Composition-Dependent Band Gap and Band-Edge Bowing in AlInN: A Combined Theoretical and Experimental Study

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A combined experimental and theoretical study of the band gap of AlInN is presented, which confirms the breakdown of the virtual crystal approximation (VCA) for the conduction and valence band edges. Composition-dependent bowing parameters for these quantities are extracted. Additionally, composition-dependent band offsets for GaN/AlInN systems are provided. We show that local strain and built-in fields affect the band edges significantly, leading to optical polarization switching at a much lower In composition than expected from a VCA approach.

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The semiconductor alloy Al1–xInxN has a direct band gap that spans a very wide energy range (0.69 to 6.25 eV).1–3 This basic property makes Al1–xInxN an ideal candidate for a range of optoelectronic devices, such as laser diodes, light-emitting diodes, and detectors.2,3 To design Al1–xInxN-based devices, an accurate knowledge of the variation of the band gaps En with varying InN content x is required. Often the variation of the band gap of a semiconductor alloy with composition x can be successfully described by the so-called virtual crystal approximation (VCA)3

\[ E_{\text{VCA}} = (1 - x)E_{\text{AlN}} + xE_{\text{InN}} - b \cdot x \cdot (1 - x), \]  

(1)

with a composition-independent bowing parameter b.

However, for Al1–xInxN systems, a large range of values for the bowing parameter b have been reported in the literature. Reported values scatter from 2.5 eV, extracted from measurements on high-x samples, up to 10 eV based on measurements with low-x values.4,5 Hence, the assumption that b is independent of composition has been questioned by several groups.6,7 Recently, based on density functional theory (DFT) results, the physical mechanisms underlying this breakdown have been clarified. It has been shown that cation-localized localized states in the conduction band (CB) and the valence band (VB) lead to the breakdown of the VCA.8 These results support the assumption of a composition-dependent bowing parameter. It is important to note that when designing polarization-matched GaN quantum wells (QWs), using AlInN barriers,9 the evolution of the CB edge (CBE) and VB edge (VBE) energies with InN content x is important, since this determines confinement energies for carriers.

To shed further light on the behavior of the band-gap bowing in Al1–xInxN and how CBE and VBE behave with varying InN content x, we have performed experimental and theoretical studies. Our results are compared with recent experimental literature data. We apply a tight-binding (TB) model to achieve an atomistic description of the electronic structure.10 This model includes local strain and built-in fields arising from random alloy fluctuations in AlInN. The same approach has been successfully applied to InGaN alloys recently.10

Our results confirm that the band-gap bowing parameter in Al1–xInxN is highly composition dependent and cannot be described by a simple VCA [Eq. (1)]. Furthermore, our calculations reveal that both CBE and VBE separately deviate from the VCA. Therefore, we also provide composition-dependent bowing parameters for CBE and VBE in Al1–xInxN, which can then be used as input parameters for continuum-based descriptions, such as k·p-models, of AlInN heterostructures. Additionally, our theoretical analysis indicates that local strain and built-in fields, arising from random alloy fluctuations, play an important role in the description of the band edges, contributing therefore to the deviation from the VCA. We extract composition-dependent CB and VB offsets for GaN/Al1–xInxN systems. Finally, we analyze the VB ordering in Al1–xInxN. We calculate an optical polarization switching from TM- to TE-polarized emission around x = 0.15.

On the experimental side, we have grown Al1–xInxN epilayers with thicknesses of about 100 nm by metal organic chemical vapor deposition, using GaN nucleation layers on c-plane sapphire, Here, Al1–xInxN samples with x ranging from 0.082 to 0.17 have been studied by photoluminescence excitation (PLE) spectroscopy. The PLE measurements have been performed at low temperatures in a closed cycle helium cryostat. The samples have been excited by a Xe-lamp and the detected wavelength has been set to the Al1–xInxN emission peak for each of the series of samples. The PLE spectra were fitted using a sigmoidal function, as introduced for InGaN epilayers in Ref. 11, to define the band gap energy together with a broadening of the absorption edge.

On the theoretical side, band-gap and band-edge bowing parameters have been studied by means of an sp3 TB model. This approach allows for a microscopic description of electronic and optical properties of AlInN. Our TB model includes explicitly local strain and built-in fields, arising from random alloy fluctuations. The theoretical framework is discussed in detail in Ref. 10 for InGaN systems. For AlInN, we used the same approach; the required material parameters are taken from Refs. 12–14, while the AlN TB parameters can be found here.15

To gain insight into the behavior of the AlInN band gap and band edges, we have performed TB calculations on supercells containing approximately 12,000 atoms. The supercell is free to relax in all three spatial directions. For
Table I. Al$_{1-x}$In$_x$N composition-dependent bowing parameters for band gap ($b$), CB ($b^{CB}$), and VB ($b^{VB}$), as functions of $x$.

| x       | 0.05 | 0.08 | 0.10 | 0.13 | 0.15 | 0.18 | 0.25 | 0.35 | 0.50 | 0.65 | 0.75 | 0.85 |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|
| $b$ (eV)| 19.81| 15.35| 13.89| 11.74| 10.72| 9.91 | 8.12 | 6.43 | 5.15 | 4.52 | 4.24 | 3.87 |
| $b^{CB}$ (eV)| 14.01| 10.67| 9.29 | 7.67 | 7.01 | 6.23 | 4.95 | 3.92 | 3.08 | 2.54 | 2.22 | 1.96 |
| $b^{VB}$ (eV)| −5.80| −4.68| −4.59| −4.07| −3.71| −3.68| −3.17| −2.51| −2.07| −1.98| −2.01| −1.92|

Figure 1 shows our theoretical TB (black circles) and experimental PLE data (red squares) together with literature data. Overall, we find that our TB results are in very good agreement with the experimental data over the full composition range. Note that the TB approach involves fitting to the band gaps of the binary materials only. Also, a closer look at the composition range $x = 0.05-0.25$, cf. inset Fig. 1, shows that both our theoretical and experimental results are in good agreement with the literature data. Furthermore, with as little as 5% InN ($x = 0.05$) in Al$_{1-x}$In$_x$N, a reduction in the band gap of over 1 eV is observed. This strong reduction in band gap can be traced back to In-related localized states in the CB. As discussed in Ref. 8, these localized states lead to the breakdown of the simple VCA description. Consequently, a composition-dependent bowing parameter is required, labeled $b$ in the following.

Table I summarizes the calculated values for $b$ in Al$_{1-x}$In$_x$N as a function of $x$, obtained from our TB model. This data is derived using Eq. (1) by fitting to the end points (binaries) and the desired $x$-value. Particularly in the low InN regime, extremely large values for $b$ are observed.

However, when modeling AlInN-based heterostructures, not only the overall band-gap bowing is important but also how the band-gap bowing is distributed between CB and VB. This quantity is of central importance for an accurate description of electronic and optical properties of heterostructures since it determines the confinement energies for the carriers.

Figure 2 shows the TB results for the CBE (circles) and VBE (squares) in Al$_{1-x}$In$_x$N as a function of $x$. A VCA fit to the TB data over the whole composition range is given by the dashed-(dotted) lines and is obtained from

$$ E_{CB}^{AlInN} = x(E_{g}^N + \Delta E_{VB}) + (1-x)E_{g}^B - b^{CB}x(1-x), $$

$$ E_{VB}^{AlInN} = x\Delta E_{VB} - b^{VB}x(1-x). \quad (2) $$

Here, $E_{CB}$ and $E_{VB}$ are composition independent and the VB offset $\Delta E_{VB}$ between InN and AlN is taken from Ref. 18. Figure 2 confirms again that composition-independent bowing parameters fail to describe the CBE and VBE in AlInN. The behavior of the CBE can clearly not be described by the VCA (dashed-dotted line). The VBE shows a similar behavior, but with a smaller deviation from a VCA-like model. To a first approximation, a composition-independent VB bowing parameter could be used ($b^{VB} = -2.64$ eV).

We apply the procedure described above for the composition-dependent band-gap bowing parameter $b$ to CBE and VBE. The values for CBE and VBE bowing parameters $b^{CB}$ and $b^{VB}$, respectively, are summarized in Table I. From Table I, we conclude that the very strong composition dependence of the AlInN band gap in the low-InN regime mainly arises from the composition dependence of the CBE. In this regime, the CBE bowing parameter $b^{CB}$ is much larger than the VBE parameter $b^{VB}$. This finding ties in with recent DFT results on the low-InN regime. However, since we observe also a significant VBE bowing parameter, the commonly applied assumption[19] in which all the bowing is attributed to the CB seems to fail in AlInN, especially when studying higher InN contents ($x > 0.5$), since $b^{CB}$ and $b^{VB}$ are comparable in magnitude for that range.

Having discussed the composition dependence of both the band gap and band edges in Al$_{1-x}$In$_x$N, we turn now and focus on the effect that local alloy, strain, and built-in field fluctuations have on the results. In Fig. 3, we disentangle the impact of these quantities on CBE [Fig. 3(a)] and VBE

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**Fig. 1.** Band gap of Al$_{1-x}$In$_x$N as a function of $x$. Our theoretical (open circles) and experimental results (squares) are compared with literature data.

**Fig. 2.** CBE and VBE in Al$_{1-x}$In$_x$N as a function of $x$. TB results for CBE and VBE ($E_{CB}^{CBE}, E_{VB}^{CBE}$); open symbols; dashed-(dotted) lines: fit obtained from Eq. (2). Solid horizontal lines: GaN CBE and VBE.

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a: Ref. 7; b: Ref. 16; c: Ref. 5; d: Ref. 17
[Fig. 3(b)]. We start with the analysis of the CBE. Comparing the results in the absence of the local strain and built-in potential contributions ($E_{CB}^{F}=0$; open stars) with data when including local strain effects only ($E_{CB}^{F}=0$; open squares), we observe a strong shift of the CBE to higher energies. This shift to higher energies arises from the deformation potential correction due to local hydrostatic strain, since the interatomic bond lengths of InN are larger ($\sim$14%) than those of AlN. When also including the local built-in potential fluctuations ($E_{CB}^{F} \neq 0$; open circles), we observe almost no difference between this full calculation and the situation where we have switched off the built-in potential fluctuations ($E_{CB}^{F} \neq 0$; open squares), at least on the energy scale shown.

Figure 3(b) shows the situation for the VBE. Taking local strain effects into account but neglecting local built-in potential contributions ($E_{VB}^{F}=0$; open squares), one observes a shift of the VBE to higher energies compared with the situation when only local alloy effects ($E_{VB}^{F}=0$; open stars) are included. The effect is mainly related to local compressive strains. In the presence of the local built-in field contributions ($E_{VB}^{F} \neq 0$; open circles), we observe a further upward bowing of the VBE compared with the situation without the local built-in potential ($E_{VB}^{F}=0$; open squares). These results are similar to our findings on the band edges in In$_{x}$Ga$_{1-x}$N.\(^{10}\)

Having discussed how band edges change in Al$_{1-x}$In$_x$N with $x$, we estimate in the following the composition-dependent CB and VB offsets $\Delta E_{CB}^{Ga}{InAlN}$ and $\Delta E_{VB}^{Ga}{InAlN}$, respectively, between GaN and AlInN. Here, we estimate band offsets in the absence of strain and polarization fields. When band offsets are included, for example, in QW calculations by means of the K-p-theory, strain and built-in potentials will be added separately.\(^{20}\) Here, the VB offset $\Delta E_{VB}^{Ga}{InAlN}$ is calculated as $\Delta E_{VB}^{Ga}{InAlN} = \Delta E_{VB}^{GaN} - \Delta E_{VB}^{AlN}$, where $\Delta E_{VB}^{AlN}$ is obtained from Eq. (2) (using data from Table I). $\Delta E_{VB}^{GaN/AlN}$ denotes the VB offset between GaN and AlN. We assume $\Delta E_{VB}^{GaN/AlN} = 0.9$ eV, which is in the range of reported literature values ($\Delta E_{VB}^{GaN/AlN} = 0.15$–1.4 eV),\(^{21–24}\) and at $x = 1$, $E_{VB}^{GaN/InN} = 0.62$ eV in accordance with Ref. 24 for the VB offset between InN and GaN. Our approach is similar to the approach used in Ref. 19. Therefore, if $\Delta E_{CB}^{Ga}{InAlN} > 0$, the VBE in GaN is at higher energies than the VBE in AlInN. The composition-dependent CB offset, $\Delta E_{CB}^{In}{InAlN}$, is calculated as $\Delta E_{CB}^{In}{InAlN} = \Delta E_{CB}^{In}{AlInN} - \Delta E_{CB}^{In}{GaN}$, where $\Delta E_{CB}^{In}{GaN}$ is the bulk band gap of GaN.\(^{11}\) $\Delta E_{CB}^{In}{AlInN}$ is calculated from Eq. (2) using data from Table I. Here, $\Delta E_{CB}^{In}{InAlN} > 0$ indicates that the CBE in GaN is at lower energies than the CBE in AlInN.

The obtained results are summarized in Table II where we estimate that the CB and VB offsets are positive up to 25% In$_x$N in AlInN. In terms of a heterostructure, neglecting strain and built-in potentials, this indicates that electrons and holes are confined in the GaN region. For $x \geq 0.25$, we observe a change in sign in CB and VB offsets, indicating that the carriers are confined in the AlInN region. We note that there is an uncertainty in the calculated composition values where CB and VB offsets change sign due to the uncertainty in the AlN/GaN VB offset\(^{21–24}\) an increase (decrease) in the assumed VB offset would, for instance, lead to the CB crossover occurring at lower (higher) InN compositions.

In the final step, we study how the optical polarization due to the VB ordering changes in Al$_{1-x}$In$_x$N with $x$. Compared with more conventional III-V semiconductors such as InAs, the spin-orbit coupling (SOC) in the group-III nitrides is small.\(^{25,26}\) Neglecting the weak SOC, the topmost VB in AlN is $p_z$-like, while in InN, it is a linear combination of $p_r$- and $p_\perp$-like states. Figure 4(a) shows the contribution of the $s$, $p_r$, $p_\perp$, and $p_z$-like orbitals to the VBE in fully
relaxed Al$_{1-x}$In$_x$N as a function of $x$. Our TB results show that below $x = 0.15$, the dominant orbital contribution is still $p_z$-like, while for $x > 0.15$, the linear combination of $p_z$- and $p_y$-like states starts to dominate. Therefore, our data indicates an optical polarization switching (TM to TE) in Al$_{1-x}$In$_x$N at $x = 0.15$. By performing calculations for AlInN systems pseudomorphically grown on GaN, the polarization switching occurs at $x \approx 0.18$ (not shown). Figure 4(b) illustrates that the charge density on the In sites ($\rho_{\text{In}}^{\text{p}_{z}}$) agrees with recent DFT data, and the polarization switching occurs at $x \approx 0.18$. The charge density on the N sites indicates a strong localization of the wave function around the In sites, in agreement with recent DFT data, and explains the surprisingly early onset of the polarization switching.

In summary, we have studied the band-gap bowing of AlInN as a function of the InN content $x$ both experimentally and theoretically. Our atomistic TB results are in good agreement with the performed PLE measurements and with experimental literature data. We confirm that the assumption of a composition-independent bowing parameter fails and provide data for the composition dependence of the bowing parameter. Moreover, we find that both CBE and VBE show deviations from a simple VCA description. Composition-dependent VBE and CBE bowing parameters have been extracted. Our microscopic analysis reveals that local strain and built-in field effects play a significant role in the composition-dependent behavior of CBE and VBE. We have used this data to study the band offsets in AlInN/GaN systems. Our analysis of the optical polarization in AlInN shows a switching from TM- to TE-polarized emission at 15–18% InN.

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1) J. Wu: J. Appl. Phys. 106 (2009) 011101.

2) G. Liu, J. Zhang, X.-H. Li, G. S. Huang, T. Paskova, K. R. Evans, H. Zhao, and N. Tansu: J. Cryst. Growth 340 (2012) 66.

3) L. Nordheim: Ann. Phys. (Leipzig) 9 (1931) 607 [in German].

4) K. S. Kim, A. Saxler, P. Kung, M. Razeghi, and K. Y. Lim: Appl. Phys. Lett. 71 (1997) 800.

5) T. Aeschbrenner, H. Dartsch, C. Kruse, M. Anastasescu, M. Stoica, M. Gartner, A. Pretorius, A. Rosenauer, T. Wagner, and D. Hommel: J. Appl. Phys. 108 (2010) 063533.

6) K. Wang, R. W. Martin, D. Amabile, P. R. Edwards, S. Hernandez, E. Nogales, K. P. O’Donnell, K. Lorenz, E. Alves, V. Matias, A. Vantommme, D. Wolderman, and I. M. Watson: J. Appl. Phys. 103 (2008) 073510.

7) E. Sakalauskas, H. Behmenburg, C. Huus, P. Schley, G. Rossbach, C. Giesen, M. Heuken, H. Kalisch, R. H. Jensen, J. Blasing, A. Dadgar, A. Krost, and R. Goldhahn: J. Phys. D 43 (2010) 365102.

8) S. Schulz, M. A. Caro, and E. P. O’Reilly: arXiv:1307.5985.

9) M. A. Caro, S. Schulz, S. B. Healy, and E. P. O’Reilly: J. Appl. Phys. 109 (2011) 084110.

10) M. A. Caro, S. Schulz, and E. P. O’Reilly: arXiv:1309.3309.

11) R. W. Martin, P. G. Middleton, K. P. O’Donnell, and W. Van der Stricht: Appl. Phys. Lett. 74 (1999) 263.

12) M. A. Caro, S. Schulz, and E. P. O’Reilly: Phys. Rev. B 86 (2012) 014117.

13) A. D. Andreev and E. P. O’Reilly: Phys. Rev. B 62 (2000) 15851.

14) Q. Yan, P. Rinke, M. Winkelnkemper, A. Qteish, D. Bimberg, M. Scheffer, and C. G. Van de Walle: Semicond. Sci. Technol. 26 (2011) 014037.

15) TB parameters for AlN: $E_{\text{c}(a,a)} = -10.20\,\text{eV}$, $E_{\text{c}(p,p)} = 0.66\,\text{eV}$, $E_{\text{c}(p,a)} = 0.92\,\text{eV}$, $E_{\text{s}(s,c)} = 2.25\,\text{eV}$, $E_{\text{s}(p,c)} = 11.08\,\text{eV}$, $V_{\text{c}(x,x)} = -8.11\,\text{eV}$, $V_{\text{s}(s,s)} = 3.20\,\text{eV}$, $V_{\text{s}(x,y)} = 5.63\,\text{eV}$, $V_{\text{ps}(sa,pc)} = 3.04\,\text{eV}$, $V_{\text{ps}(pa,sc)} = 10.31\,\text{eV}$.

16) R. E. Jones, R. Breseler, K. M. Yu, J. W. Ager, E. E. Haller, W. Walukiewicz, X. Chen, and W. J. Schaff: J. Appl. Phys. 104 (2008) 123501.

17) E. Illipoulos, A. Adikimenakis, C. Giesen, M. Heuken, and A. Georgakilas: Appl. Phys. Lett. 92 (2008) 191907.

18) P. D. C. King, T. D. Veal, P. H. Jefferson, C. F. McConville, T. Wang, P. J. Parbrook, H. Lu, and W. J. Schaff: Appl. Phys. Lett. 90 (2007) 132105.

19) O. Ambacher, J. Majewski, C. Miskys, A. Link, M. Hermann, M. Eckhoff, M. Stutzmann, F. Bernardini, V. Fiorentini, V. Tkil, B. Schaff, and L. F. Eastman: J. Phys.: Condens. Matter 14 (2002) 3399.

20) L. C. Lew Yan Voon and M. Willatzen: The k.k Method: Electronic Properties of Semiconductors (Springer, Heidelberg, 2009).

21) G. Martin, A. Botezhev, A. Rockett, and H. Morkoc: Appl. Phys. Lett. 68 (1996) 2541.

22) W. Mönch: J. Appl. Phys. 80 (1996) 5076.

23) N. Binggeli, P. Ferrara, and A. Baldereschi: Phys. Rev. B 63 (2001) 245306.

24) P. G. Moses, M. Miao, Q. Yan, and C. G. Van de Walle: J. Chem. Phys. 134 (2011) 084703.

25) I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan: J. Appl. Phys. 89 (2001) 5815.

26) I. Vurgaftman and J. R. Meyer: J. Appl. Phys. 94 (2003) 3675.