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Topical Review

Theoretical study of nitride short period superlattices

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Abstract
Discussion of band gap behavior based on first principles calculations of electronic band structures for various short period nitride superlattices is presented. Binary superlattices, as InN/GaN and GaN/AlN as well as superlattices containing alloys, as InGaN/GaN, GaN/AlGaN, and GaN/InAlN are considered. Taking into account different crystallographic directions of growth (polar, semipolar and nonpolar) and different strain conditions (free-standing and pseudomorphic) all the factors influencing the band gap engineering are analyzed. Dependence on internal strain and lattice geometry is considered, but the main attention is devoted to the influence of the internal electric field and the hybridization of well and barrier wave functions. The contributions of these two important factors to band gap behavior are illustrated and estimated quantitatively. It appears that there are two interesting ranges of layer thicknesses; in one (few atomic monolayers in barriers and wells) the influence of the wave function hybridization is dominant, whereas in the other (layers thicker than roughly five to six monolayers) dependence of electric field on the band gaps is more important. The band gap behavior in superlattices is compared with the band gap dependence on composition in the corresponding ternary and quaternary alloys. It is shown that for superlattices it is possible to exceed by far the range of band gap values, which can be realized in ternary alloys. The calculated values of the band gaps are compared with the photoluminescence emission energies, when the corresponding data are available. Finally, similarities and differences between nitride and oxide polar superlattices are pointed out by comparison of wurtzite GaN/AlN and ZnO/MgO.

Keywords: superlattices, nitrides, band structure

(Some figures may appear in colour only in the online journal)

1 Deceased 15 August 2016.
1. Introduction

During recent years properties of In(Ga)N/GaN and also other nitride short period superlattices (SLs), such as GaN/Al(Ga)N and InAlN/GaN, have been intensively studied. Tens of papers have been published covering various aspects from epitaxial growth and band gap, $E_g$, magnitude to light emitting and laser diodes with these SLs as the active region [1–10]. In particular, a large part of the works was devoted to understanding mechanisms of radiative recombination in SLs. According to theoretical considerations, the short period (few atomic layers) SL structures make it possible to cover the significant range of visible and UV spectrum by manipulating with the quantum well (QW) and quantum barrier (QB) layer thicknesses. However, it turns out that experimental realization of these structures is very difficult.

Until recently, applied and fundamental research has been focused on InGaN, AlGaN, and much less known AlInN alloy. The main interest was concentrated on covering the spectral range of emitted/absorbed light from infrared to deep ultraviolet. The most challenging part includes preparation of InGaN with tunable energy gap in the range from $E_g$ equal 0.65 eV (InN) to approximately 2.3 eV (In$_{0.3}$Ga$_{0.7}$N) crucial for optoelectronic applications from infrared to green spectral range. It is well known that ternary In$_{x}$Ga$_{1−x}$N alloys exhibit an effect of phase separation introducing macroscopic potential nonuniformities in In$_{x}$Ga$_{1−x}$N with $x > 0.25$. The pioneering work by Yoshikawa et al. [2, 3] initiated the interest in binary InN/GaN SLs, appearing as an idea to solve the above mentioned difficulties. The approach consisting in the use of mlnN/nGaN SLs, where $m$ and $n$ represent number of atomic monolayers (MLs) of InN and GaN, respectively, is very attractive since they can potentially replace In$_{x}$Ga$_{1−x}$N alloys with high $x$. Because of limited amount of experimental data on InN/GaN due to difficulties in the epitaxial growth of these SLs [11, 12] many papers concentrate on theoretical considerations of their electronic band structure and structural properties [6, 7, 10, 11].

Band gap engineering, crucial for the design of optoelectronic devices, can be realized in alloys by changing the chemical composition, whereas in SLs ‘tailoring’ of the SL band gaps can be made by varying the layer thicknesses ($m$ and $n$) and also by manipulation with lattice geometry, which we can call geometrical lattice engineering. In figure 1 we present schematically possible growth orientations of the quantum structures in the wurtzite structure. Crystal growth can be made along polar $c$-axis, two nonpolar directions, $a$ and $m$, and six semipolar orientations (s1 to s6). We illustrate schematically the valence- and conduction-band profiles for each case. Strong internal electric fields originating from the macroscopic polarization are present in polar structure changing the shape of the band profiles and leading to small, indirect gaps in a real space. The internal electric fields are weaker in semipolar structures, and there is no built-in electric fields in nonpolar SLs. Another factor influencing the band gap behavior is the internal strain caused by lattice mismatch between QW and QB layers. Analysing the influence of all these factors on $E_g$ values one has to keep in mind a specific feature of short period SLs, which is the effect of the QW and QB wave functions hybridization. Strong effect of hybridization is observed for thin QW and QB layers (usually up to 5–7 MLs.)

To realize band gap engineering it is important to understand the role of all the factors influencing the band gap behaviour and to understand their role in the evolution of $E_g$. In this work, based on first principles calculations, we discuss all these factors. By comparing band gaps in SLs grown along different directions of the wurtzite structure, or with different atomic arrangements, we demonstrate the effects of lattice geometry. To answer the question how the internal strain influences the $E_g$ values, two cases of growth conditions are compared: the pseudomorphic ($a$-lattice constant of QW matches to QB) and free-standing ($a$-lattice constant of the SL is an average of QW and QB lattice constants). It will be shown in this review that assuming given growth orientation and strain conditions, the band gaps are influenced mainly by the built-in electric field, $E_d$ (in polar structures) and by the wave function hybridization. The picture presented is somewhat simplified, but we believe that it can describe rather well the main trends in the SL band gap behavior, qualitatively and quantitatively.

In the next sections, after the description of the method of calculations in section 2, we discuss the above issues in detail. As an introduction to SL band structure calculations, and in order to obtain a suitable reference point, a short presentation of the results obtained for nitride alloys: In$_{m}$Ga$_{1−m}$N, In$_{n}$Al$_{1−n}$N, and Ga$_{1−n}$Al$_{n}$N is given in section 3. We demonstrate how to go from ordered alloy, also named in the literature as ‘digital alloy’, to short period SL. Then, in section 4, polar InN/GaN and GaN/AlN SLs are considered. Most of the issues discussed here are related to the polar structures grown along the $c$-axis (i.e. $(0001)$ direction) of the hexagonal wurtzite structure. We analyse the $E_g$ evolution in free-standing and pseudomorphically grown SLs. The contributions from the internal strain, built-in electric field and wave function hybridization are evaluated. Different methods (model and ab initio) of the electric field strength evaluation are presented. It is demonstrated that the effect of wave function hybridization is dominant for narrow wells and barriers, whereas for wider layers in polar SLs the influence of the internal electric field is more important. In particular, in order to consider the oscillator strength, crucial for light emitters, we calculate the wave function overlaps. Semipolar (we choose to study in this work two directions, $s2$ and $s6$) and nonpolar SLs are considered in section 5. The results for mlnN/nGaN SLs are compared with the polar case. The SLs containing alloys, as mln$_{m}$Ga$_{1−m}$N/nGaN, mln$_{n}$Ga$_{1−n}$N, and mln$_{m}$Ga$_{1−n}$/nGaN are analysed in section 6. The band gap behavior in these SLs is compared with the gap evolution in binary SLs. As it was already pointed out obtaining mlnN/nGaN SLs is very difficult [11]. Instead of intentionally introduced InN QWs likely In$_{x}$Ga$_{1−x}$N layers are grown in such structures [12].

Using both growth method metalorganic vapour phase epitaxy and molecular beam epitaxy (MBE), QW In$_{n}$Ga$_{1−n}$N structures with $x < 0.4$ are produced [13, 14]. The obtained photoemission energies for mln$_{m}$Ga$_{1−m}$/nGaN SLs with given In content, $x$, and layer widths, $m$ and $n$ are compared with the calculated band gaps for these SLs. As the last issue,
in section 7 we compare the polar wurtzite GaN/AlN and ZnO/MgO short period SLs pointing out similarities and differences in the band gaps behavior of these two systems. In many respects GaN and AlN are similar to ZnO and MgO, respectively, especially regarding the band gaps and the lattice parameters. We found similar evolution of the GaN/AlN and ZnO/MgO band gaps with varying number of atomic MLs, whereas band gap bowings and strength of the internal electric field existing in these two families of SLs differ significantly. Finally, we conclude with a brief outlook for the field.

2. Methodology

The electronic band structures of the nitride alloys and SLs have been analysed in a supercell model by selfconsistent calculations based on the local density approximation (LDA) to density functional theory, with the Perdew–Zunger parameterization [15] of the Ceperley–Alder exchange-correlation [16]. The calculations were performed by two different computational methods. To determine the atomic coordinates by minimization of the Hellmann–Feynmann forces the pseudo-potentials implemented in the Vienna *ab initio* simulation package (VASP) [17] were used. The converged results were obtained with a 600 Ry of energy cutoff and the *k*-space integrations were performed by summing over a 5 × 5 × 5 mesh of Monkhorst–Pack special points [18]. The obtained relaxed atomic positions were used as an input to the energy band structure calculations by the full-potential version [19] of the linear-muffin-tin-orbital (LMTO) method [20]. The semi-core 

cation $d$ states of Ga(3$d$) and In(4$d$) were treated as local orbitals [21]. The supercell contains ‘empty’ muffin-tin spheres in the interstitial regions for more accurate interpolation of the charge density. Further details of the calculations are given in [22, 23].

The semi-empirical procedure (LDA + C) has been applied to correct the underestimated by LDA band gap values. In this procedure additional external potentials, $V(r)$, are introduced at the sites of the atoms [23]:

$$V(r) = V_0 \left( \frac{r_0}{r} \right) \exp \left[ -\left( \frac{r}{r_0} \right)^{2} \right]$$

(1)

where $V_0$ and $r_0$ are adjustable parameters. The potentials are sharply peaked at the nuclear positions, and they produce ‘artificial Darwin shifts’, i.e. they push $s$-states upwards in energy. The LDA + C procedure is relatively simple and it not only corrects the fundamental gap, but also the dispersion of the conduction band and the gaps at other points of the Brillouin zone. This method for correcting $E_g$ errors caused by the LDA was originally developed and extensively used in LMTO calculations [22–27], then in linear augmented plane wave (LAPW) framework [28, 29]. Subsequently, it has also been applied in a pseudopotential method [30].

The parameters used in the external potentials are transferable. They are specific for the atomic species so they can be determined for binary compounds and subsequently applied to other systems as alloys and heterostructures. Also, they are kept unchanged while volume and composition are varied [22–26].
Table 1. The calculated (LDA + C) band gaps in nitride compounds in comparison with experimental values and other theoretical results.

<table>
<thead>
<tr>
<th>v → c</th>
<th>LDA + C</th>
<th>Experiment</th>
<th>Other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>InN</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Γ-Γ 1</td>
<td>0.69</td>
<td>0.65(^a), 0.63(^b), 0.69(^c), 0.75(^d), 0.69(^e), 0.72(^f), 1.04(^g)</td>
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<tr>
<td>M(_{4-15})</td>
<td>3.51</td>
<td>3.6, 3.5 (^h), 3.5, 3.5 (^i), 3.5 (^j), 3.5 (^k)</td>
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</tr>
<tr>
<td>M(_{4-15})</td>
<td>4.47</td>
<td>4.5, 4.5 (^l), 4.5, 4.5 (^m), 4.5 (^n)</td>
<td></td>
</tr>
<tr>
<td>M(_{4-15})</td>
<td>5.44</td>
<td>5.5, 5.5 (^o), 5.5, 5.5 (^p)</td>
<td></td>
</tr>
<tr>
<td>GaN</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Γ-Γ 1</td>
<td>6.00</td>
<td>6.1 (^q)</td>
<td>6.47(^r), 6.11(^s), 5.8(^t), 6.76(^u), 6.28(^v)</td>
</tr>
<tr>
<td>L(_{1-15})</td>
<td>3.51</td>
<td>3.6, 3.5 (^w), 3.5, 3.5 (^x), 3.5 (^y), 3.5 (^z)</td>
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<tr>
<td>M(_{4-15})</td>
<td>4.47</td>
<td>4.5, 4.5 (^aa), 4.5, 4.5 (^ab), 4.5 (^ac)</td>
<td></td>
</tr>
<tr>
<td>M(_{4-15})</td>
<td>5.44</td>
<td>5.5, 5.5 (^ad), 5.5, 5.5 (^ae), 5.5 (^af)</td>
<td></td>
</tr>
<tr>
<td>AlN</td>
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<td></td>
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<tr>
<td>Γ-Γ 1</td>
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<td>8.02 (^ag)</td>
<td>8.95(^ah), 9.4(^ai)</td>
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<tr>
<td>L(_{1-15})</td>
<td>3.51</td>
<td>3.6, 3.5 (^aj), 3.5, 3.5 (^ak), 3.5 (^al)</td>
<td></td>
</tr>
<tr>
<td>M(_{4-15})</td>
<td>4.47</td>
<td>4.5, 4.5 (^am), 4.5, 4.5 (^an), 4.5 (^ao)</td>
<td></td>
</tr>
</tbody>
</table>

3. From nitride alloys to superlattices

Firstly, in order to obtain a suitable kind of reference points for analysing the energy gap behavior in SLs, we present the results illustrating the band gap evolution in nitride alloys.

Particular attention is paid to the \(E_g\) dependence on the composition and atomic arrangements. Cation composition fluctuation (clustering) is simulated by different arrangements of atoms in the supercell and it is shown that in some cases it strongly affects the band gaps. It will be demonstrated below that for a particular clustered configuration of atoms, an alloy can be equivalent to SL.

The electronic band structures of In\(_{x}\)Ga\(_{1-x}\)N, Ga\(_{x}\)Al\(_{1-x}\)N, and In\(_{x}\)Al\(_{1-x}\)N alloys have been analysed for the compositions, \(x = 0.12, 0.19, 0.25, 0.37, 0.50, 0.56, 0.62, 0.75,\) and 0.87 realised in a supercell geometry. Different atomic arrangements have been investigated by distributing cations uniformly over the supercell or by clustering them together in a small part of the SL.

In figure 2, the calculated band gaps of In\(_{x}\)Ga\(_{1-x}\)N (a), Ga\(_{x}\)Al\(_{1-x}\)N (b) and In\(_{x}\)Al\(_{1-x}\)N (c) are shown as functions of composition, \(x\). The lines are fitted to the calculated band gaps and represent bowings for two cases: uniform distribution of cations (solid lines), and clustered distribution (dashed lines).

The determined bowing parameter, \(b\), contains an information about the rate of nonlinearity in \(E_g\) evolution in an alloy with particular composition and atomic arrangement. Generally, it is concentration dependent and for an alloy \(A_xB_{1-x}C\) is defined through:

\[
E_g(x) = xE_g^{MC} + (1 - x)E_g^{RC} - x(1 - x)b(x). \tag{2}
\]

In nitride alloys containing indium the bowing parameter is usually much larger (especially for clustered arrangement of cations) than in other alloys, such as Al\(_{x}\)Ga\(_{1-x}\)N or Al\(_{x}\)Ga\(_{1-x}\)As.

The largest \(E_g\) bowing is found for In\(_{x}\)Al\(_{1-x}\)N (figure 2(c)). It ranges from 2.1 to 6.2 eV for the uniform case, and it is almost twice as large, ranging from 3.9 to 14 eV in the clustered case. It can be compared to the experimental value of about 6 eV (for \(x\) between 0.13 and 0.24) [55] which falls in between our calculated values for both atomic arrangements (uniform and clustered). Influence of the In-content fluctuations on the band gaps (\(\Gamma\)–\(\Gamma\) and \(\Gamma\)–\(X\)) in In\(_{x}\)Al\(_{1-x}\)N were studied by Teles et al [58]. The calculations of [58] were made for the zincblende structure, but the obtained bowing parameters, 2.1 eV for uniform and 6.2 eV for clustered arrangements of In, agree well with our calculated values.

Smaller, compared to In\(_{x}\)Al\(_{1-x}\)N, \(E_g\) bowing is obtained in In\(_{x}\)Ga\(_{1-x}\)N (figure 2(a)). It ranges from 1.7 eV to 2.8 eV, for the uniform case, and from 2.5 eV to 6.5 eV for the clustered case. Experimental values reported in the literature vary between 1.43 eV [49] and 2.8 eV [51]. However, the theoretical are from 1.37 eV [59] and 1.89 eV [60] to 5.14 eV [61]. The composition dependent bowing for cubic In\(_{x}\)Ga\(_{1-x}\)N was obtained by Teles et al [61]. They found large bowing, \(b = (5.14 - 2.59x)\) eV for the minimum gap and smaller for the average band gap, \(b = (0.74 - 0.10x)\) eV.

To determine the LDA + C correction parameters for the purpose of our study, we have to know experimental values of binary nitride band gaps. The available experimental data for InN, GaN, and AlN are presented in table 1, together with our adjusted (LDA + C) band gaps and in comparison to other theoretical values. The adjustment is made simultaneously for all the binaries considered. For InN, the adjustment was made to the experimental data for the main energy gap [31–34], to the results of spectroscopic ellipsometry on MBE grown InN films [35] after the assignments made in [36], and to the results of other experiments [37, 38]. For GaN and AlN, the adjustment was made using the experimental results from [37, 39–41]. The comparison to other theoretical results consists of: LDA calculations [42, 43], calculations using the \(G_0W_0\) approximation to many-body perturbation theory [44], GW calculations by Rubio [45], ‘quasiparticle selfconsistent GW’ calculations [46], and two particularly relevant results for GaN [47], and AlN [48], obtained entirely from first principles calculations.

Optimal values of the LDA + C parameters obtained from the adjustment procedure are the following: \(V_0(\text{In}) = V_0(\text{N}) = 0\), \(V_0(\text{Ga}) = 900\) Ry, \(V_0(\text{Al}) = 990\) Ry, with the range parameter \(r = 0.015\) a.u. for all the atoms. At the empty spheres \(V_e = 0.60\) Ry, being \(r\)-independent. Subsequently, we use the above parameters in the LMTO band structure calculations of nitride alloys and SLs.
The energy gap bowing found in Ga$_x$Al$_{1-x}$N, see figure 2(b), is the weakest, and the difference between the uniform and clustered In-distribution is quite small. The theoretical values range from 0.75 eV for uniform to about 1 eV for the clustered case. A detailed discussion of the Ga$_x$Al$_{1-x}$N gap bowing was performed by Lee et al [62]. These authors divide the available experimental data, according to reliability, into three groups: A. negative bowing, B. positive large bowing, C. positive small bowing. Their analysis leads to preference of the data in group C.

The $E_g$ reduction, $\Delta E_g$, observed in the clustered case is the largest for $x = 0.25$, in both, In$_x$Al$_{1-x}$N ($\Delta E_g = 1.2$ eV) and In$_x$Ga$_{1-x}$N ($\Delta E_g = 0.5$ eV) alloys. Similar analysis was performed by Mäder and Zunger [63] for other more typical III–V alloys. The biggest reduction of $E_g$ that they obtained for In$_{0.5}$Ga$_{0.5}$P (0.13 eV) leads to the conclusion that the clustering effects are pronounced in alloys containing indium and that they are much more significant in nitrides than in other III–V semiconductor alloys, which points out a special role of indium and nitrogen.

Observing the experimental data presented in figure 2 for all the alloys considered we can see that generally they are placed between our two curves corresponding to uniform and clustered arrangements of atoms. It could indicate that the scatter in the experimental $E_g$ values could be caused by different degree of clustering in samples grown in different laboratories. It is demonstrated in figure 3 that the clustering can be realized in different ways. As an example, the case of 4 In in the 32-atom In$_x$Al$_{1-x}$N supercell ($x = 0.25$) is considered. In one possible clustered configuration 4 In atoms are the neighbours of the same N atom (figure 3(a)). In the other case (figure 3(b)) every fourth cation hexagonal layer consists entirely of In atoms. In the uniform arrangement to each N atom belong 1 In and 3 Al neighbours. Looking at figure 3(b) one can notice that clustered case where every fourth cation of the hexagonal layer consists entirely of In atoms in In$_{0.25}$Al$_{0.75}$N alloy, is exactly equivalent to 1InN/3AlN SL. This kind of ordered alloy is also known in literature as ‘digital alloy’ [64, 65].

For more details concerning band gap-bow ing and clustering effects in nitride alloys see [66–68].
SLs enables to go far beyond the limitation of fer substantially from the gaps of the alloys. The concept of effective composition $x$. Generally, the band gaps of SLs differed at first and compared with $n$ GaN/AlN SLs. The simpler $m$ InN/GaN SLs will be considered at first and compared with $m$ GaN/nAlN SLs. The simpler notation: $m/n$ will be often used.

### 4. Polar mInN/nGaN and mGaN/nAlN SLs

The main subject of this review is related to the band gap engineering, i.e. dependence of the band gaps on the thickness of the constituting layers. It will be discussed in detail including all the factors influencing the band gap behavior. As most of the issues discussed here concern the polar nitride structures grown along the $c$-axis (i.e. $(000\bar1)$ direction) of the hexagonal wurtzite structure, polar $m$InN/nGaN SLs will be considered at first and compared with $m$GaN/nAlN SLs. The simpler notation: $m/n$ will be often used.

#### 4.1. Band gaps

First, it will be shown how the $m$InN/nGaN and $m$GaN/nAlN SLs band gap values differ from the band gaps of the corresponding InGaN and GaAlN alloys (with the same effective In/Ga and Ga/Al composition). In figure 4, the calculated band gaps versus cation (In or Ga) content, $x = m/(m + n)$, for sets of $m$InN/nGaN (figure 4(a)) and $m$GaN/nAlN (figure 4(b)) SLs, are presented. The dashed lines correspond to the calculated band gaps of $m$In$_{1/2}$Ga$_{1/2}$N and $m$Ga$_{1/2}$Al$_{1/2}$N random alloys with ‘uniform’ cation distribution [64].

The first observation is that only for the sets of $m/1$ SLs the band gaps are similar to $E_g$'s of random alloys with the same effective composition $x$. Generally, the band gaps of SLs differ substantially from the gaps of the alloys. The concept of SLs enables to go far beyond the limitation of $E_g$ evolution realized in ternary alloys. It is especially visible in the case of $m$InN/nGaN SLs, where calculations give $E_g$ smaller than $E_g$ of binary InN (0.65 eV). It takes place in several cases for $m \geq 3$ and the resulting metallization (closing of the effective band gap) occurs for $m = n \geq 5$. The latter effect was also demonstrated by Miao et al [70] where the possibility of the topological insulator formation was predicted.

Band gaps of $m$GaN/nAlN SLs in accordance with expectations, demonstrate much larger magnitude than $E_g$'s of $m$InN/nGaN SLs. Their deviation from band gaps of $m$GaN/nAlN random alloy are much smaller than in case of In-containing SLs. For the $1/n$, $2/n$, and $3/n$ SLs $E_g$ increases with increasing barrier thickness. For the set $5/n$ the gap is almost independent of $n$, while for the set $7/n$ there is a slightly decreasing dependence on $n$. Only for the $7/n$ type SLs band gaps smaller than the gap of pure GaN (3.6 eV) appear.

The calculated band gaps of $m$GaN/nAlN SLs (see figure 4(b)) are compared with the PL emission energies measured for 3 samples of SLs grown by MOVPE [4]. The declared layer thicknesses, $m/n$ for these samples are: 0.9/7.2, 1.8/7.3, and 2.5/7.1 (non-integer $m$ and $n$ values reflect the fluctuations of the QW and QB layer thicknesses). The samples were grown pseudomorphically on an AlN substrate and the same pseudomorphic growth conditions were assumed in the calculations. As shown in figure 4(b), a very good agreement is obtained between the calculated $E_g$ and the emission energies measured on the set of samples.

The results for InN/GaN cannot be compared to experimental data. Earlier published experimental data for samples of nominal InN/nGaN SLs [71] likely represent SLs with InGaN alloy in a QW. It was found [11] that their real composition was 1In$_{0.33}$Ga$_{0.67}$N/nGaN. Indium incorporation lower than 100% in the QW may be a general property for all ‘InN ML’ samples presented so far. The results for the In$_{1/3}$Ga$_{1/3}$N/nGaN SLs will be presented and discussed in section 6.

To discuss further the band gap engineering in nitride SLs, an example of $m$InN/nGaN SLs will be used. Instead of using rather complicated dependence of $E_g$ on the effective In/Ga content (which was useful for comparison of SLs and alloys), we plot the band gaps as functions of barrier and well thicknesses, i.e. $n$ and $m$. Such a choice corresponds to the growth related approach.

Analysing the $E_g$ dependence on QB and QW thickness, presented in figures 5(a) and (b), respectively, one observes that the band gaps are more sensitive to the well thickness than to the barrier width. Regarding the dependence on barrier thickness (figure 5(a)) the $E_g$ at first (for $m = 1$) increases

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**Figure 4.** Calculated band gaps, $E_g$, for $m$InN/nGaN (a) and $m$GaN/nAlN (b) SLs versus chemical composition, $x$, compared with calculations performed for the corresponding In$_x$Ga$_{1-x}$N and Ga$_x$Al$_{1-x}$N alloys—the dashed curves. Free-standing growth mode is assumed, see explanation in section 4.2. Lines are fitted to the calculated values. Note a different scale for energy gaps in (a) and (b). Reprinted from [69], Copyright 2015, with permission from Elsevier. Experimental data in figure 4(b) are from [4].
rapidly up to \( n = 5 \), then saturates. In contrast, for SLs with more than one InN ML the band gap decreases with increasing well and barrier thickness. As it is shown in figure 5(b), \( E_g \) decreases strongly with increasing well thickness and this dependence is more pronounced for larger \( n \) values. The crossover from increasing to decreasing trend occurring already for well width \( m = 2 \) (figure 5(a)) is clearly seen in figure 5(b).

4.2. \( E_g \) dependence on internal strain

To study the influence of the internal strain on \( E_g \), we can simulate different strain conditions. The SL can be grown pseudomorphically on a substrate, thus having fixed in-plane lattice constant equal to the substrate lattice parameter. In this mode, the relaxation of the SL geometry is performed along the growth direction. The other strain mode corresponds to free-standing structure and involves a full relaxation of the atomic positions and lattice parameters.

In the case of the growth of In(Ga)N/GaN quantum structures, the QWs are strongly strained due to 10.6% of lattice mismatch between InN and GaN. Depending on the layer thicknesses and growth conditions, a relaxation of In(Ga)N can take place. It occurs when a thickness of indium containing layers exceeds so called critical thickness. To answer the question how the internal strain in InN wells influences the \( E_g \) values, two cases of growth conditions are compared: the pseudomorphic one, in which \( a \)-lattice constants of InN match to GaN and the free-standing one (\( a \)-lattice constant of the SL is an average of InN and GaN).

The InN/GaN band gaps presented in figures 4(a) and 5 were obtained assuming the free-standing, F-S, conditions, but some of the calculations for InN/GaN SLs were performed also for the case in which the SL is grown pseudomorphically on GaN substrate, which was motivated by the fact that In(Ga)N/GaN structures are often grown on bulk GaN substrate.

Figure 6 shows the calculated band gaps versus layer thicknesses for sets of \( m \)InN/\( n \)GaN SLs in the F-S mode and in the pseudomorphic strain mode. One can observe that all trends in the gap evolution are the same. However, the \( E_g \) values are generally smaller in the pseudomorphic mode, where closing of the gap occurs already for \( m = n \geq 4 \). In the case of 1/\( n \) SLs the difference between both strain modes is very small, but becoming larger for thicker wells, and it is quite pronounced for 5/\( n \) SLs (up to 0.5 eV). It reflects the influence of strain coming from the InN–GaN lattice mismatch on the InN layers, which causes the increasing degree of atomic relaxation along the growth direction.

To get a deeper insight into the problem of internal strain, the calculated atomic positions in three different strain modes are shown in figure 7 for 2InN/2GaN SL.

In the case of pseudomorphic growth to match the GaN barrier, called ‘ps-barrier’, InN layer is compressed to match the lattice \( a \)-constant of GaN. Consequently, the InN layer is thicker (\( c \) parameter larger). Opposite, in the case of pseudomorphic growth on InN, ‘ps-well’, the GaN layer is expanded to match the lattice constant of InN, which is larger and it results in thinner GaN layer (smaller \( c \) parameter). In the free-standing, ‘F-S’ case, the InN layer is somewhat compressed and GaN expanded, leading to an intermediate \( c \) value. The
calculated bond lengths and lattice parameters are compared to the atomic positions and bond lengths in the corresponding InN and GaN bulk materials.

We can observe similar bond lengths in all the strain modes, but different angles between them. The next observation is that the effect of strain is larger in the InN well (layer thicknesses change from 5.09 Å to 5.17 Å) than in the GaN barrier (layer thicknesses change from 5.09 Å to 5.17 Å). It could be explained by ‘softer’ InN bonds. The band gaps of 2InN/2GaN SLs being affected mainly by the InN well (layer thicknesses change from 5.17 Å to 5.19 Å). The bond lengths in 2InN/2GaN SLs in various strain modes: ‘ps-barrier’, ‘F-S’ and ‘ps-well’, see explanation in the text. Open symbols and dashed lines correspond to the corresponding bulk materials. All values are in Å. Reprinted from [69], Copyright 2015, with permission from Elsevier.

4.3. Built-in electric field

The fact that all the trends in evolution of the band gaps with barrier thickness (see figure 6) are the same, independent of the built-in strain, enables us to eliminate the strain effect from further discussion. Now, for a given strain mode, the band gap evolution may be analysed in terms of two counteracting effects: (i) the hybridization of QB on the states in the QW. In 1/5 SLs, contributions to the QB wave functions coming from GaN barrier cause an increase of the $E_g$ from 0.65 eV (bulk InN) to about 2.1 eV in the InN well. Strong influence of the wave functions of GaN QB on the states in InN QW is observed up to $n = 5$, then $E_g$ is almost constant, increasing very slowly. On the other hand, in SLs with wider QWs, the effect of the internal field dominates, leading to the reduction of the $E_g$ values.

Concluding, the effects of lattice relaxation and internal strain are quite significant in InN/GaN SLs, due to large lattice mismatch (calculated values of the $a$ lattice parameter of GaN and InN are 3.155 Å and 3.502 Å, respectively). We can compare this result for InN/GaN SLs with the case of GaN/AIN SLs, where the $E_g$ variations with the different strain conditions are almost negligible (not exceeding 0.05 eV) [72] because of small lattice mismatch (calculated values of the $a$ lattice constant are: 3.101 Å in AIN and 3.155 Å in GaN).

4.3.1. Electric field estimated from the band profiles

Analyzing the band profiles one can estimate the strengths of the internal electric fields from the slopes of the profile curves. As an example, figure 8 shows band profiles with internal electric field directed from the type A interface towards the type B interface in both well and barrier regions in 5InN/5GaN SL. The different characters of the $A$ and $B$ interfaces and strong effect of the internal electric field are clearly seen. The strength of the electric field can be estimated from a linear approximation to the band profiles inside the QW and QB. The obtained values are: $E_{el} = -6.6$ MV cm$^{-1}$ in the InN layers and $E_{el} = 7.7$ MV cm$^{-1}$ in the GaN layers. The gap is indirect in real space and equal to $E_g = 0.25$ eV. The valence band offset, VBO, equal to difference between the valence band maxima in the central layers of InN well and GaN barrier, is estimated to be about 0.5 eV.

4.3.2. Electric field calculated using the N-1s core-states as reference. Values of the internal electric fields can be found from the $ab$ initio calculations by using the N-1s core-states as reference energies. In figure 9, the energies of N-1s core-states, $E_{1s}$, within layers of the 5/5 SLs, are plotted along the [0001] growth direction (polar $c$-axis). The N-1s energy values are different in successive MLs of the SL due to the presence of the induced electric fields. The magnitude of the internal electric field can be found from the slope of the best straight-line fit. The obtained values are: $E_{el} = -7.0$ MV cm$^{-1}$.
Values of the internal electric field decrease with increasing In content from 13 MV cm\(^{-1}\) for 3/7 SL down to 0.2 MV cm\(^{-1}\) for 7/1 SL. In GaN barrier, it increases with increasing In content from 0.9 MV cm\(^{-1}\) for 1/13 SL up to 14.8 MV cm\(^{-1}\) for 7/3 SL. The second observation is that the electric field values obtained for the given effective In composition (\(x = m/(m + n)\)) are slightly different for different layer thicknesses. As an example, we can consider the sequence of 3/3, 4/4, 5/5 SLs (\(x = 0.5\)). Comparing the electric field values for this set, we observe the general trend that internal electric fields, both in QWs and QBs, decrease with increasing number of MLs. Due to this trend we expect in 6/6 SL lower values of the electric field than in 5/5 SL. However, the influence of the electric field on the \(E_g\) values depends also on QW thickness, and despite the weaker electric field in the 6/6 SL, the overall band gap is even smaller than in the 5/5 SL due to the thicker QW and we observe closing of the gap (metallization).

4.3.3. Electric field estimated using a semi-macroscopic model. A semi-macroscopic model where the built-in electric fields in the QWs and QBs of the SL can be obtained from the spontaneous polarization and piezoelectric constants of the corresponding bulk materials, enables to analyze easily the electric fields in SLs for all the compositions and layer widths. The basic equations describing the electric fields: \(E_w\) in a QW and \(E_b\) in a QB are [78]:

\[
E_w = \frac{L_b}{L_w} \left( P_b - P_w \right); \quad (3)
\]

\[
E_b = -\frac{L_w E_w}{L_b}, \quad (4)
\]

where \(P_w\) and, \(P_b\) denote the polarizations in QW and QB, \(L_w\) and \(L_b\) are the QW and the QB thicknesses, \(\lambda_w\) and \(\lambda_b\) are the static dielectric constants of the well and barrier bulk materials.

The polarization contains spontaneous and piezoelectric parts (the \((w,b)\) subscripts are omitted):

\[
P = P_{sp} + P_{pz}. \quad (5)
\]
where \( P_{\text{pz}} \) originates from the distortions due to the lattice mismatch between quantum layers. \( P_{\text{sp}} \) values for bulk materials are given in table 2, whereas \( P_{\text{pz}} \) is expressed by [79]:

\[
P_{\text{pz}} = 2e_31 \varepsilon_{xx} + e_33 \varepsilon_{zz}
\]

(6)

\[
\varepsilon_{xx} = (a_n - a)/a
\]

(7)

\[
\varepsilon_{zz} = -2e_31 \varepsilon_{xx}/e_33,
\]

(8)

where \( a \) and \( a_n \) are the lattice constants of QW or QB bulk material and the substrate, respectively.

We use the described model to get the electric field strengths for InN/GaN and GaN/AlN SLs. The values of parameters used in the calculations are presented in table 2.

Figure 11 presents the calculated built-in electric fields in QWs and QBs of \( m\text{InN}/n\text{GaN} \) (a) and \( m\text{GaN}/n\text{AlN} \) (b) SLs, as functions of the effective composition, \( x \). We observe that, the electric fields are larger in \( m\text{InN}/n\text{GaN} \) than in \( m\text{GaN}/n\text{AlN} \) SLs, reaching 18.3 MV cm\(^{-1}\) in the barrier of \( 7\text{InN}/1\text{GaN} \) and 12.5 MV cm\(^{-1}\) in the barrier of \( 7\text{GaN}/1\text{AlN} \) SL. Larger values of built-in electric fields in \( m\text{InN}/n\text{GaN} \) than in \( m\text{GaN}/n\text{AlN} \) SLs are correlated with the larger lattice mismatch between InN and GaN than between GaN and AlN.

The described model neglects the atomicistic structure of the SL structure; the resulting values of electric fields depend on the effective chemical composition \((m/n \text{ ratio})\), as follows from equations (1) and (2)), but not on the separate values of \( m \) and \( n \) (like in \textit{ab initio} calculations). This originates from using parameters of the bulk materials constituting the SL and neglecting specific SL features. Nevertheless, the agreement between ‘model’ and ‘\textit{ab initio}’ calculated values of \( E_a \) and \( E_b \) is quite good, as we can see from the comparison presented in figure 11. An advantage of the model calculations is that it easily provides the electric field strengths for any values of the QW and QB thicknesses, whereas, by \textit{ab initio} calculations, we cannot obtain the internal electric field values for very thin layers (<3 MLs) and also for rather thick layers (>10 MLs) due to computational restrictions.

![Figure 10](image-url) Absolute values of built-in electric fields in InN well (a) and in GaN barrier (b) of \( m\text{InN}/n\text{GaN} \) SLs as functions of effective In content. Lines are connecting the series of SLs with constant \( m \). Reprinted from [69], Copyright 2015, with permission from Elsevier.

**Table 2.** The spontaneous polarization, \( P_{\text{sp}} \) (in C m\(^{-2}\)), piezoelectric, \( e_{ij} \), elastic, \( c_{ij} \), and dielectric, \( \lambda \), constants used in the model calculations.

<table>
<thead>
<tr>
<th></th>
<th>InN</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>AIN</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td>GaN</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>3.533</td>
<td>3.112</td>
<td>3.186</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P_{\text{sp}} )</td>
<td>-0.035 [79]</td>
<td>-0.095 [79]</td>
<td>-0.027 [79]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \lambda )</td>
<td>15.3 [80]</td>
<td>8.5 [80]</td>
<td>10.4 [80]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( e_{31} )</td>
<td>-0.59 [8]</td>
<td>-0.67 [8]</td>
<td>-0.44 [8]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( e_{33} )</td>
<td>1.14 [8]</td>
<td>1.67 [8]</td>
<td>0.75 [8]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>( c_{13} )</td>
<td>95 [81]</td>
<td>115 [81]</td>
<td>117 [81]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( c_{33} )</td>
<td>235 [81]</td>
<td>372 [81]</td>
<td>400 [81]</td>
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</tbody>
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The dependence of the band gaps on both, wave function hybridization and built-in electric fields will be discussed in the next sections.

4.4. Wave functions hybridization

The selected structure for analyzing the contribution of the wave functions hybridization to the evolution of the band gap will be \( 1\text{InN}/5\text{GaN} \) SL.

In figure 12 the total density of states (DOS), the valence and conduction band profiles, and the valence charge density through the MLs of \( 1\text{InN}/5\text{GaN} \) SL are shown. The band-edge profiles are characteristic for the presence of the internal electric field. Two kinds of interfaces are observed: \( A \)—interface (between the last Ga layer in the GaN2 barrier and the N layer in InN1 well), and \( B \)—interface (between the In layer in the InN1 well and the adjacent N layer in the GaN6 barrier). At the interface \( A \) the valence band maximum, VBM, is in the highest energetic position, whereas at the interface \( B \) the conduction band minimum, CBM, is in the lowest position. Spatial separation of the CBM and VBM results in the band gap indirect in real space and with reduced magnitude. It is interesting to note that despite the band gap lowering due to the effect of internal electric field, the value of \( E_g \) about 1.95 eV is significantly larger than that of bulk InN, i.e. 0.7 eV. This effect
is caused by hybridization of the InN well and adjacent GaN barrier wave functions.

Separation of the VBM and CBM is reflected in an asymmetry of the charge distribution. We can see that charge is mainly localized on N sites, and interfaces A and B are not equivalent. The charge at the VBM is mainly accumulated at the interface A, in contrast, the CBM charge density is accumulated mainly at the interface B.

We observe also that the electron charge is more delocalized over the entire supercell, while localization near the InN ML mainly occurs for the hole states. Partly, this stems from the much smaller effective mass of the electrons compared to the holes. The calculations reveal an isotropically averaged effective masses for electrons of $m_e = 0.171$ and $m_{hh} = 1.118$ for the heavy holes.

4.5. Competition between internal electric field and wave functions hybridization in the band gaps determination

As was already mentioned, the $E_g$ behavior in mInN/nGaN and mGaN/nAlN SLs, shown in figures 4–6 may be understood mainly in terms of the wave functions hybridization and the influence of built-in electric field. The SL band gap can be decomposed as:

$$E_g (SL) = E_g (well) + \Delta E_{g1} + \Delta E_{g2}, \quad (9)$$

where $E_g (well)$ denotes the $E_g$ of the bulk semiconductor forming the QW, $\Delta E_{g1}$ is the change of the $E_g$ due to the internal electric field, and $\Delta E_{g2}$ includes the effects of hybridization of QW and QB wave functions, and also local atomic relaxations and strains from the substrate matching. $\Delta E_{g1}$ depends on the strength of the electric field and on the QW thickness:

$$\Delta E_{g1} = eEd_w. \quad (10)$$

In figure 13, the calculated electric fields (a) and $\Delta E_{g1}$ (b) as functions of barrier thickness are shown for mInN/nGaN SLs. We observe that the lowering of the SL band gaps for wider wells can be explained by the influence of the electric fields.

Having determined $\Delta E_{g1}$ allows us to compare the mInN/nGaN and mGaN/nAlN band gaps (figure 4) with the gaps, $E_g(\text{hyp})$ for the hypothetical case corresponding to the internal electric field ‘switched off’, i.e.:

$$E_g (\text{hyp}) = E_g (SL) - \Delta E_{g1}. \quad (11)$$
Figures 14(a) and (b) illustrate the band gaps $E_{g(hyp)}$ for the two sets of 3/n and 5/n SLs in $m$InN/nGaN and $m$GaN/nAlN SLs, respectively. We observe that the $E_{g(hyp)}$ are lying closer to the gaps of the corresponding random alloys than $E_{g(SL)}$ and show an increasing trend as a function of the number $n$ of barrier layers, in both $m$InN/nGaN and $m$GaN/nAlN SLs. Hence, we may conclude that the difference in $E_{g(SL)}$ trends between these two systems (see also figures 4 and 5) is mainly due to the stronger internal fields in the QWs of $m$InN/nGaN SLs.

Almost constant values of $E_{g(SL)}$ for both series 3/n and 5/n in $m$GaN/nAlN SLs illustrates the compensation between the effects of the internal field and the hybridization as the barrier width $n$ is varied. As a numerical example, we can consider the 5GaN/7AlN SL, where the estimated reduction of the gap due to the electric field is $\Delta E_{g1} = -0.8$ eV. Thus, $E_{g(SL)} = 3.85$ eV is decomposed into $E_{g(GaN)} = 3.50$ eV, $\Delta E_{g1} = -0.8$ eV and $\Delta E_{g2} = +1.15$ eV, i.e. $\Delta E_{g2}$ is larger than $\Delta E_{g1}$ originating from the internal electric field. On the other hand, for the other hand, for 5InN/7GaN SL we have $E_{g(SL)} = 0.05$ eV, $E_{g(InN)} = 0.7$ eV, $\Delta E_{g1} = -1.2$ eV, and hence $\Delta E_{g2} = +0.55$ eV. In this case, the contribution from the electric field dominates over that from the strain and hybridization effect.

Generally we observe that the gap evolution in thin well SLs is dominated by the hybridization effect, i.e. a wider barrier (larger $n$) leads to a larger value of $E_{g}$. In contrast, in SLs with wider wells the effect of built-in electric fields dominates influencing the band profiles and causing the band gaps to be indirect in real space, reduced in size, and eventually to vanish. This effect is larger in InN/GaN SLs than in GaN/AlN SLs, due to the stronger internal electric fields due to the larger piezoelectric part of polarization. More details can be found in [69].

4.5.1. Oscillator strength. Both effects (i) overlap reduction between hole and electron states in the valence and conduction bands caused by the presence of electric field and (ii) weakening of the wave functions hybridization with increasing barrier thickness, result in a decrease not only the $E_{g}$ values, i.e. PL energy emission, but also the PL intensity. We can connect the PL intensity with the overlap integral between the
electron and hole wave functions, the square of which reflects the oscillator strength (OS) of a band-to-band transition. Experimentally, it is related to the intensity of both a light absorption and PL.

Figure 15 shows the ratio of transition matrix elements of edge transitions for SL and bulk GaN. The OS values for different structures were obtained from an implementation of the projector augmented wave (PAW) method [83] in an existing plane-wave code supporting non norm-conserving Vanderbilt-type ultra-soft pseudopotentials [84], i.e. the Vienna ab initio simulation package VASP [17]. Based on the corresponding PAW-derived all electron wave functions, an implementation of the optical matrix elements in the VASP package is developed. The optical transition matrix elements are given by:

$$ f_{ij} = \frac{2m_e}{\hbar^2} (\varepsilon_j - \varepsilon_i) \sum_{\alpha=x,y,z} \left| \begin{array} {c} \tilde{\Psi}_i \\ \tilde{\Psi}_j \\ \tilde{R}_\alpha \end{array} \right|^2, \quad (12) $$

where $\varepsilon_i, \varepsilon_j$ are the single-particle energies, $m_e$ is the mass of an electron, $\hbar$ is the reduced Planck constant, $\tilde{\Psi}_i, \tilde{\Psi}_j$ are the conduction and the valence wave functions, respectively, and $\tilde{R}_\alpha$ is the position operator. In this formulation, excitonic effects are neglected. The details of this model can be found in [85].

As one can see from figure 15, the highest electron–hole transition probability, i.e. OS, is found for the set of SLs with the shortest barrier, $n = 1$. OS is almost the same for very thin wells, but from $m = 5$, it starts to decrease. For thin wells, it can be explained by a weak effect of the electric field and strong well-barrier wave functions hybridization, whereas, for thicker wells, influence of the electric field is dominant reducing the OS. On the other hand, considering SLs with the single ML in the well ($m = 1$), a strong reduction of the wave functions hybridization occurs with increasing barrier thickness. It causes rapid reduction of the OS at the beginning, and then for thicker barriers, starting from around $n = 5$, the transition rates show tendency to saturate (around $n = 15$ the oscillator strength is around 20% of the bulk GaN value). This saturation results from the finite penetration lengths of electron and hole states into the SL barrier (an area in the GaN barrier begins to emerge wherein overlap between hole and electron states is approximately zero).

Concluding, we demonstrated that the effect of wave functions hybridization in SLs is dominant for narrow wells, whereas for wider wells, the effect of internal electric field is more important. We predicted theoretically that the PL emission intensity should drop with the increasing widths of SL layers, especially with QB thickness, as was shown for GaN/AlN SLs [86]. Unfortunately, experimental confirmation for InN/GaN SLs is not possible, due to the lack of structures with binary InN QWs. It seems that large lattice mismatch between InN and GaN as well as low structural stability of InN requiring significantly lower growth temperature make the task of obtaining InN/GaN SL very challenging.

5. Semipolar and nonpolar $\text{minN/nGaN}$ SLs

The electric fields reduce the overlap of the electron–hole wave functions and lowers the related radiative recombination rates. Consequently, the efficiency of optoelectronic devices, both LDs and LEDs drops down [87–89]. One way to reduce or even eliminate the internal electric field is to grow the quantum-well structures and related emitters along the semipolar or nonpolar $m$ and $a$ directions. The hexagonal unit cell of the wurtzite structure with indicated polar and nonpolar planes and corresponding growth directions is presented in figure 16.

Already in 2000 it was demonstrated [90] that epitaxial growth of GaN/AlGaN in a nonpolar direction allows fabrication of quantum structures free of electrostatic fields, with an improved optical efficiency. Nonpolar and semipolar InGaN/GaN laser diodes were demonstrated already, see for example [91–94]. Beside the application oriented studies, one observes also a growing interest within the nitride community in the fundamental properties of such structures. It motivates theoretical investigations of semi- and non-polar SLs.

5.1. Nonpolar $\text{minN/nGaN}$ SLs

The band structures of nonpolar $\text{minN/nGaN}$ SLs were investigated for two possible growth directions, along the $a$ (1 1 20) and $m$ (10 10) axes. Arrangements of atomic MLs along these directions are illustrated in figure 17 for the example of 2InN/2GaN SL. In the case of SL grown in the $a$-direction, all the MLs are separated by the same distance $a/2$, whereas MLs of SL grown in the $m$-direction can be separated by about 0.29$a$ or 0.58$a$, and consequently two non-equivalent arrangements of MLs are possible. We call them $m1$ and $m2$.

Figure 18 shows the relaxed atomic positions in 2InN/2GaN SLs for the three cases: $a$, $m1$, and $m2$. We observe that the relaxation of the atomic coordinates is different in the $m1$ and $m2$ case. The bond lengths are shorter in the $m2$ case inside
the GaN layers and slightly longer inside the InN layers than in the m\textsubscript{1} case.

The calculated variations of the band gaps with effective In composition are presented in figure 19 for m\textsubscript{InN}/n\textsubscript{GaN} SLs grown in the a-direction (a) and the m-direction (b). Comparison with the band gaps of polar SLs (grown in the c-direction) is shown in figure 19(a). The dashed lines in figure 19 represent the calculations for In\textsubscript{x}Ga\textsubscript{1−x}N alloys with a quasi-random (‘uniform’) cation distribution [64–66].

Figure 19 shows that all the observed trends are alike for the a- and m- growth directions: \(E_g\) increases with increasing barrier thickness \(n\) and decreases with increasing well thickness \(m\) reflecting (as in the case of alloys) the dependence of \(E_g\) on composition. This tendency is in the case of polar SLs valid only for \(m = 1\), whereas, for higher values of \(m\), \(E_g\) decreases also with increasing barrier thickness \(n\). All the gaps of the nonpolar SLs are lying rather close to the curve for random In\textsubscript{x}Ga\textsubscript{1−x}N alloys (dashed lines), whereas they are much smaller in the polar case. We observe also that the gaps of SLs grown in the a direction (figure 19(a)) tend to be slightly larger than those of the SLs grown in the m-direction (figure 19(b)), illustrating the dependence of \(E_g\) on SL geometry, but the band gaps depend not only on the growth direction (a or m) of SL, but also on the atomic arrangement (m\textsubscript{1} or m\textsubscript{2}) for the m growth direction. Two possible arrangements of atomic layers for even/even SLs grown in the m direction lead to different values of the band gaps (represented by solid and dotted lines).

Figure 16. Sketch of the polar (a) and nonpolar-a (b) and nonpolar-m (c) crystallographic planes in the wurtzite structure.

Figure 17. Positions of MLs in 2InN/2GaN SLs grown in m and a directions in projection to the x-y plane. In atoms are indicated by red dots and Ga by open black circles. The corresponding anions are shifted in z direction. For the m growth direction, two possible arrangements of atoms: m\textsubscript{1} and m\textsubscript{2} are shown. The values of x and y are in units of the lattice parameter a. Reprinted with permission from [82]. Copyright 2013, AIP Publishing LLC.

Figure 18. Relaxed positions of atoms in 2InN/2GaN SLs grown in a direction and in m direction with two arrangements of atoms (m\textsubscript{1} and m\textsubscript{2}). In atoms are indicated by red dots, Ga atoms by open circles, and N by smaller black dots. Reprinted with permission from [82]. Copyright 2013, AIP Publishing LLC.
As already discussed, the low values of the band gaps in polar SLs originate from the strong internal electric fields present in these structures, which determines the effective $E_g$. The electric field leads to a spatial separation of the VBM and CBM density of states. Consequently, the ‘indirect in real space’ band gap becomes very small for thick layers. In contrast, in nonpolar SLs, grown along the $a$- or $m$-axis of the wurtzite structure, there is no macroscopic polarization and no internal electric field. Polar and nonpolar SPLs with the same composition show difference in the band gap values above 1 eV. A similar energy difference arises when we ‘switch off’ the electric field in polar SLs (see figure 14(a)).

In figure 20, band gaps of $3\text{InN}/n\text{GaN}$ SLs are presented for 3 growth directions, $a$, $m$ and $c$, and compared to hypothetical band gaps of $c$-SLs with ‘switched off’ electric field. We observe that indeed differences in the band gaps between polar and nonpolar SLs come mainly from the existence of electric field in polar structures, but the effect of geometry itself has to be taken into account also.

The relaxed atomic geometries, the valence and conduction band profiles, and the probability densities for the VBM and CBM states through the $1\text{InN}/5\text{GaN}$ MLs are illustrated in figures 21(a) and (b), for the $a$- and $m$-growth orientations, respectively. Figure 21 shows that the charge distribution along the growth direction is significantly different for nonpolar SLs and polar (see figure 12) SLs. In the absence of an internal electric field, the band profiles are flat, the band gap is ‘direct in real space’ and significantly larger (3.05 eV—$a$ direction, 2.75 eV—$m$ direction) than in the polar case (1.95 eV). Also, there is no noticeable charge transfer between the layers. The relaxation of atomic positions leads to In–N bond lengths slightly shorter than in pure InN, but different for $a$ and $m$ cases due to different geometry of the supercell.

In conclusion, comparing the $E_g$ behavior for three differently oriented SLs, two aspects should have been in focus: the influence of internal electric fields (comparison of polar and nonpolar SLs) and the dependence on lattice geometry (comparison of $a$- and $m$-oriented nonpolar SLs). It is interesting to note that the band gaps depend not only on the growth direction and the widths of the layers, but also on the arrangements of layers, and atomic positions inside the layers. This was illustrated by the band gaps in two different types of $\text{InN}/\text{GaN}$ SLs grown in the $m$ direction.

As has been discussed for a variety of semiconductors, the pressure coefficient of the band gap $dE_g/dp$ supplies an important information about mechanisms controlling a behavior of the band gap [95]. In particular, in the case of polar nitride quantum structures $dE_g/dp$ exhibits a significant reduction with respect to the alloys with equivalent composition [96]. The internal electric field present in quantum structures is responsible for this effect. In this context it is interesting to study the dependence of $dE_g/dp$ on the growth directions. The calculated $dE_g/dp$ for selected polar and nonpolar SLs is shown in figure 22. One can see that, in agreement with expectations, the band gap pressure coefficients in nonpolar SLs are
lying very close to the curve presenting $dE_g/dp$ obtained for In$_x$Ga$_{1-x}$N quasi-random alloys and close to the InN band gap pressure coefficient (28 meV GPa$^{-1}$). In contrast, $dE_g/dp$ calculated for polar In$_x$Ga$_{1-x}$N alloys has significantly lower values, which decrease further with QW ($m$), and QB thickness ($n$). The gaps and their pressure coefficients for nonpolar SLs (especially those grown in the $m$ direction) vary with composition in a similar fashion as those calculated for ‘bulk’ In$_x$Ga$_{1-x}$N alloys.

Figure 21. Relaxed positions of atoms (in Å)—top, band-edge profiles—middle, and band-edge electron densities—bottom, through MLs of 1InN/5GaN SL grown in $a$-direction (a), and $m$-direction (b). $A$ and $B$ denote two different interfaces. The gray areas represent planes shifted up by 0.8 Å in (a) and 1.6 Å in (b). Reprinted with permission from [82]. Copyright 2013, AIP Publishing LLC.

Figure 22. Calculated band gap pressure coefficients, $dE_g/dp$, for nonpolar 1InN/nGaN SLs grown along the $a$- and $m$-directions in comparison with the $dE_g/dp$ calculated for polar SLs [19]. Results of the calculations performed for In$_x$Ga$_{1-x}$N quasi-random alloys are represented by the dashed curve. [97] John Wiley & Sons. Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

More details on the nonpolar SLs can be found in [97].

5.2. Semipolar $m$InN/nGaN SLs

Significant efforts during the last 15 years have been devoted to studies of semipolar nitride quantum structures and devices [10, 70, 93, 98]. It is interesting to consider theoretically their electronic band structure and verify the expectation that their properties represent intermediate cases with respect to polar and nonpolar SLs.

There is a wide variety of the growth directions enabling realization of the semipolar type of structures. For the purpose of illustration, two selected cases will be used: SLs grown along the $s_2$ and $s_6$ directions. Figure 23 shows the hexagonal unit cell of the wurtzite structure with the $s_2$-plane...
Figure 24. Top view of the relaxed atomic structure of the 1/5 SLs grown in the s2-direction (a), and the s6-direction (b) of the wurtzite structure. Only the atoms within the SL unit cell are shown. A and B denote two different interfaces. The bond lengths and ML widths are indicated (in Å). In the lower panel, the corresponding local valence- and conduction-band edges are traced through the SLs. Reprinted with permission from [101]. Copyright 2014, AIP Publishing LLC.

(a) and s6-plane (b) indicated. The s2-plane is defined by the orthogonal directions [1 1 0 0] and [1 1 2 3], corresponding to the vectors \( \vec{v}_1 = \vec{a}_1 - \vec{a}_2 \) and \( \vec{v}_2 = \vec{a}_1 + \vec{a}_2 - \vec{c} \) (in terms of the lattice vectors shown in figure 23(a)). The s2 growth direction is then given by the direction of \( \vec{v}_1 \times \vec{v}_2 \), which is along \( \vec{b}_1 + \vec{b}_2 + 2\vec{b}_3 \), in terms of the reciprocal lattice vectors \( \vec{b}_i \). Similarly, the s6-plane, illustrated in figure 23(b), is defined by the orthogonal directions [1 2 1 0] and [1 0 1 4], which correspond to the vectors \( \vec{w}_1 = -\vec{a}_2 \) and \( \vec{w}_2 = 2\vec{a}_1 + \vec{a}_2 - 4\vec{c} \), with the normal given by the direction of \( \vec{w}_1 \times \vec{w}_2 = 2(2\vec{b}_1 + \vec{b}_3) \).

The electronic structures of semipolar mInN/nGaN SLs have been calculated and compared to similar calculations for polar SLs (grown along the c-direction) and nonpolar SLs (grown along the a- and m-directions).

In figure 24, the relaxed atomic positions are shown through the MLs of the 1/5 SLs grown in the s2 (a) and s6 (b) directions. For the s2-SL, the constructed supercell contains two cations and two anions in one ML, whereas there are four cations and four anions in one ML in the s6-SL geometry, which lie at different coordinates along the growth direction leading to the formation of characteristic staggered interfaces [99, 100]. The average ML separation is indicated in figure 24, showing a local enhancement at the InN ML. In both cases (s2 and s6), the bonds in the vicinity of the interfaces A and B are generally shorter than in the corresponding binaries (InN: 2.15 Å, GaN: 1.95 Å). We observe also that the atomic relaxations are more complicated in the s6 case (the local bonds around the four cations within each ML are not identical).

In the lower panel of figure 24, the valence and conduction band edges are traced through the SL showing typical band edge profiles of a SL with an internal electric field directed from the A interface towards the B interface in both QW and QB regions. The SL band gap (‘indirect in real space’) is the difference between the overall VBM (which is found at the InN layer at interface A) and the overall CBM (which is found at the InN layer at interface B). Its magnitude is \( E_g = 2.9 \text{ eV} \) for the s2-SL and \( E_g = 2.4 \text{ eV} \) for the s6-SL. The above results can be compared to the polar case where much stronger asymmetry in the bond lengths and charge distribution is leading to larger slopes of the band edge profiles and even smaller ‘indirect’ band gaps. Thus, semipolar SLs, with weaker influence of the electric field on the band structure than found for polar SLs, represent ‘intermediate’ case between polar and nonpolar SLs.

To further investigate the relation between the internal electric field and the band gap, the electric fields were estimated for several s2- and s6-SLS and compared with the values obtained for polar SLs. The electric field strengths were obtained by using the N-1s core-levels as reference energies by the procedure described in section 4.3.2. Examples of the obtained values of the electric field for semipolar and polar SLs are given in table 3. As it was already mentioned, it is not possible to find the electric field value for one or even two MLs. As it results from table 3, the electric field strengths are quite similar for the s2- and s6-SLS ranging from 1 MV cm\(^{-1}\) to 4.9 MV cm\(^{-1}\), but much smaller than those obtained for polar structures (between 3.6 MV cm\(^{-1}\) and 15.6 MV cm\(^{-1}\)) for the same range of compositions.

The calculated band gaps, \( E_g \), versus In content, \( x = m/m + n \), for semipolar \( m/n \) s2-SLS are compared in
The effects of internal strain and cation clustering are discussed in detail. The hybridization of well and barrier wave functions is discussed in their behavior. The role of the built-in electric field and the polar structures are also taken into account. The discussion includes comparison with existing experimental data. It turned out that obtaining mInN/nGaN SLs is very difficult. There has been an increasing amount of structural studies which show that instead of intentionally introduced mInN QWs InGaN SLs grown along the wurtzite axis with the corresponding random alloys (In, Ga1−yN) are presented. The band gaps are shown as functions of barrier: well ratio, In content, x, and layer widths, m and n are compared with the calculated band gaps for these SLs.

In conclusion, studying different types of SLs two aspects have to be taken into account: the influence of internal electric fields (comparison of polar, semipolar, and nonpolar SLs) and the dependence on lattice geometry (comparison of nonpolar SLs in the a- and m-direction, as well as semipolar SLs in the s2- and s6-direction).

6. SLs containing nitride alloys

In the following we discuss the band gaps of short period mGaN/nGaN SLs grown in the c-axis (polar structures) and we analyze the main factors influencing their behavior. The role of the built-in electric field and the hybridization of well and barrier wave functions is discussed in detail. The effects of internal strain and cation clustering are also taken into account. The discussion includes comparison with existing experimental data. It turned out that obtaining mInN/nGaN SLs is very difficult. There has been an increasing amount of structural studies which show that instead of intentionally introduced mInN QWs InGaN SLs grown in such structures. Using both growth method MOVPE or MBE structures with x not larger than 0.4 are obtained. The photoemission energies for mInN/GaN SLs with given In content, x, and layer widths, m and n are compared with the calculated band gaps for these SLs.

6.1. mInGaN/nGaN and mGaN/nGaN SLs

Figure 26(a) shows the calculated band gaps, E_g, for sets of mInGaN SLs with three different compositions in the InGaN well: y = 0.25, 0.33 (one set, 1/n) and y = 0.5 (various choices of m/n). In figure 26(b) the gaps for mGaN/nGaN and mGaN/nGaN SLs with the composition in the GaN barrier: y = 0.5 (selected sets m/n) and y = 0.67 (one set, m/1) are presented. The band gaps are shown as functions of effective cation composition in order to compare to the E_g’s of the corresponding random alloys (InGaN and GaN). The calculated band gaps in both, the mGaN/nGaN and mGaN/nGaN SLs increase with increasing barrier thickness and decrease with increasing well thickness. They deviate from the E_g’s of the corresponding alloys, especially for wider QWs and QBs. This effect is more pronounced in mInGaN/nGaN SLs.

Table 3. The values of the electric fields (in MV cm−1) in semipolar m/n SLs grown in s2 and s6 directions in comparison with those calculated for nonpolar (a and m) SLs and polar (c) SLs. Reprinted with permission from [101]. Copyright 2014, AIP Publishing LLC.

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Figure 25. The calculated band gaps for semipolar s2 (a) and s6 (b) mInN/nGaN SLs in comparison with those calculated for nonpolar (a and m) SLs and polar (c) SLs. Reprinted with permission from [101]. Copyright 2014, AIP Publishing LLC.
Analysing figure 26(a) we observe that the calculated band gaps for $1\text{In}_y\text{Ga}_{1-y}\text{N}/n\text{GaN}$ SLs with lower $y$ ($y = 0.25$ and $0.33$) are significantly larger compared to the analogical set ($1/n$) of SLs with $y = 0.5$ and they are also lying much higher than the gaps of $1\text{InN}/n\text{GaN}$ SLs (see figure 4(a)). And even higher than the band gaps of the In$_x\text{Ga}_{1-x}\text{N}$ alloy. It can be explained by the fact, that for lower $y$, gaps are less affected by the internal electric field (decreasing the gaps) due to smaller lattice mismatch between QW and QB and more dominated by the hybridization effect which increases the $E_g$ values.

The main factors influencing the band gap behavior will be discussed in more details in the next sections.

6.1.1. Comparison with experimental data. The calculated band gaps are compared to PL energies measured on a set of $1\text{In}_{0.33}\text{Ga}_{0.67}\text{N}/n\text{GaN}$ samples with $m/n = 1/2$, $1/3$, $1/4$, $1/10$, and $1/40$ (red dots in figure 26(a)) [11]. Intentionally, these samples were grown as $1\text{InN}/n\text{GaN}$ short-period SLs [2], and it was believed that they contain one ML of pure InN. Consequently, the previous theoretical works [72, 103, 104] on InN/$n$GaN SL indicated on significant discrepancy between theory and experiment. The calculated $1\text{InN}/n\text{GaN}$ band gaps were about 1 eV lower than the PL energies measured on the mentioned samples.

Several hypotheses were proposed to explain this discrepancy, including the suggestion that optical transitions are due to GaN excitons partially localized in the InN region [11], or that the observed light emission originates from the recombination of carriers located in different spatial regions, i.e. from the GaN QB to the InN QW [25, 69] and that the observed discrepancy was caused by screening of the internal electric fields in the polar structures by free carriers originating from unintentional defects, an effect which was not included and...
in the calculations [82]. The last hypothesis suggested that the inserted layer is not pure InN, but actually consists of a ternary InGaN alloy [70, 71, 99]. To check this hypothesis, quantitative high resolution transmission electron microscopy (TEM) studies were performed on the set of nominal InN/nGaN short-period SLs. It was revealed that the SLs consist of an In$_{x}$Ga$_{1-x}$N ML with an indium content of $x = 0.33$ instead of the intended $x = 1$. Figure 26(a) shows that the calculated gaps of In$_{0.33}$Ga$_{0.67}$N/nGaN SLs are lying close to PL energies measured for the set of samples with In content corrected to the value $y = 0.33$. Lower In incorporation may be a general property for all InN-ML samples presented so far. To make a further comparison between the experiment and theory, under the assumption that the SL samples studied have the same trend as observed in InN/nGaN short-period SLs. It was revealed that the SLs consist of an In$_{x}$Ga$_{1-x}$N ML with an indium content of $x = 0.33$ instead of the intended $x = 1$. Figure 26(a) shows that the calculated gaps of In$_{0.33}$Ga$_{0.67}$N/nGaN SLs are lying close to PL energies measured for the set of samples with In content corrected to the value $y = 0.33$. Lower In incorporation may be a general property for all InN-ML samples presented so far. To make a further comparison between the experiment and theory, under the assumption that the SL samples studied have the same trend as observed in InN/nGaN short-period SLs. It was revealed that the SLs consist of an In$_{x}$Ga$_{1-x}$N ML with an indium content of $x = 0.33$ instead of the intended $x = 1$. Figure 26(a) shows that the calculated gaps of In$_{0.33}$Ga$_{0.67}$N/nGaN SLs are lying close to PL energies measured for the set of samples with In content corrected to the value $y = 0.33$. Lower In incorporation may be a general property for all InN-ML samples presented so far.

6.12. **Influence of electric field and wave function hybridization on the band gaps.** Due to the possibility of comparison with the experimental data, we will concentrate in our analysis on the mIn$_{0.33}$Ga$_{0.67}$N/nGaN SLs.

Figure 29 illustrates the internal electric fields in wells ($E_w$) and barriers ($E_B$) of mIn$_{0.33}$Ga$_{0.67}$N/nGaN and mGaN/nAl$_{0.33}$Ga$_{0.67}$N SLs as functions of number of barrier MLs.

Another set of mIn$_{x}$Ga$_{1-x}$N/nGaN samples, that we can compare to was grown recently [13] by MOVPE technique. Quantum wells thicknesses were 1 MLs and In content, $x$, was in the range from 0.30 to 0.33. The results of PL measurements brought a new information on SL properties since the reported so far experimental results were obtained on SLs with 1 or 2 MLs in QW, only. Figure 28 shows the calculated band gaps of mIn$_{0.33}$Ga$_{0.67}$N/nGaN versus QB thickness for different values of $m$ in comparison with PL emission energies obtained on the fabricated samples. Good agreement between theoretical and the experimental gaps is observed.

Analysing figure 28, we can see that the band gaps increase with increasing barrier thickness for all the considered well widths (up to $m = 5$). Contrary to the case of binary InN/nGaN SLs (figure 5(a)), we do not observe the change of the increasing trend observed for $m = 1$ to decreasing one, for $m > 1$, however, $E_g$ increases more slowly for higher $m$ values. We can interpret it in terms of much weaker, than in InN/nGaN SLs, built-in electric field, which is sensitive to indium content, $x$, in QW. Higher In content leads to higher lattice mismatch between InGaN and GaN layers, resulting in increases the piezoelectric polarization and consequently the electric field strength.
bulk QW material, $\Delta E_{g1} = eE_d w$ is the reduction of $E_g$ due to the internal electric field, $E_d$, and $\Delta E_{g2}$ include the effects of strains, local atomic relaxations, and hybridization of well and barrier wave functions. In figure 30(a), the energy gap shift, $\Delta E_{g1}$, due to the internal electric field, is shown for the set of $mn_{0.33}Ga_{0.67}N/nGaN$ SLs. One can observe that $\Delta E_{g1}$ depends strongly on $m$ and $n$ values. The largest values of $\Delta E_{g1}$, are in SLs with wide QWs and QBs, where the influence of internal electric fields is dominant, whereas, in SLs with thin layers the hybridization of well and barrier wave functions is more significant. The highest estimated reduction of $E_g$ due to the electric field, $\Delta E_{g1} = -0.57$ eV, is found for $7/10$ SL.

By correcting the calculated band gaps for the effect of the electric field, one can obtain gaps, $E_g(hyp)$, for the hypothetical case with the internal electric field ‘switched off’: $E_g(hyp) = E_g(SL) - \Delta E_{g1}$. They are shown in figure 30(b) for three sets of $mn_{0.33}Ga_{0.67}N/nGaN$ SLs: $1/n$, $3/n$ and $5/n$ (solid lines) in comparison with the SL gaps, $E_g(SL)$ (dashed lines).

It can be concluded from figure 30(b) that the $E_g(hyp)$ are lying even higher compared to the gaps of the equivalent random alloy $In_{0.33}Ga_{0.67}N$ than $E_g(SL)$, which effect can be explained by strong wave function-hybridization effect in these SLs.

6.1.3. Oscillator strength. Figure 31 shows the oscillator strength ratio of SL and bulk GaN for the set of $1In_{x}Ga_{1-x}N/nGaN$ SLs with $In$ content $x = 0.33, 0.25$ and $1$. We observe that the oscillator strength ratio increases with decreasing $In$ content in the QW, reaching the strength for $1In_{0.25}Ga_{0.75}N/1GaN$ SL almost equal $0.9$. Also, the character of the dependence on barrier thickness changes drastically. Contrary to $1In_{x}Ga_{1-x}N/nGaN$ SLs, the dependence on layer thickness is quite weak for thin barriers and does not saturate so fast. In particular, the SLs $1/1$ and $1/3$ with $x = 0.25$ are characterized by almost the same oscillator strength ratio. It can be explained by much stronger penetration of well wave functions into the barrier region (especially for thin barriers) than could occur in the case of binary $1In_{x}Ga_{1-x}N$ SLs and also by lower strength of the internal electric fields.

6.1.4. Influence of atomic arrangement on the band gaps—cation clustering. The band structure calculations discussed in the previous section were performed in a supercell geometry modelling a uniform distribution of cations in the GaAlN and InGaN layers of the SL. In practical sample preparation, it is a severe issue whether ideal homogeneity of the random ternary alloys can be achieved, or rather regions of varying relative cation concentration are formed during growth (cation clustering). This may have significant bearings on the predictions of the properties of the SLs, as clustering tends to decrease the effective band gap of the random alloy.

The effects of cation clustering in nitride alloys were studied earlier [66, 67] and a noticeable lowering of the alloy band gap was demonstrated. Here, we undertake a similar study for the SLs.

In figure 32, the calculated band gaps of polar $1In_{0.33}Ga_{0.67}N/nGaN$ SLs for uniform and clustered arrangements of the In atoms in the InGaN QW are compared. Generally, the clustering can be realized in different ways as was already discussed in [66]. Here, we simulate...
Figure 32. Calculated band gaps, $E_g$, of In$_{0.33}$Ga$_{0.67}$N/nGaN SLs for two cases: uniform (blue open circles) and clustered arrangement of In atoms (green dots) in comparison with the experimental data (big red dots) [11]. The values of $n$ are indicated for both experimental and theoretical data. Lines are spline fits to guide the eye. The dashed curves correspond to the calculations performed for In$_{Ga1−x}$N alloys with uniform and clustered arrangements of In atoms [64]. Reprinted with permission from [102]. Copyright 2015, AIP Publishing LLC.

In$_{0.33}$Ga$_{0.67}$N/nGaN SLs by In$_{Ga1−x}$N/$n$GaN SLs are also indicated (blue star, dot and triangle), see description in the text.

Figure 33. Calculated band gaps, $E_g$, for In$_{x}$Al$_{1−x}$/n/nGaN and nGaN/In$_x$Al$_{1−x}$/In$_{x}$Al$_{1−x}$/nGaN SLs (solid lines) in comparison with $E_g$ calculated for In$_x$Al$_{1−x}$/Ga$_{1−x}$/N alloy (red dashed lines) with the same chemical composition. Experimental PL results for nGaN/In$_x$Al$_{1−x}$/nGaN SLs are also indicated (blue star, dot and triangle), see description in the text.

Specific role of In cations was demonstrated above. The observation that the band gaps of SLs with clustered In-arrangements in alloys are substantially smaller than those for the SLs with uniformly distributed In atoms is similar to the trend found for In-containing alloys.

6.2. $m$In$_y$Al$_{1−y}$/N/nGaN

The InAlN band gap can be tuned from about 0.7 eV–6.2 eV. Due to such a large spectral range, quantum structures based on this material are very promising for applications. In this context, studies of band structure evolution in the system of the combined multilayers of In$_x$Al$_{1−x}$/N and GaN forming SLs are interesting and important. The aim of this Section is to show that there is a number of physical problems which require a better understanding. Among them are: (i) expected strong internal strain and built-in electric field, both caused by large InN–AIN and InN–GaN lattice mismatches, (ii) properties of nIn$_x$Al$_{1−x}$/In$_x$Ga$_{1−x}$/N SLs with equal GaN and In$_x$Al$_{1−x}$/N band gap values (3.5 eV) for $y < 0.20$; as a consequence, for $y < 0.2$, we deal with nGaN/mIn$_x$Al$_{1−x}$/N SL, whereas for $y > 0.2$, it is $m$In$_x$Al$_{1−x}$/In$_x$GaN SL, according to the commonly used convention to denote QW/QL in a SL.

In figure 33, the calculated band gaps of mIn$_x$Al$_{1−x}$/In$_x$GaN SLs for $y = 0.83, 0.67, 0.50, 0.33, 0.7, 0.50, 0.33, 0.7, 0.50, 0.33$ and $n$GaN/mIn$_x$Al$_{1−x}$/N SLs with $y = 0.17, 0.12$ are shown for $y = 0.17, 0.12$ as functions of the effective Ga composition $n$. This way of presentation enables a comparison with the quaternary alloys In$_{x−y}$Al$_{1−x−y}$/Ga$_y$N with the same effective contents of In, Al and Ga. More details can be found in [107], where the case $m = 3$ is considered also.
where the band gap increases first, exceeding the bulk value for higher Ga composition, but different layer thicknesses. They are: discussed in the next subsections. 

characteristic features of SLs, as built-in strain, internal electric fields and the wave functions hybridization, which will be explained for SLs in two strain modes; pseudomorphic growth on InAlN substrate (ps-InAlN). 

An exception is the band gap of both types of SLs (y-value either larger or lower than 0.2) we observe that for higher values of n their $E_g$ approaches the GaN band gap (3.5 eV) from the opposite directions (increasing or decreasing with n). An exception is the In$_{0.12}$Al$_{0.88}$N/GaN SL, where the band gap increases first, exceeding the bulk values of both of the constituents for n = 1, then decreases for higher n. As it is shown in figure 33, the band gaps of nGaN/mIn$_{1-y}$Al$_y$N SLs agree well with these In$_{(1-x)}$Al$_x$(1−y)logyy−y−yGaN alloys with the same effective composition. On the other hand, $E_g$ values of mIn$_{1-y}$Al$_y$N/GaN SLs show, especially for thicker barriers, significant deviations from the alloy band gaps. These differences come from the characteristic features of SLs, as built-in strain, internal electric fields and the wave functions hybridization, which will be discussed in the next subsections.

The calculated gaps are compared in figure 33 with PL emission energy measured on the samples with the same effective Ga composition, but different layer thicknesses. They are: 3GaN/3In$_{0.12}$Al$_{0.88}$N [108] (blue dot), 1GaN/7In$_{0.18}$Al$_{0.82}$N [8] (blue star) and 3GaN/7In$_{0.18}$Al$_{0.82}$N [8] (blue triangle). Experimental data for the first two samples are lying close to the calculated curves for SL with the same (or similar) In composition. Observed deviation for the third sample can be explained by the slightly different In composition and by the fact that layer thicknesses in the calculations are different from those in the measured samples. Taking the above into account, one can conclude that the agreement between experiment and calculations is quite reasonable.

6.2.1. Influence of internal strain on the SLs band gaps. To illustrate the role of internal strain, the band gaps are calculated for SLs in two strain modes; pseudomorphic growth on a GaN substrate (ps-GaN), and pseudomorphic growth on InAlN substrate (ps-InAlN).

6.2.2. Influence of electric field and wave function hybridization on the band gaps. An internal electric field of 3.64 MV cm$^{-1}$, due to spontaneous polarization, was reported as obtained from PL measurements performed on a set of nGaN/mIn$_{0.18}$Al$_{0.82}$N quantum structures [8].

The internal electric fields in wells of nGaN/mIn$_{1-y}$Al$_y$N and mIn$_{1-y}$Al$_y$N/GaN SLs estimated from the semi-macroscopic model described in section 4.3.3, are illustrated in figures 35(a) and (b), respectively. The obtained electric fields are compared for selected SLs with the values calculated ab initio by the method described in section 4.3.2 (open circles in figure 35) and quite a good agreement is found, taking into account the model limitations. As it was already mentioned in section 4.3.3, the estimates from the model values of electric fields depend only on well to barrier thickness ratios (as follows from equations (1) and (2)), but not on the separate values of well and barrier thicknesses.

Considering nGaN/mIn$_{1-y}$Al$_y$N SLs (figure 35(a)), strong internal fields are found for very small values of well-barrier thickness ratios, whereas for higher ratios (above 4), they change rather slowly, approaching zero for the ratios above 10. A similar behavior of the electric field was observed in wells of mIn$_{1-y}$Al$_y$N/GaN SLs, with y = 0.67 and y = 0.50 (figure 33(b)). Comparing figures 33(a) and (b) we can conclude that the highest electric fields are obtained for SLs with highest In content, y (up to 9 MV cm$^{-1}$ for y = 0.67) and weaker for SLs with smaller y values. An exception here is mIn$_{0.33}$Al$_{0.67}$N/GaN SL where the electric field almost vanishes for all m/n values. It will be shown that this is due to the compensation of the spontaneous and the piezoelectric polarizations.

The semi-macroscopic model enables to analyze the electric fields in SLs in terms of contributions from the piezoelectric and spontaneous parts of polarization. The calculated spontaneous and piezoelectric components of polarization in nGaN/mIn$_{1-y}$Al$_y$N and mIn$_{1-y}$Al$_y$N/GaN SLs, being differences in polarization between the InAlN and GaN layers, are shown in figure 36. We observe that both, spontaneous, $P_s$, and piezoelectric, $P_p$, parts of the polarization depend almost linearly on In content, y. Around $y = 0.17$ (where well and barrier layers are lattice matched) the piezoelectric polarization vanishes, and only the spontaneous part contributes to

![Figure 34. Calculated band gaps, $E_g$, for 1In$_{1-y}$Al$_y$N/GaN and nGaN/1In$_{1-y}$Al$_y$N SLs in two different strain modes. Solid lines correspond to SLs in ps-GaN strain mode, dashed red lines correspond to SLs in ps-InAlN mode. The vertical blue arrow indicates the largest difference, $\Delta E_g$, between the two strain conditions. Reprinted figure with permission from [107], Copyright 2016 by the American Physical Society.](image-url)
the total polarization. The total polarization vanishes around $y = 0.33$, at the crossing of $P_{sp}$ and $-P_{pz}$ lines, so the model confirms the finding that in $m$In$_{0.33}$Al$_{0.67}$N/nGaN SLs the internal electric field is close to zero.

Summarizing, SLs containing In$_{y}$Al$_{1-y}$N alloys can be analysed in three different regions of $y$ values:

1. Low In content, $y < 0.33$
   Wells and barriers of the SLs are nearly lattice-matched. The internal strains are small and the electric fields are mostly due to the spontaneous polarization. Their influence on the band gaps is compensated to some extent by the hybridization of wave functions. At $y \sim 0.17$, the piezoelectric polarization vanishes due to the matching of GaN and InAlN lattice constants and the internal strain also vanish. The band gaps are similar to the gaps of the quaternary alloys with equivalent compositions.

2. $y \sim 0.33$
   The spontaneous and piezoelectric polarizations cancel and the built-in electric fields vanish. The band gap behavior is mostly due to other effects, as internal strain and hybridization of wave functions. The In$_{0.33}$Al$_{0.67}$N/GaN SL represent somehow the border case between GaN/In$_{y}$Al$_{1-y}$N and In$_{y}$Al$_{1-y}$/In$_{y}$Al$_{1-y}$/N/GaN SLs.

3. Large In content, $y > 0.33$
   Strong internal electric fields are observed in thin wells of the SLs with high In content (up to 9 MV cm$^{-1}$ in In$_{0.67}$Al$_{0.33}$N/GaN SL). It results in band gaps much lower compared to the gaps of InAlGaN alloy with the equivalent composition.

7. Comparison of nitride and oxide superlattices

Oxide and nitride semiconductors have many similar physical properties. In particular, concerning three binary nitrides, GaN,
Characterized by much larger exciton binding energy in ZnO, and both crystallize in the wurtzite structure. However, variations. Experimental data for Zn (dashed red line). The lines represent fits to the calculated gap has been observed for the last two decades [109, 110].

Moreover, in contrast to wide and successful applications of AlN, and InN with corresponding oxides, ZnO, MgO, and CdO, it is easy to realize similar lattice constants and band gaps, as it is shown schematically in figure 37. On the other hand, the ionicity of oxides is much larger than that characterizing nitrides. Furthermore, in contrast to wide and successful applications of nitrides in optoelectronics and electronics, oxides are not used on such a large scale in the semiconductor industry. However, an increasing scientific interest in these latter semiconductors has been observed for the last two decades [109, 110].

To illustrate the similarities and differences between the two groups of materials, we will compare the nitride alloys and SLs based on AlN and GaN with oxide structures based on ZnO and MgO. The main representatives of these groups of semiconductors, ZnO and GaN are formed from neighboring atoms in the Periodic Table (Z(N) = 31, Z(Zn) = 30, Z(Ga) = 31, Z(Al) = 13). And have similar lattice parameters and similar direct energy gap, $E_g$, of 3.35 eV and 3.43 eV, respectively, and both crystallize in the wurtzite structure. However, ZnO has some advantages over GaN. The first one is characterized by much larger exciton binding energy in ZnO ($E_{ex} \approx 60$ meV) compared to GaN ($E_{ex} \approx 25$ meV); consequently, it is expected that ZnO-based light emitters should be much brighter than GaN light emitters. The next advantage is that large bulk monocrystals of ZnO are easily available, suitable as cheap substrates for epitaxy.

Alloys and quantum structures are formed in the case of GaN by adding elements from Group III of the Periodic Table (Al or In), and in the case of ZnO by adding elements from group II (Mg, Cd or Be). In figure 37, a schematic illustration shows similar ranges of available band gap energies for nitrides and oxides, crystallizing in the wurtzite structure; however CdO and MgO are stable in the rocksalt phase and experimental data on their wurtzite phase are very scare [111].

7.1. GaAlN and ZnMgO alloys

Due to different MgO and ZnO crystallographic structures (rocksalt and wurtzite, respectively), Mg,Zn$_{1-x}$O alloys have a tendency to be metastable. Phase segregation has been reported to occur in Mg$_x$Zn$_{1-x}$O for, $x > 33\%$, with a maximum $E_g$ of about 4.0 eV [112, 113]. It is interesting to observe that in Mg,Zn$_{1-x}$O an increase of band gap with $x$ is accompanied by a reduction of the lattice constant. This behavior is different from usually observed trends (see e.g. AlGaN case).

Our calculated band gaps for Zn$_x$Mg$_{1-x}$O alloy in the wurtzite structure are compared in figure 38 with the band gaps obtained for Ga$_x$Al$_{1-x}$N (see figure 2(b)), see also [114]. Additionally, our results for Mg,$Zn_{1-x}$O are compared with the experimental data from the literature [112, 115–119] and a very good agreement is found.

In both alloys we observe similar $E_g$ dependence on composition, but different composition dependent band gap bowings, $b(x)$, which are defined through equation (2). In a linear approximation: $b(x) = \alpha + \beta x$.

The band gap bowing of Ga$_x$Al$_{1-x}$N alloy is small, $b = 0.71$ eV for $x = 0.5$, $\alpha = 0.75$, $\beta = 0.07$). The calculated bowing parameter of Zn$_x$Mg$_{1-x}$O is larger, and with increasing Zn content, $x$, changes from 1 to 3eV, being equal to 2.6 eV for $x = 0.5$, $\alpha = 0.8$, $\beta = 3.4$). Larger is also the difference in size of the cations. The covalent radius for Zn is equal to 1.22 Å and is 1.41 Å for Mg. In this respect, we can compare Zn$_x$Mg$_{1-x}$O to In$_x$Ga$_{1-x}$N where $E_g$ bowing is also quite large and similar as in Zn$_x$Mg$_{1-x}$O, ranging from 1.4 to 2.8 eV Covalent radii of the cations are equal to 1.22 Å for Ga and 1.21 Å for Al and similar lattice parameters.

The calculated bowing parameter of Zn$_x$Mg$_{1-x}$O is larger, and with increasing Zn content, $x$, changes from 1 to 3eV, being equal to 2.6 eV for $x = 0.5$, $\alpha = 0.8$, $\beta = 3.4$). Larger is also the difference in size of the cations. The covalent radius for Zn is equal to 1.22 Å and is 1.41 Å for Mg. In this respect, we can compare Zn$_x$Mg$_{1-x}$O to In$_x$Ga$_{1-x}$N where $E_g$ bowing is also quite large and similar as in Zn$_x$Mg$_{1-x}$O, ranging from 1.4 to 2.8 eV Covalent radii of the cations are equal to 1.22 Å for Ga and 1.21 Å for Al and similar lattice parameters.

The above finding differ from the one obtained by Toporkov et al [115] where the $E_g$ bowing for the Zn$_x$Mg$_{1-x}$O alloy was found to be very small ($b = 0.237$ eV). The experimental Mg,$Zn_{1-x}$O bowing parameter is unknown due to a limited range of available compositions (up to 40% of Mg), but the good agreement with the calculated band gaps (figure 38) indicates that the experimental $E_g$ bowing should likely be also large.

7.2. GaN/AIN and ZnO/MgO SLs

To compare the short period SLs of the form: $m$GaN/$n$AlN and $m$ZnO/$n$MgO, we choose the most typical growth direction along the wurtzite c-axis. Such a comparison is interesting because not only QWs (GaN and ZnO), but also QBs (AIN and MgO) are similar (Z(Al) = 13, Z(Mg) = 12).

In figure 39, energy band gaps versus number of barrier MLs, $n$, are presented for $m$ZnO/$n$MgO (a) and $m$GaN/$n$AlN...
Comparing figures 39(a) and (b), we observe surprisingly similar \( E_g \) behavior in both kinds of SLs. The range of the \( E_g \) variation is almost the same, and they exhibit the same trends with changing \( m \) and \( n \). In both cases, with an increasing number of QW layers, \( m \), \( E_g \) is significantly reduced. On the contrary, increasing the barrier width, i.e. \( n \), leads to increase (smaller \( m \)) or decrease (larger \( m \)) of \( E_g \).

Analysing the contributions to the band gap evolution, we can estimate the influence of the internal strain as not substantial, due to similar lattice constants of quantum layers and substrates (GaN in \( m\)GaN/\( n\)AlN and ZnO in \( m\)ZnO/\( n\)MgO). The interplay of the built-in electric field and wave functions hybridization should mostly influence the \( E_g \) behavior. The effect of the internal electric field will be discussed in the next section.

### 7.3. Internal electric field

The electric fields in the wells (\( E_w \)) and barriers (\( E_b \)) of the \( m\)ZnO/\( n\)MgO SL structures are estimated from the semi-macroscopic model described in section 4.3.3 and presented in figure 40. The values of the parameters for ZnO and MgO used in the model calculations are listed in table 4. Note that lattice matching to ZnO substrate is assumed.

Figure 40 illustrates the internal electric fields in wells (\( E_w \)) and barriers (\( E_b \)) of \( m\)ZnO/\( n\)MgO SLs as functions of the effective Zn content. [114] John Wiley & Sons. © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Table 4. Lattice constants \( a \) (Å), ML thicknesses \( l_{wb} \) (Å), spontaneous polarizations \( P_{sp} \) (C m\(^{-2}\)), piezoelectric coefficients, elastic constants, and dielectric constants, \( \chi \), used in the calculations of the electric fields.

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>3.198</td>
<td>3.228</td>
</tr>
<tr>
<td>( l_{wb} )</td>
<td>2.578</td>
<td>2.500</td>
</tr>
<tr>
<td>( P_{sp} )</td>
<td>–0.053 [120]</td>
<td>–0.080 [120]</td>
</tr>
<tr>
<td>( e_{31} )</td>
<td>–0.55 [120]</td>
<td>–0.78 [120]</td>
</tr>
<tr>
<td>( e_{33} )</td>
<td>1.24 [120]</td>
<td>0.14 [119]</td>
</tr>
<tr>
<td>( c_{13} )</td>
<td>84 [120]</td>
<td>88 [120]</td>
</tr>
<tr>
<td>( c_{33} )</td>
<td>176 [120]</td>
<td>222 [120]</td>
</tr>
<tr>
<td>( \chi )</td>
<td>7.4 [121]</td>
<td>9.8 [121]</td>
</tr>
</tbody>
</table>
and $m\text{ZnO}/n\text{MgO}$ SLs, we observe a similar evolution of the band gaps with varying number of atomic MLs, whereas the strengths of the built-in electric fields, existing in these two families of SLs differ significantly.

8. Summary and outlook

In summary, a study of the band gap engineering in short period nitride SLs based on first principles calculations was presented. All the factors influencing the band gap behaviour were analysed and discussed.

The evolution of the band gaps and electric fields was illustrated and discussed using two ways of presentation. The first one consists of dependences on effective cation concentration. Such a choice was motivated by the concept of comparison with corresponding alloys. The second way uses the numbers of barrier and well monolayers. The latter approach is based on more intuitive understanding and enables to expose new microscopic mechanisms leading to SL formation (discussion of the wave functions overlaps and oscillator strength).

It was shown that, for superlattices, it is possible to exceed by far the range of band gap values which can be realized in ternary alloys. By comparing band gaps in SLs grown along different directions of the wurtzite structure, or with different atomic arrangements, we demonstrated the effects of lattice geometry. To evaluate the effect of internal strain, two cases of growth conditions were compared: the pseudomorphic and free-standing. It was shown, assuming a given growth orientation and strain conditions, that the band gaps are influenced mainly by the built-in electric field, $E_g$ (in polar structures) and by the wave function hybridization. The contributions of these two important factors to the band gap behavior are illustrated and estimated quantitatively. It appears that there are two interesting ranges of layer thicknesses; in one (few MLs in barriers and wells) the influence of the wave function hybridization is dominant, whereas in the other (layers thicker than roughly 5–6 MLs) the effect of the internal electric field is more important.

Finally, to show the specifics of nitride structures, a comparison of GaN/AlN and ZnO/MgO SLs was performed, pointing out the similarities and differences between nitride and oxide SLs. Comparing GaN/AlN and ZnO/MgO SLs, we found a large difference in the internal electric field strengths. In light of the above findings, it is very surprising that the band gaps of ZnO/MgO and GaN/AlN SLs are so similar, covering the same range of values and exhibiting the same trends. Additionally, we found substantial differences in Ga$_{0.33}$Al$_{0.66}$N and Zn$_{0.33}$Mg$_{0.66}$O band gap bowings.

The obtained results provide insight in the properties of nitride SLs with relevance to band gap engineering and consequently to device optimization. The idea of short period SLs is very complex and crucial to understand in detail for the realization in optoelectronics based on nitride quantum structures. Many problems remain to be solved. It is important to comment on the availability of real structures. Up to now the most popular crystal growth orientation was the polar one, but we observed increasing interest, within the nitride community, in the properties of semipolar and nonpolar structures including, both, theoretical and experimental investigations. It is quite challenging to obtain binary $m\text{InN}/n\text{GaN}$ SLs. Instead of intentionally introduced InN QWs, In$_{x}$Ga$_{1−x}$N layers are grown in such structures. Using both growth methods metalorganic vapour phase epitaxy or molecular beam epitaxy, produce In$_{x}$Ga$_{1−x}$N/GaN structures with $x$ not higher than 0.3–0.4. Low In incorporation may be a general property for all SL samples presented so far. Concerning the comparison of the measured band gaps in such $m\text{InN}/n\text{GaN}$ SLs ($x \leq 0.35$) with theoretical predictions, demonstrated in this work, the agreement is satisfactory. Moreover, measured hydrostatic pressure dependence of $E_g$ in different samples goes along with the theoretical calculations. It represents a strong experimental verification of the used approach and strongly suggests much lower In-concentration in quantum wells of considered SLs than the intended ones. Another interesting issue is the ordering of In cations in ultrathin InGaN layers. Preferential concentrations of $x = 0.33$ and 0.66 has been considered by Limperakis et al. [106].

Below we present a partial list of issues which are important for understanding properties of In(Ga)N/GaN SLs, i.e. structures which demonstrate anomalies in both their growth parameters and physical mechanisms of band structure, lattice vibrations, heat transport, and doping. Developing a controllable growth processes of In$_{x}$Ga$_{1−x}$N/GaN short period superlattice will lead to:

(a) a solution to limitations in obtaining high In-content quantum structures and devices based on InGaN QWs that operate in amber, red and infrared spectral regions;
(b) a description of atoms arrangement in alloys for the case of ions with significantly different size and chemical bond strength (e.g. In versus Ga and In–N versus Ga–N, correspondingly), in particular ordering of cations, and its relation to growth conditions;
(c) the experimental verification of SPSLs properties grown on N-side of GaN substrate or InGaN pseudo-substrate;
(d) an opportunity for the verification the theoretical predictions concerning the realization of topological insulators based on InGaN/GaN superlattices [70, 122].

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