $x_c =$ 0.63 and zb-AlN amount to -0.41 and -0.24 eV, respectively.

IV. SUMMARY AND CONCLUSION

We have used exact-exchange adjusted hybrid functional based DFT and the branch-point alignment technique to analyze the natural band alignment at unstrained heterojunctions of nonpolar ternary $Al_xGa_{1-x}N$ alloys. The alignment of bulklike direct $\Gamma_v \rightarrow \Gamma_c$ and indirect, *pseudodirect*, respectively, $\Gamma_v \rightarrow X_c$ type energy states in *zb*-Al_xGa_{1-x}N show a rather complex composition dependence of fundamental band discontinuities in the zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N material system, which is characterized by the direct-indirect band-gap crossing of zb-Al_xGa_{1-x}N alloys and a type-I-to-type-II bandalignment type transition. The *zb*-GaN/Al_xGa_{1-x}N band edges consistently show a type-I alignment. In addition, the presence of a direct-indirect band-gap transition in the investigated cubic zb-Al_xGa_{1-x}N semiconductor alloys gives rise to a notable composition dependence of band discontinuities with weak nonlinear character in the predominantly Ga-rich direct-alloy regime below the critical direct-indirect Al/Ga-crossover concentration $x_c = 0.63$ but substantial bowing characteristics in the Al-rich alloy regime. The relative position of fundamental band edges changes to a staggered type-II alignment in the Al-rich composition ranges of zb-Al_xGa_{1-x}N/AlN and the zb-Al_xGa_{1-x}N/Al_yGa_{1-y}N system, in general.

Our results indicate that semiconductor alloys with mixed direct-indirect band-gap characteristics, systems obeying a direct-indirect band-gap crossing, respectively, possess nontrivial fundamental band-alignment features that not only deviate from the trivial linear dependencies expressed in Vegard's law but also exhibit quite sharp derivative discontinuities that prevent straightforward fitting of composition dependencies to monotonic power laws. Likewise, there is no straightforward justification for the assumption of composition independent band-offset ratios in the band discontinuities between group-III nitrides or comparable semiconductor systems. Therefore, we emphasize the general need for detailed numerical studies on the composition dependence of multicomponent composite semiconductors using state-of-the-art first-principles approaches as a sound basis for interpretation of experimental data as well as reliable input to highly parametrized calculation approaches on the basis of more phenomenological model theories.

Despite being fundamentally unaffected by the strain conditions of a real heterostructure, the efficient calculation of natural band offsets via branch-point alignment allows the systematic study of composition dependent band-alignment trends, which are of vital interest for the design of optoelectronic devices. The natural band offsets itself can further be utilized alongside volume deformation potentials as input to effective mass theory based simulation approaches (e.g., see Refs. [29,119]) allowing effective modeling of nanometer sized semiconductor heterostructures. Albeit providing a sound data basis, remaining uncertainties, as possible accuracy limits due to the utilized branch-point alignment (see Ref. [49]) or limited availability of volume deformation potentials across the entire composition range, still leave room for future verification and refinement of the identified trends by ab initio studies on strained band offsets at the interfaces between cubic group-III nitride materials.

The promotion of charge separation via spatially separated localization of electrons and holes is, in general, a committed heterostructure-alignment feature in the design of photovoltaic devices in order to prevent charge-carrier recombination. Even though the band gap of Al-rich zb-Al_xGa_{1-x}N semiconductor alloys exceeds the size desirable for utilization in visible light-emission applications and energy harvesting devices, a

limitation that can be overcome by alloying zb-Al_xGa_{1-x}N with InN, the large accessible range of band gaps and band offset promotes fabrication of intersubband devices working in the technology eminent THz wavelength regime. Especially, the spatial separation of electron and hole wave functions within the type-II aligned heterostructures, a property rarely observed in the group-III nitride material system, allows individual tuning of charge carrier confinement potentials through variations of the layer widths.

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UNDERSTANDING BAND ALIGNMENTS IN ...

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